Adsorption desorption study of Chromium (VI) from Chromium contaminated soil in the industrial belt of Bhilwara, Rajasthan

A THESIS

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Submitted by

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Under the supervision of

Supervisor

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Dedicated to

my beloved parents,

and Prateek

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Certificate

It is to certify that the

(i) The thesis entitled **"Adsorption desorption study of Chromium (VI) from Chromium contaminated soil in the industrial belt of Bhilwara, Rajasthan"** submitted by **Priya Vijayvergiya** is an original piece of research work carried out under my supervision.

(ii) Literary presentation is satisfactory and the thesis is in a form suitable for publication.

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(v) Candidate has put in at least 200 days of attendance every year.

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A word of gratitude

“Feeling gratitude and not expressing it is like wrapping a present and not giving it”

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(Priya Vijayvergiya)

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(Priya Vijayvergiya)

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Introduction

ABSTRACT

A brief review of natural, anthropogenic and industrial sources of Chromium(VI), chemistry of Chromium in soil and aquatic environment, hazardous effect of Chromium(VI), kinetics and metabolism of Chromium in human, Adsorption/ desorption of Chromium(VI) in soil and factors affecting the mobility of Chromium(VI) in soil such as clays, soil matrix and pH. Adsorption mechanism and kinetics, and some previous studies of adsorption desorption of Chromium on different adsorbent have been included in this chapter. The scope of the present work has been outlined at the end of this chapter.

One of the serious threats to our fascinating and fragile environment is the discharge of untreated effluent into the soil and water bodies. Among the various contaminants, discharge of heavy metal ions into the environment are of prime concern because of their persistent nature, toxicity, and non-biodegradability leading to ecological problems. These heavy metals which have transferred to the environment are highly toxic and can bio accumulate in the human body, aquatic life, natural water bodies and also possibly get trapped in the soil.

Soil contamination by heavy metals is extremely pernicious because these contaminants are environmentally persistent, unlike most organic contaminants, metals are generally stubborn and cannot be degraded or readily detoxified biologically. Toxic metals pose a particularly difficult long-term pollution problem [1].

The rapid development and proliferation of process industries have made wastewater treatment a major concern in industrial areas. Advances in science and technology have brought tremendous progress in many spheres of development, but in the process, also contributed to degradation of environment all over the globe due to very little attention paid to the treatment of industrial effluents. Thus the presence of metal ions in natural (mainly by volcanic activity and weathering of rocks) or industrial wastewater and their potential impact has been a subject of research in environmental science for a long time.

Chromium is one of the most commonly found metal contaminants in soil. Chromium has been extensively studied and their effects on human health are regularly reviewed by international bodies such as the WHO [2]. These Chromium compounds coming to the earth's surface not only contaminate surface water (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow.

Elemental Chromium is a transition-group metal belonging to group VIB of the periodic table and has oxidation states ranging from –2 to +6, of which the Chromium(III) and Chromium(VI) forms are the most important. Elemental Chromium does not occur naturally in the environment. Trivalent Chromium [Cr(III)], which occurs naturally and is an essential nutrient, and hexavalent

Chromium [Cr(VI)], which, along with the less common metallic Chromium (Cr), is most commonly produced by industrial processes. Chromium(III) is essential to normal glucose, protein, and fat metabolism and is thus an essential dietary element while the Chromium(VI) is carcinogenic. Chromium(VI) compounds are strong oxidizing agents and are highly corrosive. In environment, they generally are reduced to Chromium(III) compounds. The Chromium(VI) compounds most commonly encountered in industry are potassium chromate and dichromate, chromium trioxide, sodium chromate and dichromate, calcium chromate and dichromate, lead chromate, strontium chromate, and zinc chromate [3].

Chromium is seventh most abundant elements in the earth's crust with an average concentration of 100 mg L^{-1} [4]. Chromium has four stable isotopes with masses of 50 (natural abundance 4.35%), 52 (83.8%), 53 (9.50%) and 54 (2.37%) [5]. Chromium is the only elemental solid which shows anti ferromagnetic ordering at or below room temperature [6]. It has also high corrosion resistance and hardness. Many of its compounds are intensely colored. Because of its unique characters, Chromium was widely used in electroplating, tanning, pigments, dyes, industrial water cooling, metal finishing, magnetic tapes, paper pulp producing, photographic film, automotive parts, chemical manufacturing, wood protection, ore and petroleum refining, metallurgical and refractory producing, and other industrial activities [7-9].

1.1 Sources of Chromium(VI)

Some important sources of Chromium(VI) in Lithosphere are as given below:

1.1.1 Natural Sources

Chromium was discovered later than other metals because of its relatively low concentration in the earth's crust-detected at approximately 100 ppm in Chromium rich rocks. Additionally, Chromium does not appear terrestrially as a native metal, but is strongly bonded to minerals in which it occurs. Naturally occurring Chromium is usually present as trivalent Chromium. Hexavalent Chromium in the environment is almost totally derived from human activities [10]. Chromium in water originates from natural sources, such as weathering of rock constituents, wet precipitation and dry fallout from the atmosphere, and runoff from the terrestrial systems. Natural sources of Chromium accumulation in soil are due to the weathering of parent rock. 30-40% of Chromium in atmosphere is from the natural sources [11, 12]. Chromium is a naturally occurring element in rocks, animals, plants, soil, and volcanic dust and gases. In nature Chromium occurs in more than fifty different ores. The following are some important ores:

- Barbertonite: $Mg_6Cr_2(CO_3)(OH)_{16}.4H_2O$
- Brezinaite: Cr_3S_4
- Chromite: $(Mg,Fe^{2+})(Cr,Al,Fe^{3+})_2O_4$
- Chromatite: $CaCrO_4$
- Nichromite: $(Ni,CoFe^{2+})(Cr,Fe^{3+},Al,)_2O_4$

Chromium minerals are generally resistant to weathering. Therefore, 75% of the annual transfer of Chromium into the environment is by mining activities [13]. Its concentrations in industrial wastewaters range from 0.5 to 270.0 $mg{\cdot}L^{-1}$ [14]. The tolerance limit for Chromium(VI) for discharge into inland surface waters is 0.1 $mg{\cdot}L^{-1}$ and in potable water is 0.05 $mg{\cdot}L^{-1}$ [15].

In order to comply with this limit, it is essential that industries treat their effluents to reduce the Chromium(VI) to acceptable levels [16]. Central pollution control board in India has set the maximum permissible limit of chromium in waste water to be below 0.01 mg L^{-1} for hexavalent Chromium and 5 mg L^{-1} for the trivalent Chromium salts [17]. It is therefore important to not only recover/reuse Chromium from waste stream prior to disposal for economic reasons but also to confirm the stringent laws.

1.1.2 Anthropogenic Sources

Many industrial and other anthropogenic activities (e.g. disposal of products or chemicals containing Chromium, or burning of fossil fuels) are responsible for discharging huge amounts of Chromium compounds into the environment, including air, soil, and water [18].

The content of Chromium in soils is generally low. The range of mean concentrations of Chromium varies from 7 to 150 ppm and its content and distribution in the soil mainly depends on the type of the soil's mother rock. The presence of additional amounts of the element in the soil is caused by human activities, including emission of furnace or coke dust or combustion of fluid fuel or tannery waste water or communal solid waste. [19-21]. Chromium and its compounds are extensively used in textile, electroplating, leather tanning, metal finishing, nuclear power plant, dyeing and photography industries [22, 23]. Out of the total chrome ore production 90% is used in metallurgical industries for steel, alloy and nonferrous alloy production. Only 5% each has been used in refractory (iron & steel, cement, glass, ceramics and machinery) and chemical (leather tanning, plating, wood preservation and pigment) industries (**Figure 1.1**) [24].

Heavy metal release to the environment has been increasing continuously as a result of industrial activities and technological development, posing a significant threat to the environment, public and soil health [25]. Chromium is released into the environment by a large number of industries such as mining, iron sheet cleaning, chrome plating, leather tanning, wood preservation [26], electroplating, metal finishing, textile industry and nuclear power plants [27]. These industries contain Chromium(III) and Chromium(VI) at a concentration ranging from 10 to 100 mg/L [28, 29]. Long-term release of such wastewater may result in the accumulation of heavy metals in soil.

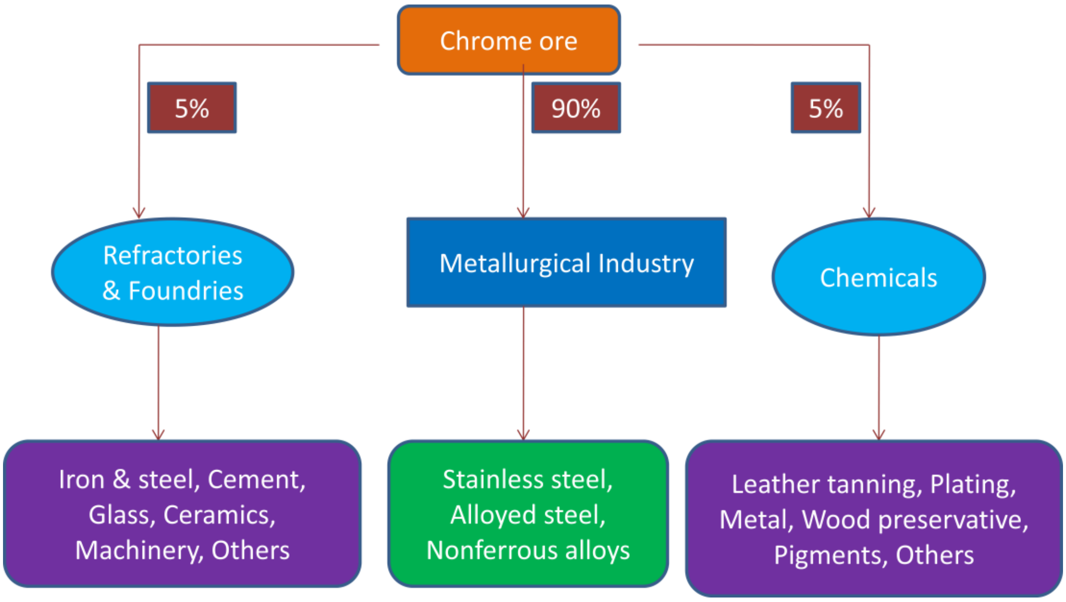

Figure 1.1: Percentage use of Chromium in different industry.

1.1.3 Industrial Sources

The most important industrial sources of Chromium in the atmosphere are those related to production of ferrochrome which is an alloy of Chromium and Iron containing 50% to 70% Chromium. Hexavalent Chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing and fertilizer and photography industries and causes severe environmental and public health problems [30]. The tanning process is one of the largest polluters of chromium all over the world. Most of the tanneries in India adopt the Chromium tanning process because of its processing speed, low costs, and light color of leather and greater stability of the resulting leather. In the Chromium tanning process, the leather takes up only 60–80% of applied Chromium, and the rest is usually discharged into the sewage system causing serious environmental impact. Chromium ion in liquid tanning wastes occurs mainly in trivalent form, which gets further oxidized to Chromium(VI) form, due to the presence of organic substances [31].

1.1.4 Mordant in Textile Industry

Demands of clothing and apparel increase with the improving sense of fashion and lifestyle; thus textiles are manufactured to meet the growing demand. Mordants, are substances, (such as Chromium), used to “fix” color onto the fabric. They may be are very toxic and may have a high impact on the wastewater quality. Many natural dyes (plant extracts, etc.) require a mordant and natural dyestuffs require large quantities of water for dyeing (Almost equal to or double that of the fiber’s own weight). About 80 percent of the dyestuffs stay on the fabric, while the rest go down the drain. Since Chromium is almost exclusively used as the mordant on wool, chrome dye has become essentially synonymous with mordant dye. Consequently natural dyes prepared from wild plants and lichens can have a very high impact on the environment [32].

Thousands of small-scale dyeing units, employing millions of people, generate enormous amount of polluted water. Mostly, the areas situated around industrial belts are under stress due to the continuous disposal of the untreated water. The quality of water is continuously deteriorating due to addition of toxic dyeing effluents. Dyeing effluents from textile industries are highly toxic as they contain a large number of metal complex dyes (e.g. Chromium and cobalt complexes) [33, 34]. The high concentration of such dyes causes many water borne diseases and increases the BOD of receiving waters [35]. Hundreds of small-scale dyeing industries are facing closure since they are not treating their effluents. It is not economical for them to treat the effluent [36]. S. S. Patel et al (1999) was found that, the textile, dyeing and printing industrial effluents have an adverse effect on the soil and ground water eco systems. It is mainly due to leachates of cationic and anionic species from textiles effluents through soil strata. A comparison of collected data clearly indicates that about 3-8 folds increase in the concentration of all parameters of effluent amended soil near the industrial area [37].

Textile, dyeing and printing industrial effluent contain following metals:

Ca > Na > Mg > K > Zn > **Cr** > Fe > Hg > Pb > Cu > Cd > As > Ni

Ground water near industrial area

Ca > Mg > Na > K> Zn > Fe > **Cr** > Pb > Hg > Ni > Cu > Cd > As

Soil affected by industrial effluents

Ca > Mg > Na > K > Fe > Zn > **Cr** > Cu > Pb > Ni > Hg > Cd

Unless, these soils are managed properly, it may lead to severe land and ground water pollution affecting various component of the soil eco system [38].

1.2 Chemistry of Chromium in Environment

1.2.1 Chemistry of Chromium in Soil

The literature indicates that Chromium behavior in soil is complex, and depends on environment conditions such as pH, oxidation reduction potential, and ionic composition of the soil and groundwater. Very little information is available concerning the chemical form of the element in the soil, but it is generally assumed to occur as the trivalent Chromium oxide. Natural α-Al_2O_3 contains occasional Chromium(III) ions in place of Aluminium(III) ions. The migration of Chromium takes place only in a strongly acidic and reducing medium, where it occurs in the form of the Cr^{3+} cation, or a strongly basic and oxidizing medium, where it occurs as the CrO_4^{2-} anion. Due to low solubility of its compounds and their high availability, Chromium plays an important role in the soil processes [39-41]. During weathering, Chromium oxide in rocks tends to oxidize soluble Chromium(VI) anions. Chromium(VI) is relatively stable and mobile in soils that are sandy or contain low organic matter concentration. In soils with high pH and low organic matter content, Chromium(VI) is readily mobilized by groundwater, but at lower pH and higher organic matter content Chromium(VI) may adsorb or be reduced to Chromium(III) and then adsorbed onto the soil. Chromium(VI) in soil is divided into two categories; exchangeable fraction, which is the fraction of Chromium easily removed from the soil, and non exchangeable fraction, which includes the fraction either very tightly adsorbed by the soil or precipitated on the soil [42]. Chemical and physical processes that control the rate of transport and mobility of chromium in soil include diffusion, adsorption-desorption, precipitation-dissolution, oxidation-reduction, and complexation [43].

R. J. Bartlett (1991) [44] showed that Chromium(VI) is capable of moving towards groundwater due to its extreme mobility, and it is in thermodynamic equilibrium with the atmosphere. Chromium(VI) is the product of oxidation of Chromium(III) with atmospheric oxygen and its presence is greater into the earth crust. Since the natural oxidation of Chromium(III) is extremely low, most of the Chromium(VI) found in soil and groundwater results from pollution. The Chromium(III) reactivity increase when the inert crystals and amorphous mineral are transformed into organic and hydroxide forms which are smaller and more mobile.

The equilibrium between the two Chromium forms, Chromium(VI) and Chromium(III) in soil depends upon soil physical and chemical characteristics. The oxidation process is only controlled by the reaction kinetics, due to Chromium(III) species immobility and insolubility. Chromium(III) tends to be strongly bound by soil humic acid polymers, and this affinity restricts the availability of Chromium(III) to be oxidized and reduce the organic matter decomposition [45, 46]. The presence of manganese oxide in soil favors trivalent Chromium oxidation, thus increasing the hazards connected to hexavalent Chromium contamination of groundwater.

Some previous studies found that the stable Chromium(III) form in soil is oxidized to Chromium(VI) by manganese dioxide, which serves as the electron acceptor in **Equation 1.1**. The rate of Chromium(III) oxidation by β-MnO_2 was found to increase with decreasing pH [47, 48]. Chromium(III) concentration, pH, and the amount of initial available β-MnO_2 surface are the parameters controlling the degree of oxidation [49]. The amount of Chromium(III) oxidized to Chromium(VI) was proportional to the manganese reduced. The following oxidation equation was proposed:

$$CrOH_2^{+} + 1.5\ MnO_2(s) = HCrO_4^{-} + 1.5\ Mn^{2+} \qquad (1.1)$$

Both oxidation of Chromium(III) and reduction of Chromium(VI) can be thermodynamically favorable in soil. The transformation of Chromium(VI) to Chromium(III) within soils is likely to occur in the presence of electron donors such as Fe (II) [50]. The rate and amount of reduction of Chromium(VI) in soil is difficult to predict. Reduction of Chromium(VI) with organic compounds to insoluble Chromium(III) forms has been studied by several workers. Organic matter present in clays provides a sufficient source of electrons for reduction of Chromium(VI) to Chromium(III). Another source of Chromium(VI) reduction to Chromium(III) is from Fe(II) in hematite and biotite. Past studies with pure mineral phases have shown that even the small amounts of Fe (II) contained in hematite and biotite can reduce aqueous Chromium(VI) species to Chromium(III), resulting in the precipitation of $(Fe,Cr)(OH)_3$ [48]. Reduction of chromate by the ferrous ions produced by dissolution of the ferrous iron components of hematite and biotite in acidic media is described by the following reaction:

$$3[FeO]_{biotite} + 9H^{+} + HCrO_4^{-} = CrOH^{2+} + 3FeOH^{2+} + 3H_2O \qquad (1.2)$$

1.2.2 Chemistry of Chromium in Aquatic Environment

Oxidation reduction processes play a major role in the mobility, transport, and fate of inorganic and organic chemical constituents in natural waters. Of the possible oxidation states of Chromium, only hexavalent and trivalent Chromium are of interest in environmental systems. Chromium speciation in groundwater is affected by pE and pH conditions (**Figure 1.2**) [51]. Chromium in natural waters exists in two oxidation states: +3, Chromium(III) or trivalent form; and +6, Chromium(VI) or hexavalent form. Chromium (VI) species are anionic (i.e., $HCrO_4^-$ and CrO_4^{2-}) and are generally mobile in most neutral to alkaline systems. The proportion of each ion in solution depends on pH and total chromium concentration. The following are the important equilibrium reactions for different Chromium(VI) species in aquatic environment [52]:

$H_2CrO_4 = H^+ + HCrO_4^-$	log K (25 °C)	- 0.8	(1.3)
$HCrO_4^- = H^+ + CrO_4^{2-}$	log K (25 °C)	-6.5	(1.4)
$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$	log K (25 °C)	1.52	(1.5)
$HCr_2O_7^- = H^+ + Cr_2O_7^{2-}$	log K (25 °C)	0.07	(1.6)

Equations 1.3, 1.4, and **1.6** shows that the predominant species present, as a function of the pH, are H_2CrO_4 at pH less than 0.8, $HCrO_4^-$ at pH between 0.8 to 6.5, and CrO_4^{2-} at pH above 6.5. **Equation 1.5** does not contain any H^+ terms, and therefore, in a certain pH range (2-5) this reaction is nearly independent of pH and depends only on total Chromium(VI) concentration. When the concentration of chromium exceed 10 mM and under acidic conditions bichromate ($HCrO_4^-$) polymerizes to form dichromate ($Cr_2O_7^{2-}$). Chromium(VI) species are strong oxidants that are reduced to the trivalent state by aqueous Fe(II) and organic compounds [52-54]. As the pH becomes lower, Chromium(VI) species are removed from solution by adsorption onto positively charged sorption sites [55]. The dominant Chromium(III) species occurring in groundwater also depend on pH. Apparent stability constants (298 K, K=0.75) calculated for pertinent reactions, relevant for Chromium(III) speciations are [56]:

$Cr^{3+} + H_2O = CrOH^{2+} + H^+$	log K (25 °C)	- 4.4	(1.7)
$Cr^{3+} + 2 H_2O = Cr(OH)_2^+ + 2 H^+$	log K (25 °C)	10.6	(1.8)
$Cr^{3+} + 3 H2O = Cr(OH)_3 + 3 H^+$	log K (25 °C)	-19.2	(1.9)
$Cr^{3+} + 4 H_2O = Cr(OH)_4^- + 4 H^+$	log K (25 °C)	-28.2	(1.10)

$Cr(OH)_2^+$ is the dominant species in natural ground waters with a pH between 6-8, $CrOH^{2+}$ and Cr^{3+} predominate in more acidic environment. $Cr(OH)_3$ and $Cr(OH)_4^-$ predominate in more alkaline environment (**Figure 1.2**). Chromium

(III) solubility is limited due to the formation of hydrous oxides, $Cr(OH)_3(s)$ and chromite $(Fe,Cr)(OH)_3(s)$, and the strong tendency to adsorb onto clays and other solid phases. Chromium(III) can also form soluble organic complexes, particularly under acidic conditions. However, Chromium(III) could be converted to the more soluble Chromium(VI) if the redox state changes from reducing to highly oxidizing [47, 57].

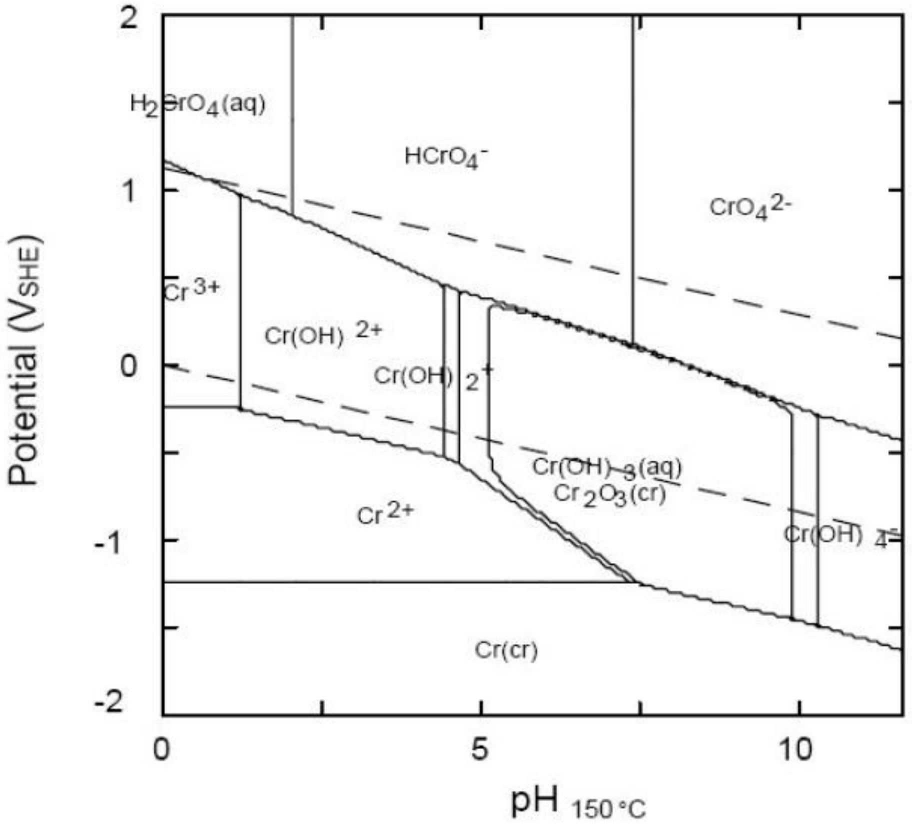

Figure 1.2: A simplified Pourbaix diagram for chromium species at 150°C and $[Cr(aq)]_{tot} = 10^{-8}$ [58, 59].

1.3 Hazardous Effects of Chromium(VI)

In the array of heavy metal ions, chromium is of special interest because it is an essential nutrient as well as a carcinogen [60]. Dietary deficiency of Chromium(III) has found to cause faulty sugar metabolism [61], although in combination with insulin, it removes glucose from the blood and also plays a key role in fat metabolism [62]. On the other hand, Chromium(VI) is lethal to human system because of its mutagenic and carcinogenic properties [63, 64]. Trivalent

Chromium is an essential micronutrient whereas Chromium(VI) is listed as a Group 1 human carcinogen by the International Agency for Research on Cancer [65].

1.3.1 Acute (Short Term) Health Effects

Short-term effects of Chromium(VI) exposure (for example, from chromic acid droplets or chromate dust) include eye irritation and respiratory irritation, sneezing, or sensitization; acute exposure to high levels of Chromium(VI) can produce nervous system damage and liver disorder [66]. In high concentrations, acute inhalation can cause ulcers in the nasal septum. In sensitive individuals, inhalation of Chromium(VI) can cause an asthma attack. If very small quantities are ingested, the body converts it to the trivalent form in the stomach. In larger quantities or concentrations, however, ingestion of hexavalent Chromium compounds can result in acute gastroenteritis, vertigo, gastrointestinal hemorrhage, convulsions, ulcers, kidney damage or failure, and liver damage or failure; approximately 1 g of potassium chromate is considered a lethal dose. Significant acute exposure of the skin to Chromium(VI) can cause burns, liver damage or failure, kidney damage or failure, and anemia [67] .

1.3.2 Chronic (Long Term) Health Effects

Hexavalent Chromium compounds are highly toxic when ingested or inhaled. Carcinogenesis caused by Chromium(VI) may result from the formation of mutagenic oxidative DNA lesions following intracellular reduction to the trivalent form [68]. Excessive exposure to toxic Chromium(VI) results in various health problems such as chronic ulcers, dermatitis, hemorrhage, and pulmonary cancer [67]. Chromium(VI), generally occurs in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), has the ability to diffuse through cell [69] and modifies DNA transcription process which can lead to digestive tract and lung cancer [70]. If inhaled through the mouth, it can cause periodontitis and gingivitis. Impacts of chronic skin exposure include dermatitis, hypersensitivity reactions, eczema, and kidney or liver damage. The characteristic lesions resulting from Chromium(VI) exposure are referred to as "chrome holes" or "chrome ulcers." Chronic eye exposure can result in conjunctivitis [71].

1.3.3 Exposure Routes

Ingestion of Chromium(VI) in drinking contaminated groundwater or surface water. This is still being debated within the scientific community. Dermal contact through bathing or washing in Chromium(VI) contaminated water is another exposure pathway. Chromates can enter the bloodstream through breaks in the skin. CrO_4^{2-} blood poisoning occurs when CrO_4^{2-} destroys red corpuscles. Inhalation is also an important human exposure pathway; however, it is less likely to be associated with exposure to Chromium(VI) contaminated soil and groundwater and more likely associated with industrial processes such as welding, cutting, heating of Chromium alloys, and work related practices. With low pH rain or fruit juice (orange juice and lemon juice), the Chromium can be leached off the wood surface [72].

1.3.4 Worker Health

Workers, rather than consumers, have the highest risk of adverse health effects from Chromium(VI) exposure. The industries with the greatest risk of occupational exposure to Chromium(VI) are chrome electroplating, stainless steel welding, metal coating and painting, printing, textiles, leather tanning, wood preservation, and cement or masonry work. Inhalation risk may be from fumes (welding), mists or droplets (electroplating, spray painting.) Dermal exposure can result from contact with fluids, such as those used in electroplating, or materials containing Chromium(VI), such as wet cement; smoking can increase the risks from Chromium(VI) exposure [73].

1.3.5 Public Health

Chromium may enter in human body through food, water, air, or adsorption through the skin when they come in contact with humans in, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults [74]. Chromium is found naturally in the soil in trace amounts, which pose few problems. Exposure may occur from natural or industrial sources of Chromium. The average daily intake from air, water, and food is estimated to be less than 0.2 to 0.4 μg, 2.0 μg, and 60 μg, respectively [75].

1.3.6 Environmental Hazards

There are both naturally occurring and anthropogenic sources of Chromium compounds in the air, soil, and water. Natural sources include volcanic activity and the weathering of Chromium-containing rock. The dumping of industrial waste materials significantly increases Chromium concentration in soil and is usually accompanied by groundwater contamination [76]. Chromium in the air is in the form of particles or droplets, which may be transported by wind and deposited onto soil or water. The behavior of Chromium compounds in soil and water is complex. Chromium (VI) can leach out of soil into groundwater and migrate over time [73, 77]. Factors that determine whether the Chromium is in trivalent or hexavalent form in different environmental media (air, soil, surface water, ground water) include pH, oxygen levels, temperature and the presence of other chemicals and organic matter [78].

1.4 Kinetics and Metabolism of Chromium in Human

In mammals, Chromium(III) is an essential trace element involved in lipid and glucose metabolism. It is usually considered that almost all the Chromium in food is present as Chromium(III) [79]. About 0.5-1% of Chromium(III) present in the normal diet is absorbed [80]. Adsorption of ingested Chromium(VI) compounds is greater than for Chromium(III) compounds, ranging from approximately 2-8%, although most of ingested Chromium(VI) is considered to be reduced to Chromium(III) in the stomach prior to absorption [79, 81]. The behavior and toxicity of Chromium is strongly dependent on the valency, physical-chemical properties of the substance, the particle characteristics and the route of exposure/administration.

Chromium(VI) chromate ions are transported into cells, whereas Chromium(III) compounds enter into cells by passive diffusion and phagocytosis. Furthermore, water soluble Chromium(III) aerosols of respirable size are more efficiently absorbed from the respiratory system than from the gastrointestinal tract, with approximately 5% being absorbed within hours of exposure, followed by further slow systemic absorption over weeks or months. Uptake of deposited and retained insoluble Chromium(III) oxide particles is a very slow process and particles containing Chromium may be retained in the lung for years following occupational exposure. In contrast, once deposited in the lungs, Chromium(VI) compounds are generally transferred to the systemic circulation more readily than Chromium(III) compounds [79-82].

Chromium(VI) is more efficiently adsorbed through the skin than Chromium(III) compounds. Chromium compounds are widely distributed in the body, with a greater distribution reported following exposure to Chromium(VI) compounds compared to Chromium(III), reflecting the greater tendency of Chromium(VI) to cross plasma membranes. Chromium(VI) is unstable in the body and is reduced to Chromium(V), Chromium(IV), and ultimately to Chromium(III) by endogenous substances such as ascorbate and glutathione and it is believed that the toxicity of Chromium may result from damage to cellular components during this process (e.g. through the generation of free radicals) [12].

1.5 Adsorption Desorption of Chromium(VI) in Soil

Various methods of Chromium removal include filtration, chemical precipitation, adsorption, electrodeposition and membrane systems or even ion exchange process. Among these methods, adsorption is one of the most economically favorable and a technically easy method [82]. In most soil environment adsorption is the dominating speciation process and thus the largest fraction of heavy metal in a soil is associated with the solid phase of that soil. Pollution problem arise when heavy metals are mobilized into the soil solution and taken up by plants or transported to the surface/ground water. The properties of the soil are thus very important in the attenuation of heavy metals in the environment. The solubility of heavy metals in soil is controlled by reactions with solid phases [38]. Once introduced into the soil, the heavy metal species undergo several possible fates including adsorption/desorption reactions, precipitation/dissolution reaction, plant uptake and mobility through soil profile.

Adsorption is a major process responsible for accumulation of heavy metals. Therefore the study of adsorption processes is of most importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase [83]. There are two general surface complexes formations are described by the configuration geometry of the heavy metal at soil surface. These include inner- and outer-sphere surface complexes and are defined by the presence, or absence, of the hydration sphere of the adsorbate molecule upon interaction. When at least one water molecule of the hydration sphere is retained upon sorption, the surface complex is referred to as outer-sphere. When the ion is bound directly to the adsorbent without the presence of the hydration sphere, an inner-sphere complex is formed [84-87].

Chemicals like heavy metals once introduced to the environment by one particular method may spread to various environmental components. Heavy metals may chemically or physically interact with the natural compounds, which change their forms of existence in the environment. In general they may react with particular species, change oxidation states and precipitate [88]. Heavy metals may be bound by particular natural substances, which may increase or decrease mobility. Studying the dissipation of heavy metals is called speciation [89, 90].

The most important interfaces involved in heavy metal adsorption in soil are predominantly inorganic colloids such as clays [91], metal oxides and hydroxides [8], metal carbonates and phosphates. Also organic colloidal matter of detrital origin and living organisms such as algae and bacteria provide interfaces for heavy metal adsorption [92-95]. Adsorption of heavy metals onto these surfaces regulates their solution concentration, which is also influenced by inorganic and organic ligands. Those ligands can be of biological origin such as humic and fulvic acids [96, 97] and of anthropogenic origin such as NTA, EDTA, polyphosphates, and others [98-101], which can be found frequently in contaminated soils and wastewater.

The most important parameters controlling heavy metal adsorption and their distribution between soil and water are soil type, metal speciation, metal concentration, soil pH, solid: solution mass ratio, and contact time [102-105]. In general, greater metal retention and lower solubility occurs at high soil pH [106]. To predict fate and transport of heavy metals in soils both conceptual and quantitative model approaches have been developed. These models include the determination of the nature of the binding forces, the description of the chemical and physical mechanisms involved in heavy metal–surface reactions and the study of the influence on variations of parameters such as pH, Eh, ionic strength and others on adsorption [83].

Some important factors influencing chromium mobility in soil are discussed here:

1.5.1 Clays

Several low cost adsorbents such as agricultural/industrial wastes and natural/synthetic clay minerals have been used as effective adsorbents for removal of heavy metals, organics and radionuclides [107, 108]. Hence, in the past decades, clay minerals have been used as effective adsorbents for heavy metal removal in water treatment because of their strong ion-exchange and complex formation abilities with the heavy metals [109, 110]. Knowing the sorption and desorption characteristics of the heavy metals on the clay mineral, will in no small measure, aid in modeling the behavior of the soil when contaminated by these heavy metals. It will also be achieved through studying adsorption and desorption behavior of clay minerals [108].

The clay buffer capacity and the initial pH play an importance role in the mobility of the heavy metals in the clay. Alkaline pH condition enhances the precipitation of the heavy metals, thereby reducing their mobility [111]. Clay minerals exhibit a strong affinity for heavy metals. They possess a wide pore size distribution, ranging from micro (< 20A^o) to mesopores (20-500 A^o). The ionic charges on the clay surface can also increase the adsorption capacity by attracting oppositely charged polluting substances and convert them into harmless or easily removed forms. A number of clay minerals have been investigated for water and waste water treatment, including sepiolite [112], kaolinite [113], montmorillonite [114], smectite [115] and bentonite [116].

1.5.2 Soil Matrix

Soil is a very complex heterogeneous medium, which consists of solid phases (the soil matrix) containing minerals and organic matter and fluid phases (the soil water and the soil air), which interact with each other and ions entering the soil system [117]. The ability of soil to adsorb metal ions from aqueous solutions has consequences for both agricultural issues such as soil fertility and environmental questions such as remediation of polluted soil and waste deposition. The solid state of soil composes an average of 45% of soil bulk. It consists of mineral particles, organic matter and organic-mineral particles. They all play a very important role in giving the soil the ability to adsorb, exchange, oxidise, reduce, catalyze and precipitate chemicals and metal ions [90].

Heavy metals added to soil will normally be retained at the soil surface. Movements of metals into other environmental compartments, i.e., ground water, surface water, or the atmosphere, should be minimal as long as the retention capacity of the soil is not exceeded. The extent of movement of a metal in the soil system is intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix. The retention mechanisms for metals added to soil include adsorption of the metal by the soil solid surfaces and precipitation. The retention of cationic metals by soil has been correlated with soil properties such as pH, redox potential, surface area, cation exchange capacity, organic matter content, clay content, iron and manganese oxide content, and carbonate content. Anion retention has been correlated with pH, iron and manganese oxide content, and redox potential.

Changes in the soil environment over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of soil matrix with reference to the metal and waste matrix. It has been found that the relative mobility of nine metals through Montmorillinite and Kaolinite to be **Cr(VI)** > Se > As(III) > As(V) > Cd > Zn > Pb > Cu > Cr(III) [118, 119].

1.5.3 Soil pH

Soil pH appeared to be greatest determination of Chromium solubility and mobility in a light textured sandy soil [120]. The mobility and bioavailability of heavy metals increases with decreased soil pH [121-123], thus enhancing the uptake of heavy metals by plants and thereby posing a threat to human health [124, 125]. Thus the soil pH was found to play the most important role in determining metal speciation, solubility from mineral surfaces, movement, and eventual bioavailability of metals, due to its strong effects on solubility and speciation of metals both in the soil as a whole and particularly in the soil solution [126, 127].

The soil components responsible for element adsorption include, soil humic substances, phyllosilicates, carbonates and variable charge minerals (constituents such as Fe, Al, Mn and Ti oxides, short-range ordered aluminosilicates as well as phyllosilicates coated by OH-Al or OH-Fe species whose charge varies with the pH of the soil solution). Unlike phyllosilicates, the variable charge minerals (crystalline and short range ordered Fe, Al, Mn-oxides, allophanes, imogolite) strongly retain heavy metals for their dependency on pH. On these materials a hydroxylated or hydrated surface, positive or negative charge is developed by adsorption or desorption of H^+ or OH^- ions [87].

The pH at which the net variable charge on the surfaces of these components is zero is called the point of zero charge (PZC). The reported PZC of Fe-oxides, range from pH 7.0 to 9.5, whereas that of Al-oxides ranges from pH 8.0 to 9.2 [128-130]. Variable charge minerals selectively adsorb polyvalent cations, even when their surfaces are positively charged (solution pH values lower than the point of zero charge [PZC] of the adsorbent). Some previous studies suggested that chromate forms an outer-sphere complex on the surfaces of Fe and Al oxides. However, spectroscopic studies have shown that chromate forms inner-sphere complexes on goethite [131, 132]. The pH value of the investigated soil is naturally alkaline (8.2) which promotes heavy metals precipitation and adsorption onto the clay surface. Soil organic matter plays an important role in the adsorption of heavy metal ions even in soils where its value is very low [85].

1.6 Adsorption Mechanism and Kineticts

The adsorption efficiency is often described by means of adsorption equilibrium isotherms and kinetic studies. Chemical kinetics can be defined for the soil chemical interaction as the study of the rate of chemical reaction and of molecular process by which the reaction occurs where transport is not limiting

[133]. The application of kinetic theories to heterogeneous soil constituents is one of the most important and challenging areas to be investigated. Chemical reactions in soils are generally heterogeneous, soil liquid reactions involve a solid component of the soil and the soil solutions. In the agriculture fields, interaction of soils with fertilizers ions, pesticides, insecticides, chemicals in irrigation water etc lead to several ion-exchange, adsorption, desorption and transport processes accompanied by displacement of solutes and adsorbates in a liquid phase, solid-phase and at the interface. The processes of ion-exchange, simultaneous adsorption and desorption of species bonded to charged surface of soil by electrostatic forces. Some methods commonly adopted to study kinetics of soil chemical interactions resulting in adsorption-desorption are as follow:

1.6.1 Kinetic Methodologies

Kinetics deals with description of time dependent processes which are path dependent. Methods helpful in obtaining kinetic data for studying various types of reaction in soil are mainly the following:

(i) Relaxation methods
(ii) Batch methods
(iii) Flow methods

Relaxation and batch methods are most suitable for adsorption studies only, while flow methods are widely applied for desorption and leaching studies. A good review on these methods is by D. L. Sparks (1989) [134]. R. A. Ogwada et al (1986) [135] have investigated the effect of kinetic methodologies and degree of agitation on rate parameters using five different methods. In the static technique, there was no mixing, in continuous flow and batch method agitation was done. The stirred method was based on stirring of the mixture. In a vortex batch technique, the mixture was rapidly mixed on a vortex mixer. Results showed that significant diffusion exist in the static and miscible displacement methods because of limited mixing.

Flow methods have been used in a number of kinetics studies on soil and soil constituents [136]. Flow methods have also been used on soil reactions by D. L. Sparks et al (1981), [137] and S. C. Hodge et al (1987) [138] for solute transport in soils.

1.6.2 Adsorption Equilibrium Study

Adsorption is usually described through an isotherm. The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [139]. The adsorption isotherm is useful for representing the capacity of an adsorption catalyst for providing description of the functional dependence of capacity on the concentration of pollutant. The steeper the isotherm, the more effective is adsorption that is, the sharper the rise of the isotherm to a given ultimate capacity as concentration increases, the higher will be the effective capacity at the concentration level desired for the treated water.

Experimental determination of the isotherm is a routine practice in evaluating the feasibility of adsorption process. The adsorption isotherm relates to an equilibrium condition, however any practical detention time used in most treatment applications do not provide sufficient time for true equilibrium to obtain. Rates of adsorption are thus significant, as more rapid the approach to equilibrium, the greater is the fraction of equilibrium capacity utilized in a given contact time.

Equilibrium adsorption isotherm is of important in designing the adsorption system. Several isotherm equations are available and three important isotherms i.e. Langmuir, Freundlich and Temkin isotherms have been used extensively by early researchers in this field [140].

Some of the studies conducted on adsorption-desorption of Chromium (VI) on different adsorbents have been summarized in **Table 1.1**.

Table 1.1: Some Previous Studies on Adsorption – desorption of Chromium (VI)

S. No.	Adsorbent	Experimental method	Reference
1.	Cellulose –clay composite biosorbent	Batch method	[141]
2.	EDTA modified cross linked chitosan resin	Batch method	[142]
3.	Eucalyptus bark	Batch method	[31]
4.	Activated carbon developed from Tamarind wood activated with Zinc Chloride	Batch method	[143]
5.	Tamarindus indica seeds	Batch method	[144]
6.	Polypyrrole magnetic nanocomposite	Batch method	[145]
7.	Waste Marigold Flowers	Batch method	[146]
8.	Flyash	Batch method	[36]
9.	Seeds of Artimisia absinthium	Batch method	[147]
10.	Modified and unmodified bentonite clay	Batch method	[148]
11.	Divinylbenzene copolymer resin	Batch method	[149]

12.	Mangrove leaf powder	Batch method	[150]
13.	Sulfuric acid - modified Avocado seed	Batch method	[67]
14.	Activated Carbon derived from Water Hyacinth	Batch method	[151]
15.	Activated Carbon primed from sugarcane bagasse	Batch method	[152]
16.	Chitosan powder	Batch method	[76]
17.	Organobentonite	Batch method	[153]
18.	Admixtures of rice husk, shredded tyre and fly ash	Batch method	[154]
19.	Natural clay used as Landfill liner	Batch method	[155]
20.	Chemically modified Okra Powder	Batch method	[156]
21.	One step steam pyrolysis corn cobs activated carbon	Batch method	[157]
22.	Tamarind Pod Shell and Carbon	Batch method	[2]
23.	Soil Colloids	Batch method	[158]
24.	Palm tree branches	Batch method	[66]

1.7 Scope of the Work

The main objective of the present study was to understand the process of the adsorption desorption of the Chromium(VI) onto the soil. The study aimed to investigate natural processes involved in adsorption of Chromium(VI) through physical and chemical processes. The effect of variation of different parameters on migration and adsorption of Chromium(VI) on soil has also been included. The studied parameters mainly consist of initial Chromium(VI) concentration, contact time, particle size of soil, amount of soil, pH of solution, and temperature. The experiments were conducted and the best fitted kinetic model and adsorption isotherm for the adsorption of Chromium(VI) onto the soil evaluated. The parameters which influence mobility of Chromium(VI) in the subsurface soil and groundwater have been studied to predict further contamination trends under various soil conditions. Thermodynamic parameters, for instance enthalpy, Gibbs free energy and entropy were evaluated to predict feasibility of adsorption processes.

Remediation of the Chromium(VI) contaminated sites is often an costly and time consuming process. Understanding of the physico-chemical processes which affect adsorption and chemical state of Chromium(VI) is required to work out any preventive/remedial strategy for remediation of Chromium contaminated soil.

This study emphasizes to determine remediation of already contaminated sites and to work out possible preventive measure to protect soil and water resources from getting contamination. Results may also provide guidance for selection of appropriate and cost-effective remediation methods for contaminated sites, and the study will help in designing the remedial/precautionary measure to check the environmental pollution through soil and ground water. The study may also be helpful for Pollution Control Board in framing guide line for disposal of chemical waste from industries.

1.8 References

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Chapter – 2

Materials, Methods and Physico-Chemical Characterization of the Soil

ABSTRACT

The chapter incorporates the details of various chemicals and reagents, equipments, method of spectrophotometric determination of Chromium(VI) by 1, 5 Diphenylcarbazide, sample collection, geography of study area and ground water scenario of Bhilwara district. Method of Batch sorption experiment, physico-chemical characteristics of soil samples, analysis of soil by XRF, XRD, FTIR techniques, SEM image analysis of soil before and after adsorption of Chromium(VI) and point of zero charge have also been described in this chapter.

This chapter describes the details of various chemicals and reagents, equipments and analytical procedures adopted to study of the adsorption of Chromium(VI) on Chromium contaminated soil. Soil characteristics, geography of study area and analysis of soil by XRF, XRD, FTIR and SEM, techniques have also been described in this chapter.

2.1 Chemicals and Reagents

1. **Potassium dichromate stock solution:** Stock standard solution of Chromium(VI), obtained by weighing 0.2829 g amount of potassium dichromate and diluting it with deionized water making solution of 1000 ml; 1 ml of thus-prepared solution contained 0.1 mg of chromium (VI)
2. **Potassium dichromate standard solution:** Working solution of desired strength of Chromium(VI) was prepared by diluting the stock standard solution with doubly distilled water.
3. **Sulfuric acid, 10% (v/v):** Dilute 10 mL of AR grade (Ranbaxy) sulfuric acid, H_2SO_4, to 100 mL with deionized water.
4. **Diphenylcarbazide solution:** 0.5% solution of 1,5-diphenylcarbazide $(C_6H_6NHNH)_2CO$, obtained by dissolving 0.5 g of 1,5-diphenylcarbazide in acetone up to 100 ml and stored in a brown bottle. Discarded when the solution became discolored.
5. **Acetone:** Acetone of AR grade of Sigma-Aldrich was used for making Diphenylcarbazide solution.
6. **Concentrated orthophosphoric acid:** AR grade orthophosphoric acid of Sigma-Aldrich was used.
7. **Ammonium peroxydisulphate solution:** solution of ammonium peroxydisulphate was used as oxidizing agent.
8. **EDTA Solution:** EDTA solutions of desired strength were prepared by using AR grade disodium etylenediaminetetraacetate (Na_2EDTA) of Merck.
9. **Sodium Hydroxide (NaOH):** The solution of sodium hydroxide was prepared by dissolving an approximately weighed pellets of NaOH (BDH, AR grade) in doubly distilled water for maintain the pH of solutions and for preaparing the desired strength solutions.

10. **Concentrated HCl:** AR grade HCl of sigma Aldrich was used for preparation of HCl solution of desired strength and for maintaing the pH of solutions.
11. **Calcium Chloride solution ($CaCl_2$):** AR grade $CaCl_2$ of sigma Aldrich was used for preparation of solution of desired strength.
12. **Sodium Nitrate ($NaNO_3$):** AR grade $NaNO_3$ of BDH was used for preparation of solution of desired strength.
13. **Sodium Sulphate (Na_2SO_4):** Na_2SO_4 from Ranbaxy AR grade was used for preparation of solution of desired strength by dissolving in deionized water.
14. **Magnesium Chloride ($MgCl_2$):** $MgCl_2$ from Himedia was used for preparation of solution of desired strength by desolving in deionized water.

2.2 Equipments

1. **pH-Meter:** The Systronics digital pH meter model, 335 was used for measuring pH of the reaction mixtures and for calculating pH_{pzc} with the maximum uncertainity in pH of ± 0.01 unit..
2. **Mini Rotatory Flask Shaker:** Mac Mini rotator flask shaker (MSW 303) was used to obtained supernatant liquid from solution.
3. **Centrifuge:** Centrifuge with 8×15 ml swing out heads was used to obtained supernatant liquid from solution.
4. **Electronic Balance:** K. Roy electronic balance was used for weighing purposes. The least count of balance is 0.0001 mg.
5. **Stirrer:** Abron exports magnetic stirrer with hot plate was used for stirring soil suspension at a fixed and suitable rpm.
6. **Test Sieve:** Different types of test sieves ranging from 100 BSS to 300 BSS were used for sieving the soil samples.
7. **Thermostate:** For maintaining the temperature of the solution Chino fabricated thermostate with electronic relay was used.
8. **UV-Visible Spectrophotometer:** Systronics UV-Visible Spectrophotometer 118 model was used for calculating the concentration of Chromium(VI) by measuring absorbance at $\lambda = 540$ nm.
9. **X-Ray Diffractometer:** Soil sample was characterized for structural analysis using X-Ray diffractometer at Panjab University Chandigarh.

10. **Scanning Electron Microscope (SEM):** Morphological studies soil sample were performed on Scanning Electron microscope of EVO 18 carlzeiss model at USIC Department, University of Rajasthan, Jaipur.

11. **FT-IR Spectrometer:** FT-IR analysis was carried out by using FT-IR spectrophotometer to study the chemical bonding present in the adsorption of Chromium(VI). It delivers excellent sensitivity reproducibility and stability. FTIR spectrophotometer (Alpha-T model, Bruker, Germany) is used to record the FTIR spectra in the range of 400-4000 cm^{-1} by mixing the sample with dried KBr (in 1:20 weight ratio) with a resolution of 4 cm.

12. **Wave-Dispersive X-Ray fluorescence Spectrometer (WD-XRF):** Analysis of soil sample was done by using Wave-Dispersive X-Ray fluorescence Spectrometer at SAIF, Panjab University Chandigarh.

2.3 Sample Collection and Treatment

The soil samples were collected from the process house, IV phase, RIICO industrial area, BHILWARA from different depths which are given below:

1. From (0-15) cm. Depth, IV Phase, RIICO Industrial Area, BHILWARA, $\mathbf{[S_1]_{0-15}}$
2. From (15-30) cm. Depth, IV Phase, RIICO Industrial Area, BHILWARA, $\mathbf{[S_2]_{15-30}}$

The soil samples were dried in air for about three weeks. After drying the soil was sieved in order to obtain different particle size distribution (100-300 BSS).

2.4 Geography of Study Area

Bhilwara is famous as "the city of textiles & looms". 25.35°N and 74.63°E. It has an average elevation of 421 metres (1381 feet). It falls between the districts of Ajmer (in north) and Chittorgarh and Udaipur (in south). Major rivers flowing through the district are Banas, Bedach, Kothari, Khari, Mansi, Menali, Chandrabhaga and Nagdi. There is no natural lake in the district but there are number of ponds and dams so the district is the most irrigated in the state of Rajasthan.

The major industry is textiles, with more than 850 manufacturing units in the town. The main textile product is synthetic fabric used in trousers. The city boasts of producing around a billion metres p.a. of trouser fabric, making Bhilwara one of the major textile centres in India. The city has nine major and five small spinning mills. The total spindlage installed at Bhilwara are approximately 4.50 lacs, about 40% of the state capacity. It has 18 modern process houses to process polyester/viscose suiting with the annual capacity of a billion metrers of fabric. In the weaving sector it has approximately 13,500 looms out of which about 9000 are modern shuttleless ones [1].

2.5 Ground Water Scenario of Bhilwara District, Rajasthan

Soils of the district are classified as follows: ‘Clay loam or medium black’, this type of soil is found in the hilly areas in the central parts of the district. ‘Loam’, this type of soil is found in the entire district. ‘Sand and sandy loam’, this type of soil is found mostly near the banks of rivers and nallahs. ‘Loam pebbly and stony’, these types of soils are met within the hilly areas of the eastern blocks of the district [2].

Textile industries of Bhilwara produce 75 per cent of the country's textile. There are hundreds of synthetic textile units in outskirts of Bhilwara on Chittorgarh, Gangapur and Mandal roads. Most units are involved in spinning, dyeing and weaving. The industry's poor effluent management system has long poisoned the area affecting air, surface and subsurface water, agricultural lands and human health. A study by the state public health engineering department in 2004 found that most open wells in villages near the Kothari river that flowed beside the industrial belt had Chromium (Cr), lead (Pb), iron (Fe), zinc (Zn) and sodium (Na) above the norms set by the Bureau of India Standards. These chemicals were similar to those found in textile unit's waste. The untreated and partially treated effluents from the factory are either flowing into the *nala* that joins the major rivers, or percolating in the sandy river bed. Villages downstream had been affected. Water in open wells in these villages has turned green and water from handpumps smells and tastes of chemicals [3].

A study through National Geochemical mapping (NGCM) programme of Geological Survey of India (GSI) reveals that the areas with agricultural land use and stream water near the Banas and Kothari rivers (**Figure 2.1)**, those flow beside the industrial belt had Cr, Pb, Zn, Fe_2O_3 and Na_2O above the toxicity limit which corroborate the fact mentioned above. Agricultural activity in 8-10 other villages located downstream of the Banas river towards village Mangroop has reached a standstill.

Chromium is one of the important micro-nutrients, which regulates the plant growth and it is taken up as chromate by plants. Its mobility in plants is very low, and leads to enrichment and toxicity in soil. As far as the agricultural practice is concerned, soil with Chromium concentration more than 64 ppm is considered to be toxic. Most part of the area shows concentration more than this value (**Figure 2.2)**, which probably have been derived from the effluents released from the textile industries and resulted in toxicity of the soil [3].

In Bhilwara, there are many Textile industries and according to study based on NGCM programme in Rajasthan certain areas of Bhilwara having Chromium up to 160 to 190 ppm [3]. So in this area Chromium should be considered in the critical range of toxicity.

2.6 Batch Adsorption Experiments

The Batch tests were carried out in 250 ml flask using a contaminated soil as a adsorbent. A stock solution of Chromium(VI) is prepared by weighing 0.2829 g amount of potassium dichromate and diluting it with deionized water making solution of 1000 ml and this solution is diluted as required to obtain solution containing different initial concentration. A 2 g soil was mixed with 100ml of the aqueous solutions of various initial concentration (0.5 mg, 1 mg, 2 mg, 3 mg and 5 mg) of chromium (VI) in each flask. The stirring speed was kept constant at 120 rpm. The flasks were shaken at a constant rate, allowing sufficient time for adsorption equilibrium. It was assumed that the applied shaking speed allows all the surface area to come in contact with heavy metal ions over the course of the experiments. The study was performed at room temperature to be representative of environmentally relevant condition. The effects of various parameters on the rate of adsorption process were observed by varying initial Chromium(VI) concentration, amount of soil, particle size, pH of solution and temperature of the

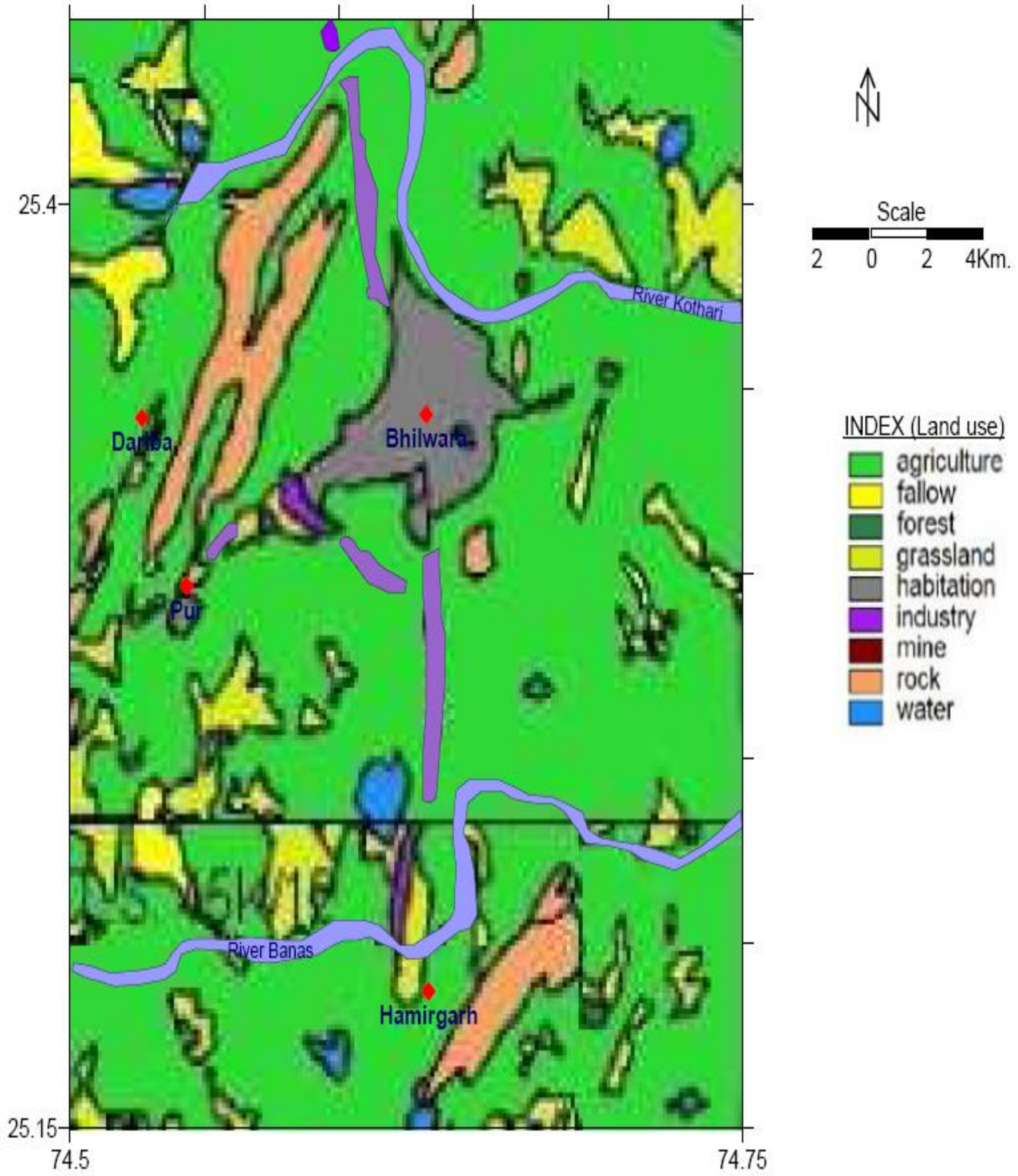


Figure 2.1: The land use map of the industrial belt of Bhilwara (Based on the satellite imagery data) [3].

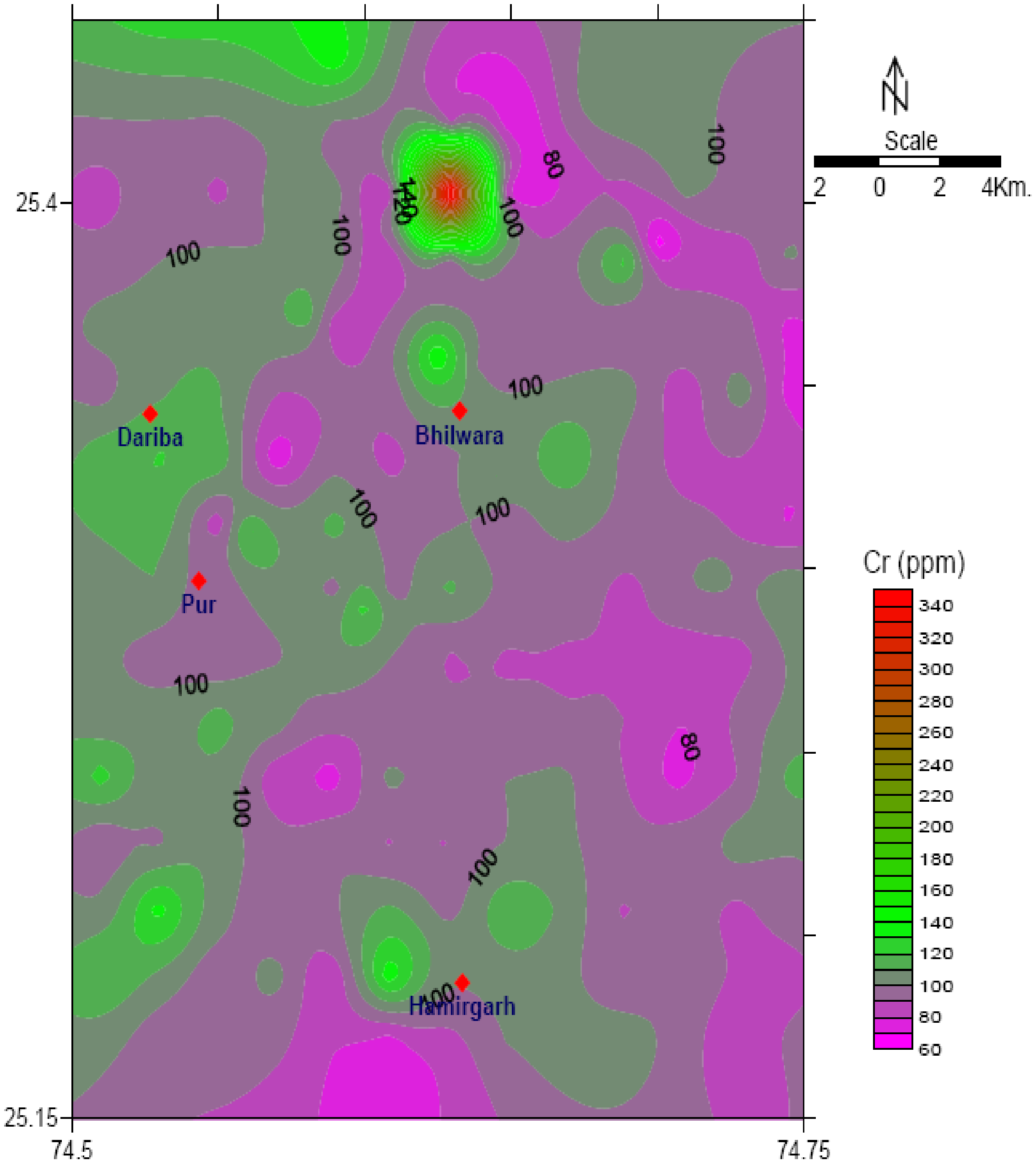


Figure 2.2: Geochemical contour map showing the distribution of Chromium in the industrial belt of Bhilwara, Rajasthan. [More than 90% of the areas of agricultural land use shows Chromium toxicity (>64ppm)] [3].

solution. The solution volume (V) was kept constant. The change in Chromium(VI) concentration due to adsorption was determined spectrophotometrically according to standard method [4]. The measurements were made at the wavelength λ=540nm, which corresponds to maximum absorbance [5]. A purple-violet colored complex was developed in the reaction between Chromium(VI) and 1, 5-diphenylcarbazide in acidic condition. Using the **Equation 2.1**, the concentrations of Chromium(VI) at different time adsorbed in soil solids was calculated,

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{2.1}$$

Where q_t is the amount of Chromium(VI) adsorbed onto the soil at time t, C_o is the initial concentration of Chromium(VI), C_t is aqueous phase concentration of Chromium(VI) at time t, V is the volume of the aqueous phase, and M is the weight of soil sample.

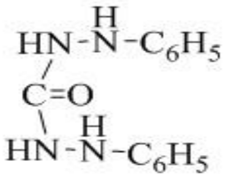
2.6.1 Color Development and Measurement of Chromium(VI) by Diphenylcarbazide Method

Figure 2.3: Development of color by Diphenylcarbazide method.

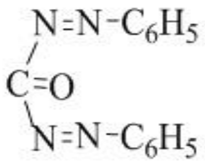
A colorimetric method was used to determine soluble Chromium(VI) in soil. 1 ml of the extract to be tested was transferred to a 50-mL volumetric flask. 1:1 H_2SO_4 solution to give a pH of 2 and 2.0 ml diphenylcarbazide solution was added in it and mixed. Then diluted to 50 ml with doubly distilled water, and was stand for 5 to 10 min for full color development (**Figure 2.3**). An appropriate portion of the solution was transferred in to a 1-cm absorption cell and measures its absorbance at 540 nm. Doubly distilled water was used as a reference. From the absorbance, amount of Chromium present in sample was determined by reference to the calibration curve [6].

2.6.2 Principle of Chromium(VI) Determination by U. V. Visible Spectrophotometric Method

The diphenylcarbazide method involves the formation of a purple-red complex of Chromium(VI) with 1, 5- diphenylcarbazide in the acidic medium. Its molar absorption coefficient at λ=540 nm is 4.3 x 10^4. The obtained color is a result of the redox reaction (**Equation 2.2**) of 1, 5-diphenylcarbazide with Chromium(VI) in acidic solution to form the Cr(III)-diphenylcarbazone complex that absorbs electromagnetic energy at 540 nm [7]. The acidity of the analyzed solution influences the intensity of the color, so it should be maintained at the same level. The recommended pH is about 1-2 since it ensures high sensitivity of the reaction. The color is stabilized by the presence of orthophosphoric acid. The diphenylcarbazide method of determination of Chromium(VI) can be considered selective. [8-10].



diphenylcarbazide



diphenylcarbazone

$$2Cr(VI)+3diphenylcarbazide \rightarrow Cr(III)+3diphenylcarbazone \tag{2.2}$$

2.6.3 Determination Procedure for Preparation of Calibration Curve

In order to plot the calibration line, 0.0, 0.2, 0.6, 1, 1.5, 2.0, 3.0, 5.0, 6.0, 8.0, and 10.0 ml of the working Chromium(VI) solutions were measured in turns into 50 ml flasks, which corresponded with the Chromium(VI) content in a sample ranging from 0.0 to 0.05 mg. 1.0 ml of H_2SO_4 (1:1) and 0.3 ml of concentrated H_3PO_4 were added and the solution was diluted with distilled water up to the mark. After 5 minutes, 2.0 ml of 1, 5-diphenylcarbazide was added to each sample. After another 10 min, the absorbance of the solutions was measured in 1 cm cells at λ=540 nm against blank test. The dependence between the concentration of Chromium(VI) and absorbance is rectilinear over the whole range of the examined concentrations (**Figure 2.4**) and its correlation coefficient is 0.993.

A similar procedure was used to determine the content of Chromium in the soil samples. The content of Chromium in the soil was calculated according to the **Equation 2.1**.

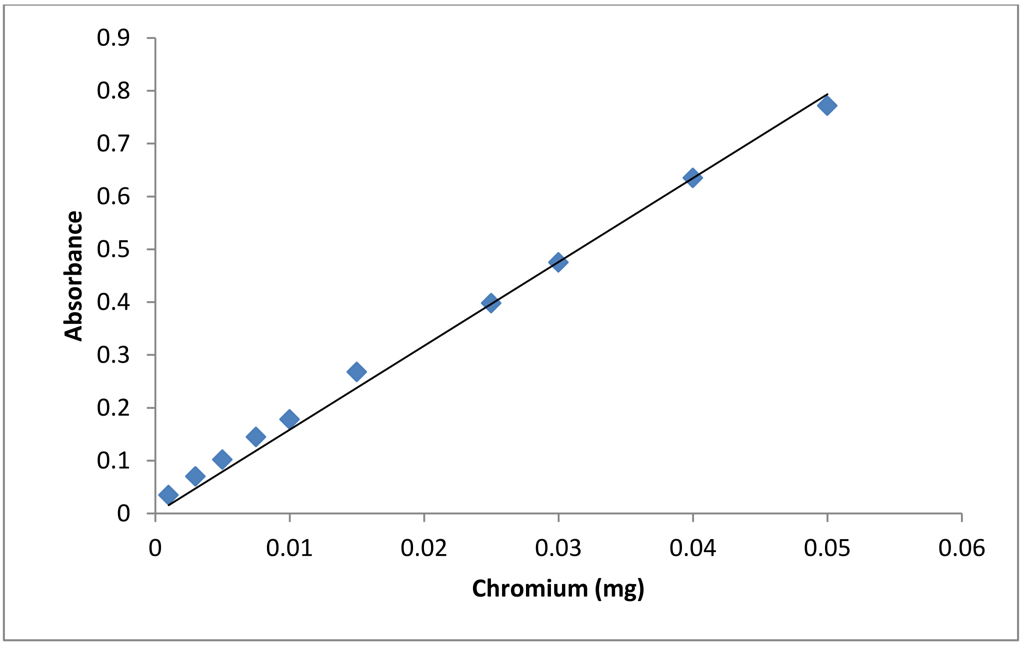


Figure 2.4: Calibration line for determination of Cr(VI) in the form of a complex with 1, 5-diphenylcarbazide.

2.7 Physico-Chemical Characterization of Soil Sample

The experimental portion of this research was conducted in two phases. The first phase was pretreatment and characterization of soil sample collected from RIICO Industrial Area, Bhilwara. The second phase was a series of Chromium experiments to determine the kinetics of the adsorption reactions, the amount of adsorption as a function of initial Chromium(VI) concentration, particle size, pH of solution and amount of soil. Best suitable adsorption isotherm was determined for adsorption process. Desorption experiments was carried out by soil washing, by NaOH and EDTA.

2.7.1 Physico-Chemical Characteristics of Soil

The tests were Performed with the help of CEG test house and research centre Jaipur, and RARI, Durgapura Jaipur and given in **Table 2.1** and **Table 2.2**

Table 2.1: The Physico-chemical characteristics of the soil $[S_1]_{0-15}$.

S. No.	**Parameters**	**Soil**
1.	**pH**	**8.2**
2.	**Conductivity (dS/m)**	**0.21**
3.	**Organic Carbon**	**0.18 %**
4.	**Phosphate (per Kg)**	**24**
5.	**Potash (per Kg)**	**254**
6.	**Clay Content**	**3.67 %**
7.	**Sand Content**	**72.57 %**
8.	**Silt Content**	**23.76 %**
9.	**Sodium absorption ratio**	**28.59**
10.	**Cation Exchange Capacity (meq/100gm)**	**5.10**

According to Rajasthan State Pollution Control Board, soil sample collected from RIICO Industrial Area, Bhilwara, IV Phase (Process House) have 202.91 mg/kg Total Chromium.

Table 2.2: **The Physico-chemical characteristics of the soil $[S_2]_{15-30}$.**

S. No.	**Parameters**	**Soil**
1.	**pH**	**8.3**
2.	**Conductivity (dS/m)**	**0.22**
3.	**Organic Carbon**	**0.19 %**
4.	**Phosphate (per Kg)**	**21**
5.	**Potash (per Kg)**	**249**
6.	**Clay Content**	**4.66 %**
7.	**Sand Content**	**71.37 %**
8.	**Silt Content**	**23.97 %**
9.	**Sodium absorption ratio**	**29.69**
10.	**Cation Exchange Capacity (meq/100gm)**	**5.86**

2.8 X-Ray Fluorescence Study

The XRF method was used for analysis of an element's total concentration in examined soil [11]. As soil are ensemble of elements, therefore a multi element technique capable of determining elements with accuracy is preferable. One such technique is XRF in which major elements were analyzed on a fused glass beads at 50 kV and 50 mA tube operating conditions. The intensity obtained for the elements were calibrated by using standards for both major and minor element analysis [12].

X-ray Flourescence (XRF) analysis is a widely used method of elemental analysis and chemical analysis providing both qualitative and quantitative compositional information. XRF can measure the wide range of measurable elements covering nearly the entire periodic system. X-ray fluorescence model Bruker S8 Tiger is used for the present work. It is a wavelength dispersive X-ray fluorescence (WD-XRF), which separates the characteristic wavelength with a very high degree of resolution. Optimized analyzer, crystals and detectors are used to separate and count the emitted X-rays. WD-XRF is unsurpassed in terms of analytical accuracy and precision. In this method, the sample is excited with a primary X-ray beam, causing the sample to have fluorescence. The primary X-rays eject electrons out of the inner atomic shells (K- and L-shell). The resulting "vacancy" is filled by an electron transition takes place only between the inner shell of the atom, which are not involved in chemical bonding. Hence the samples can be analyzed directly without advanced sample preparation.

X-ray fluorescence (XRF) spectrometry has also been used for analysis and speciation of Chromium(III) and Chromium(VI) [13-16]. The main advantage of this technique is its capability of direct analysis of solid and liquid samples, avoiding sample handling or at least reducing it to a minimum.

2.8.1 Results and Discussion

The XRF analysis of soil sample before and after adsorption of Chromium(VI) shown in **Table 2.3** XRF analysis confirm the following composition of the elements in the soil before adsorption of Chromium(VI) : CaO (64377 ppm), MnO (0.26%), SiO_2 (61.66%), Fe_2O_3 (8.94%), Ni (407 ppm), Cr (203 ppm), Co (26 ppm) and Zn (121 ppm). After adsorption of Chromium(VI), XRF revealed the following results: CaO (61675 ppm), MnO (0.25%), SiO_2 (60.23%), Fe_2O_3 (7.80%), Ni (305 ppm), Cr (226 ppm), Co (23 ppm) and Zn (119 ppm). The result confirmed the adsorption of Chromium(VI) by soil sample by the increase in its composition from 203 ppm to 226 ppm. Amount of CaO decreases from 64377 ppm to 61675 ppm which indicates that Chromium bind with the Calcium after its adsorption onto soil sample. It is also in good agreement with the result of XRD in **Section 2.9** which confirm the formation of

Table 2.3: Chemical Composition of $[S_1]_{0-15}$, before and after Cr(VI) adsorption, determined by XRF technique

Chemical Components	**$[S_1]_{0-15}$, Before adsorption of Cr(VI) ppm**	**$[S_1]_{0-15}$, After adsorption of Cr(VI) ppm**
CaO	**64377**	**61675**
Sc	**18**	**16**
SiO_2	**61.66 %**	**60.23 %**
TiO_2	**0.88 %**	**0.87 %**
V	**511**	**532**
Cr	**203**	**235**
MnO	**0.26 %**	**0.25 %**
Fe_2O_3	**8.94 %**	**7.80 %**
Co	**26**	**23**
Ni	**407**	**305**
Cu	**132**	**135**
Zn	**121**	**119**
Ga	**21**	**19**
As	**9**	**12**
Rb	**59**	**59**
Sr	**123**	**117**
Y	**30**	**26**
Zr	**202**	**169**
Nb	**16**	**14**
Mo	**3**	**2**
Sn	**0.0**	**1**
Sb	**2**	**4**
Cs	**5**	**7**
Ba	**222**	**239**
La	**35**	**37**
Ce	**77**	**75**
Pb	**32**	**34**
Th	**9**	**9**
U	**2**	**2**
Compton	**77.40 %**	**77.13 %**

Chromatite ($CaCrO_4$). The composition of the other elements also changes after Chromium(VI) adsorption indicates that these metals solubilize with water due to constant stirring at the time of adsorption experiment.

2.9 X-Ray Diffraction Study

X-ray diffraction (XRD) pattern for soil samples before and after Chromium(VI) adsorption was recorded with pananalytical X-ray diffractometer using CuKα radiation ($\lambda = 1.5406$ A^o). The Kα radiation was selected with a diffracted beam monochromator at 25 kV, and the diffraction pattern was collected from 4 to 80 º 2θ with a step size of 0.4–0.5° 2θ for 50 minutes in order to acquire X-ray patterns with sufficiently high intensities to identify the minerals present.

In XRD the parallel planes inside the crystal called lattice planes are designated by their integers *h, k,* and *l* called miller indices, which are of the reciprocals of the intersection between the lattice plan and the three crystallographic axis that span the unit cell of the crystal. A given set of planes with indices *h, k, l* cut the a-axis of the unit cell in h section, b axis in k sections and the c-axis in l sections. The incident X-ray beam and the lattice planes have to be oriented in a certain angle (θ) to allow diffraction. Beams reflected at parallel lattice planes in the distance (d_{hkl}) interfere and give intensity maximum, which occurs as a peak in x-ray diffractogram, if their path difference $2d_{hkl}$ is an integer of wavelength (λ). This relationship can be expressed mathematically in Bragg's law [17, 18] as given in **Equation 2.3**.

$$n\lambda = 2.d_{hkl}.\sin\theta \qquad (2.3)$$

The X-ray diffractogram consists of a plot of reflected intensity versus the diffracted angle 2θ. In powder samples with randomly oriented crystallites, the same amount of the crystallites has the right orientation for the diffraction for all lattice planes. If instead a certain pattern is preferred the intensity of some reflection is lowered or increased. Information about the lattice parameters is available from peak position. The sharpness of the diffraction lines is determined from their intensity together with their breadth, which is called the full width at half maximum (FWHM). The breadth of the peak is increased with decreasing crystallites size. The XRD patterns of a sample show the intensity of X-ray diffracted by different planes of the crystal at different angles. The crystal phase identification is based on the comparision of the set of reflections of the specimen with that of pure references phases or with database [19]. X-ray diffraction line broadening analysis is used to determine crystallite size of the crystalline phase using the Scherrer formula [20, 21] as in **Equation 2.4** where,

$$Crystallite \quad size = K\lambda / W.\cos\theta \tag{2.4}$$

K = shape factor, λ = wavelength of X-ray radiation use, W = difference of broadened profile width of the experimental (W_b) and standard profile width of the reference sample (Ws), θ = angle of diffraction.

Compounds were identified by comparing with the Joint Committee on Powder Diffraction Standards (JCPDS) cards in the conventional way.

2.9.1 Results and Discussion

The XRD pattern of the soil sample, before adsorption of Chromium(VI) shows sharp and pointed diffraction peaks (**Figure 2.5**) at 2θ values corresponding to 5.94^o, 10.46^o and 26.63^o, which indicates the crystalline nature of the soil with certain degree of exfoliation. After the adsorption of Chromium(VI) the new sharp peaks obtained at 2θ values corresponding to 20.82^o, 21.96^o, 27.87^o, 42.41^o, 49.11^o, 50.67^o and 59.88 respectively [22]. Interestingly, the crystalline nature of the soil is not disturbed after the adsorption of Chromium (**Figure 2.6**) and the new sharp peaks obtained at 2θ values corresponding to 42.41^o, 49.11^o, are attributed to the adsorption of Chromium which concurs with the reported values in literature [23]. The peak with 2θ 50.67^o correspond to Cr_2O_3 [24].

The characteristic peaks of quartz (SiO_2) at $2\theta = 26.63^o$ [25], (JCPDS card 33 – 1161) [26], But after the adsorption of Chromium(VI) the spectrum appears with a peak at $2\theta = 26.58^o$, which indicates that the material is amorphous and contain pure SiO_2 [27, 28]. The X-ray diffraction analysis (**Figure 2.6**) showed the presence of chromatite, $CaCrO_4$ (JCPDS card 8-0458) identified by 49.1^o 2θ peak [26, 29-30], like a main crystalline phase.

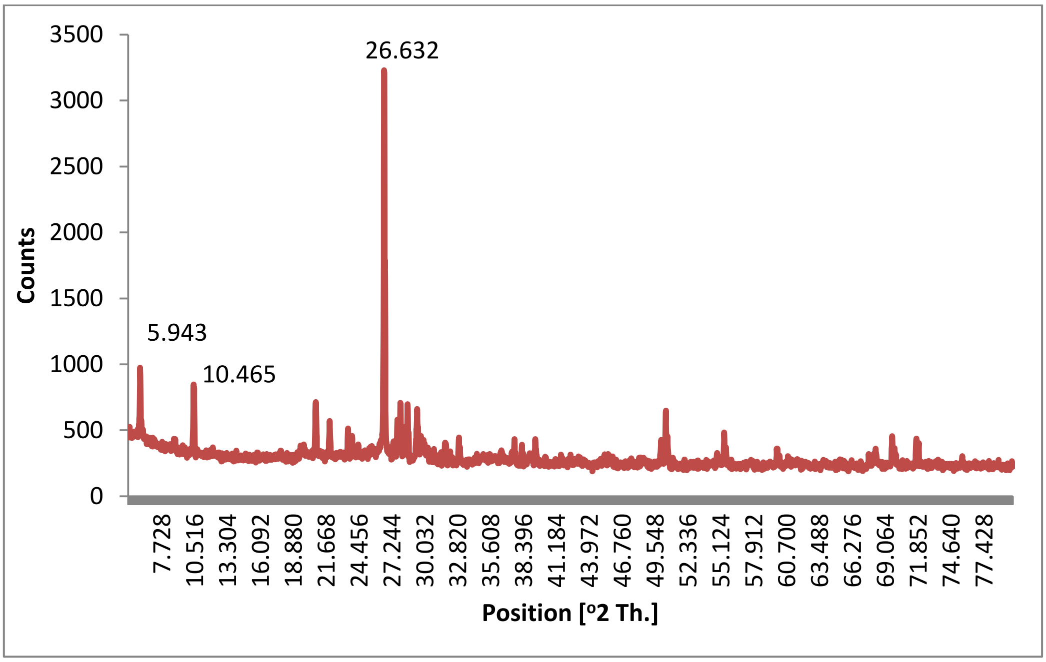


Figure 2.5: X-ray diffraction pattern of soil sample before adsorption of Chromium(VI).

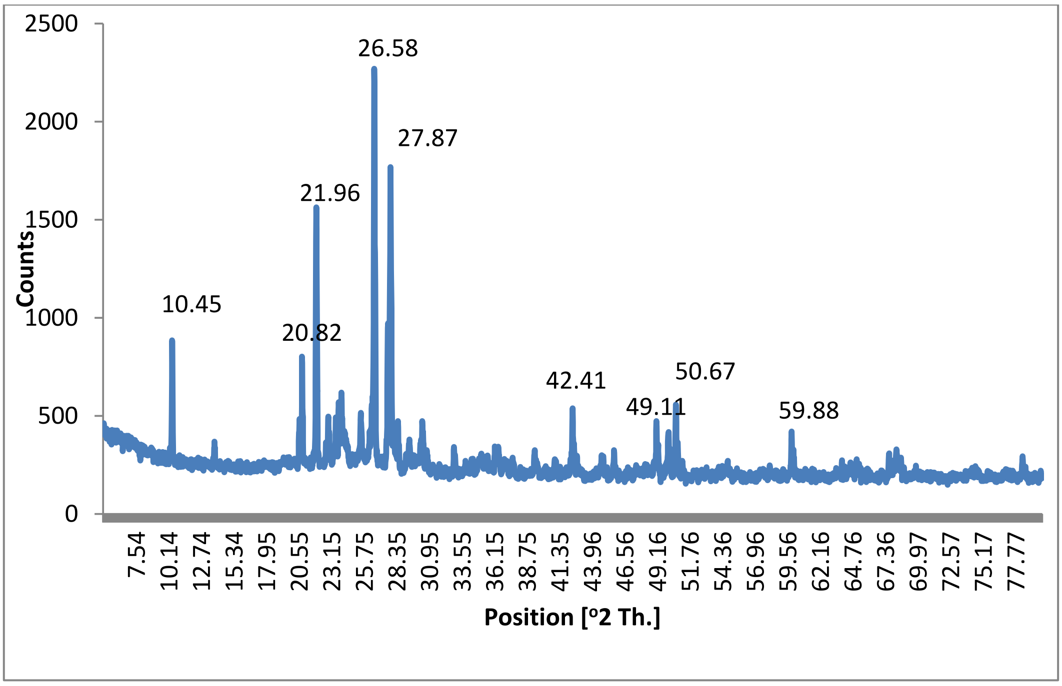


Figure 2.6: X-ray diffraction pattern of soil sample after adsorption of Chromium(VI).

2.10 Fourier Transform Infra-Red (FT-IR) Spectroscopy

The FT-IR spectrum of soil was used to investigate the functional groups present on the soil that could be responsible for the adsorption of heavy metal species [31]. By the help of this technique we can identify unknown materials, can determine the quality or consistency of a sample and the amount of components in a mixture. An infrared spectrum represents a fingerprint of a sample with adsorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. This technique works on the fact that bonds and groups of bonds vibrate at characteristic frequency. The interactions of IR radiation with molecules result to variation in the dipole moment and therefore, the transition take place in vibrational energy levels of the molecules, which are quantized. The activation of the molecule leads to different mode of fractional motions such as stretching (symmetric and asymmetric) and bending, promotes the molecule in higher vibrational energy level. The energy of the stretching vibrational motion is higher than that of the bending vibration and the asymmetrical stretching motion (asymmetrical stretching frequency) is higher in energy than symmetrical stretching (symmetrical stretching frequency). The transition in vibrational energy levels of the molecules gives IR spectrum, which is the graph between the wave number and the % transmittance or absorbance. FT-IR was performed by mixing the sample with KBr in 1:20 weight ratio. Spectra were recorded in the range 400-4000 cm^{-1} with a resolution of 4 cm^{-1} by using FT-IR spectrophotometer (Alpha-T model, Bruker, Germany).

2.10.1 Results and Discussion

The FTIR spectra of the soil sample before adsorption of Chromium(VI) are shown in **Figure 2.7**. A broad peak at 3421 cm^{-1} is due to –OH stretching (surface –OH of SiOH) [32, 33], which indicate the presence of hydroxide group in the sample and that at 2924 cm^{-1} is attributed to C-H stretching vibration in soil. A peak around 2514 cm^{-1} shows ν–OH stretching [34]. The band at 1629 cm^{-1}

and 1428 cm^{-1} could be ascribed to the H-OH bonding in water and CaO/ CO_3^{-2} respectively [35]. The peak characteristics of soil were observed at 1028 cm^{-1} (Si-O- Ca stretching) [36], 781 cm^{-1} (Si-O stretching of quartz and silica), 485 cm^{-1} (Si-O-Fe deformation) and 416 cm^{-1} (Si-O-Si deformation), respectively [37-40].

The FTIR spectra of the soil sample after adsorption of Chromium(VI) are shown in **Figure 2.8**. After adsorption, the FTIR spectrum of Chromium(VI)-soil shows that peaks at 2924 cm^{-1} and 2514 cm^{-1} almost disappear and the peak 3421 cm^{-1}, 1629 cm^{-1}, 1428 cm^{-1}, 1028 cm^{-1}, 781 cm^{-1} and 485 cm^{-1} was shifted to 3418 cm^{-1}, 1631 cm^{-1}, 1425 cm^{-1}, 1027 cm^{-1}, 775 cm^{-1} and 483 cm^{-1} respectively. The new peaks also appear at 689 cm^{-1} and 447 cm^{-1}. The appearance of some of the functional group in the range of 400-800 cm^{-1} may be due to C-metal bonds present at the surface of soil [41].

Comparison of the characteristic absorbance range of various functional groups/vibrational bands of soil samples before and after adsorption of Chromium(VI) are given in **Table 2.4**.

There are considerable amendments in the spectral features after the adsorption of hexavalent Chromium and the change is more obvious in the O-H region of the FT-IR spectrum. Chromium(VI) exists primarily as bichromate ion ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) in acidic medium [42]. A shifting in the peak 3421 cm^{-1} to 3418 cm^{-1} indicating interaction between hydroxyl group and Chromium ions. This fact is also substantiated through the appearance of characteristic Cr-O and Si-O deformation peaks at 775 cm^{-1} and 689 cm^{-1}, respectively [43].

Hydrogen bonding interaction is also probable between the hydroxyl protons in soil and the oxygen atoms in the bichromate anion. Furthermore, it is also probable that the silanol groups in soil could be protonated as $SiOH^{2+}$ in acidic medium and this would further reinforce the interaction of bichromate anion with the positively charged soil surface [44, 45]. This is in agreement with the discussion in **Section 3.3.4** of **Chapter 3** on the effect of solution pH. The shift in the wave number corresponds to the change in the energy of the functional groups, indicates the existence of Chromium binding process on the surface of the soil [46].

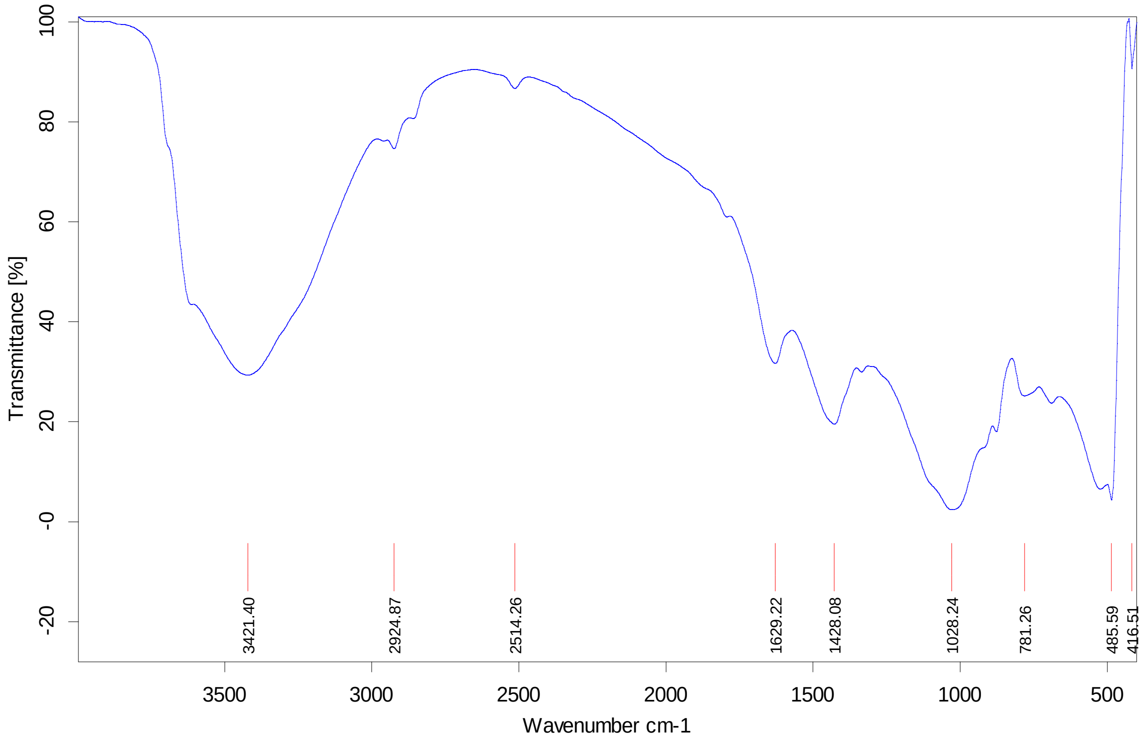


Figure 2.7: FT-IR spectra of soil sample before adsorption of Chromium(VI).

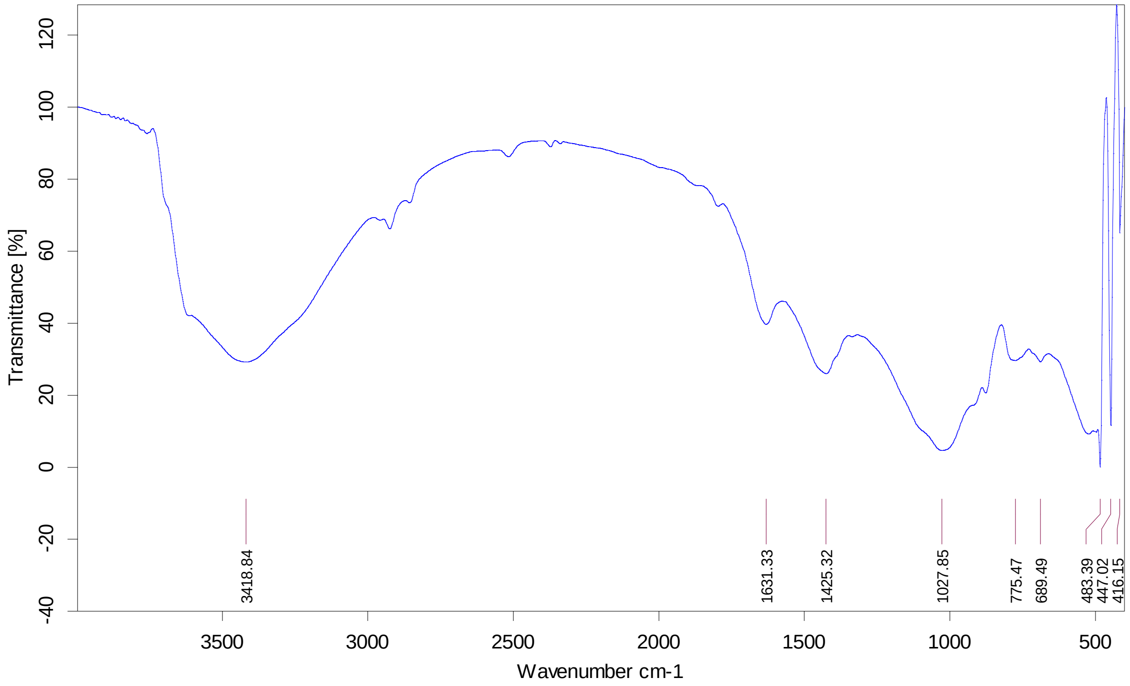


Figure 2.8: FT-IR spectra of soil sample after adsorption of Chromium(VI).

Table 2.4: Results of FTIR bands for soil sample collected from IV phase RIICO industrial area, Bhilwara.

S. No.	**Chemical functional group/ Vibrational band**	**Characteristics absorption range, Wavelength (cm^{-1})**		**Ref.**
		Before adsorption of Cr(VI)	**After adsorption of Cr(VI)**	
1.	**Surface -OH of SiOH**	**3421**	**3418**	**[32, 33]**
2.	**C-H stretching vibration**	**2924**	**-**	**[34]**
3.	**ν–OH stretching**	**2514**	**-**	**[34]**
4.	**H-OH bonding in H_2O**	**1629**	**1631**	**[35]**
5.	**CaO/CO_3^{-2}**	**1428**	**1425**	**[35]**
6.	**Si-O-Ca**	**1028**	**1027**	**[36]**
7.	**Si-O stretching of quartz and silica**	**781**	**775**	**[37]**
8.	**Si-O-Fe deformation**	**485**	**483**	**[38]**
9.	**Si-O-Si deformation**	**416**	**416**	**[39, 40]**
10.	**Cr-O**	**-**	**775**	**[43]**
11.	**Si-O deformation**	**-**	**689**	**[43]**
12.	**C- Metal bonds**	**-**	**447**	**[41]**

2.11 SEM Analysis

A scanning electron microscope (SEM) is a type of electron microscope that produces images of sample by scanning it with a focused beam of electrons. The morphological and topographical studies were carried out electron microscope, which is a straight forward technique for the determination of morphology and size of solid catalysts [21]. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures. The most common SEM mode is detection of secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons that can be detected depends, among other things, on the angle at which beam meets surface of specimen, i.e. on specimen topography. By scanning the sample and collecting the secondary electrons that are emitted using a special detector, an image displaying the topography of the surface is created.

2.11.1 Results and Discussion

Scanning electron micrograph of soil before and after adsorption of Chromium(VI) has been recorded and the spectrum is shown in **Figure 2.9**. From **Figure 2.9 (a)** it could be observed that prior to Chromium adsorption, soil are having very fine pores on it and irregular surface structure, indicating soil is a heterogeneous powder. **Figure 2.9(b)** and **2.9(c)** shows that after adsorption, the surface became abnormal and a great deal of crystal adhered to the surface, these images prove that, the Chromium(VI) ion was adsorbed by soil into its pores and developed a layer of Chromium(VI) on the surface.

2.12 Point of Zero Charge

The pHpzc is defined as the pH of the suspension at which the surface (acidic or basic) functional groups of absorbents no longer contribute to the pH value of the solution[47]. The relationship between pHpzc and adsorption

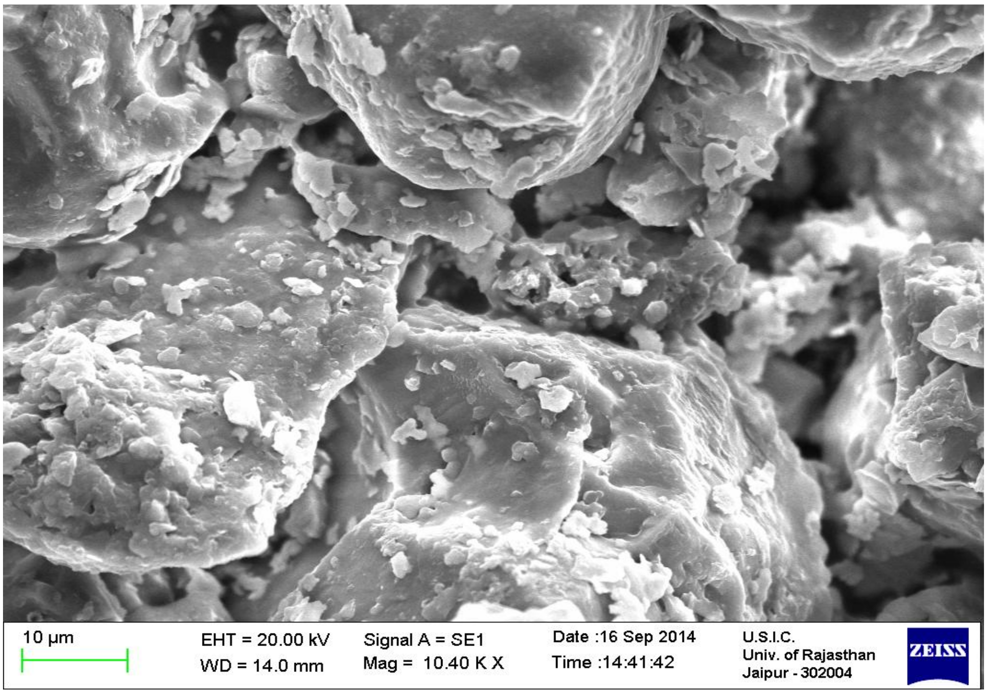


Figure 2.9 (a): SEM image analysis before Chromium(VI) adsorption onto soil sample.

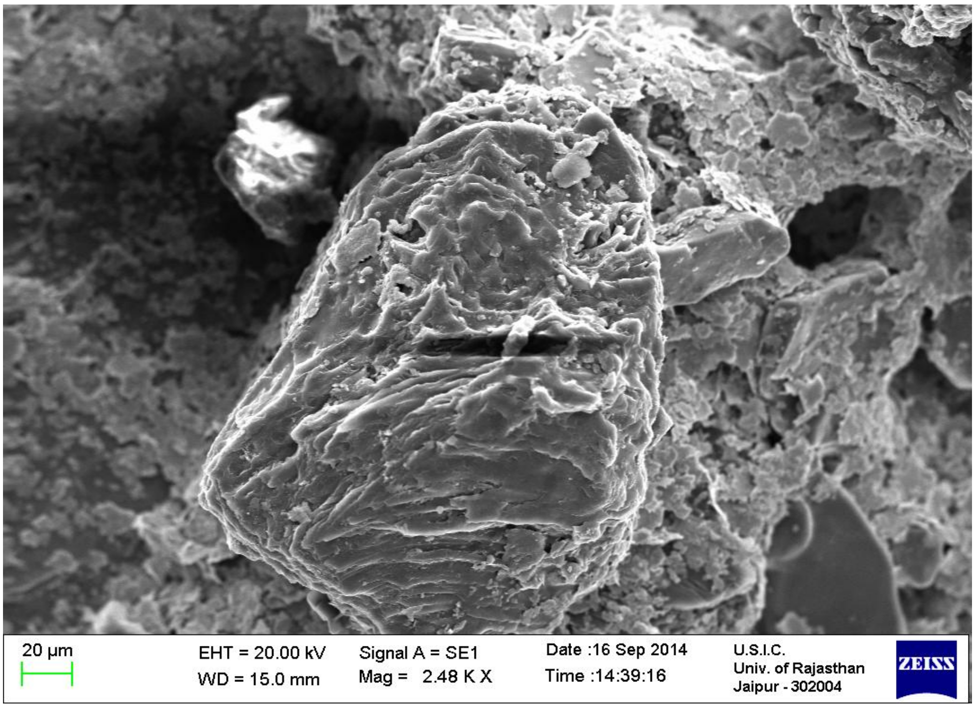


Figure 2.9 (b): SEM image analysis of soil sample after adsorption of 0.5 mg Chromium(VI).

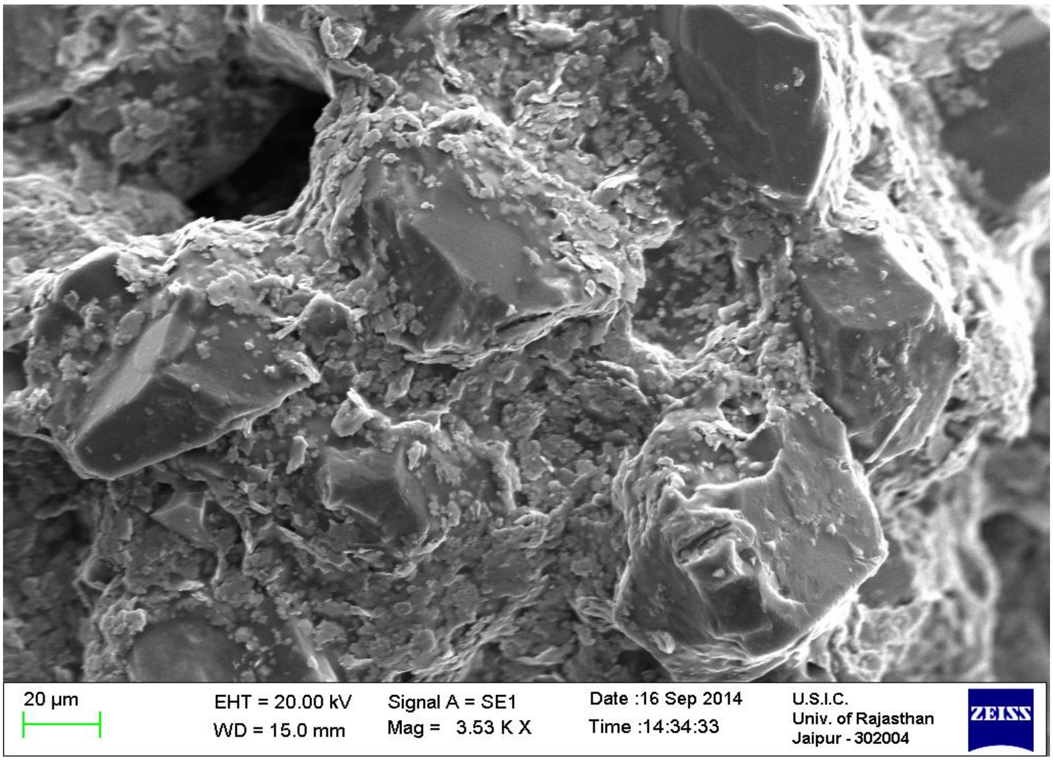


Figure 2.9 (c): SEM image analysis of soil sample after adsorption of 2 mg Chromium(VI)

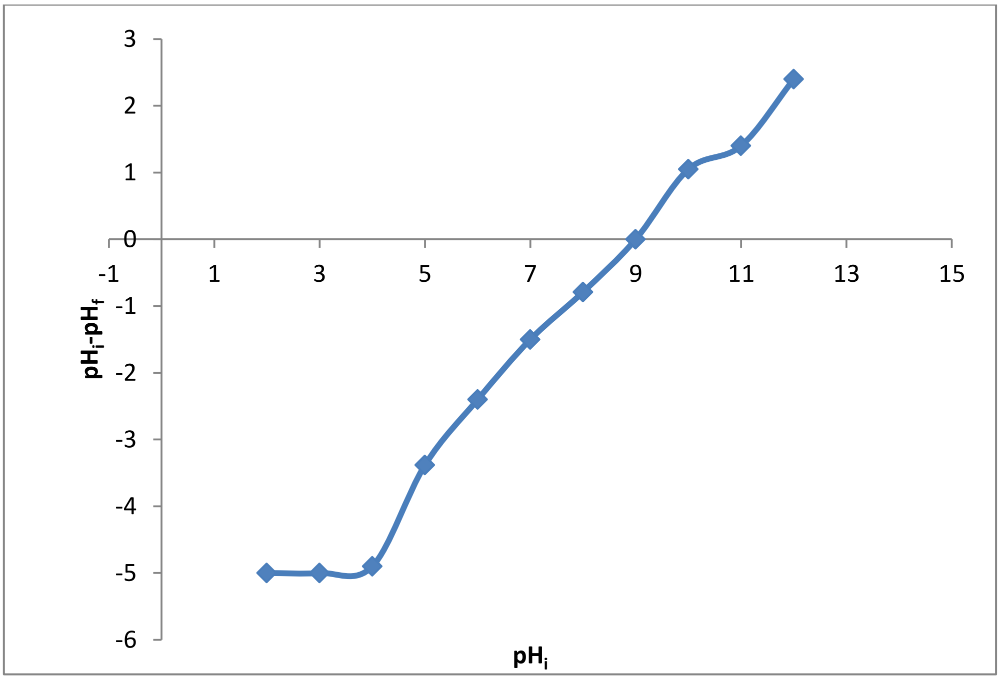


Figure 2.10: Point of zero charge of soil sample.

capacity is that cation adsorption on any adsorbent will be expected to increase at pH value higher than the pHpzc while anions adsorption will be favorable at pH values lower than pHpzc. It has been reported by earlier researcher [48, 49] that the pHpzc of an adsorbent decreases with increase in acidic groups on the surface of the adsorbents. The effects of pH on the adsorption process may also be explained in terms of pH of the point of zero charge, (pHpzc) at which the surface of adsorbent is neutral [49]. The effect of pHpzc can be represented by considering that (-SH) represent the adsorbent type bearing zero charge by the following equation:-

$$-SH_2^+ \xleftrightarrow{below \quad pH_{pzc}} -SH \xleftrightarrow{above \quad pH_{pzc}} -S^- \qquad (2.5)$$

The pH drift method was used to measure the pH at the potential of zero charge (pHpzc) of soil [50, 51]. The pH of a solution of 0.01M NaCl was adjusted between 2 and 12 by adding either HCl or NaOH. 1 gm soil was added to 50 ml of the solution. After the pH had stabilized (typically after 24 hr), the final pH was recorded. A plot between initial pH and pH_i-pH_f is drawn for determination of Point of Zero charge is shown in **Figure 2.10.**

2.12.1 Results and Discussion

As it can be seen in the **Figure 2.10** that for soil sample used in present study, the pHpzc value is found to be 9 and below this pH (pH< 9), the surface charge of the adsorbent is positive while above this pH, surface charge of adsorbent surface is negative. The relationship between pHpzc and cation adsorption will be expected to increase at pH value higher than the pHpzc while anions adsorption will be favorable at pH values lower than the pHpzc [52, 53].

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Chapter – 3

Adsorption Study of Chromium(VI) in Chromium Contaminated Soil by Batch Method

ABSTRACT

In the present study adsorption of Chromium(VI) on the contaminated soil samples of Bhilwara industrial belt have been described. Adsorption studies have been done on two different depths soil; $[S_1]_{0-15}$ and $[S_2]_{15-30}$ using the batch adsorption technique. Influence of variation of initial Chromium(VI) ion concentration, contact time, particle size, amount of soil, pH of solution and effect of co-existing ions have been discussed on adsorption of Chromium(VI) onto the both depth soil. Adsorption of Chromium(VI) was increased with initial concentration of Chromium(VI) and amount of soil due to availability of vacant sites on the soil. Adsorption of Chromium(VI) was increased with decreasing particle size. To check the effect on adsorption the pH was varied from pH 2 to 10. Any significant effect was not shown by anions and cations other than phosphate.

3.1 Introduction

Chromium is released into the environment by a large number of industries such as dyeing, mining, iron sheet cleaning, chrome plating, leather tanning & wood preservation [1]. These industries contain Chromium(III) and Chromium(VI) at a concentration ranging from 10 to 100 mg/L [2]. In Bhilwara most of the areas under cultivation show Chromium values exceeding 65 ppm with certain areas having values between 160-190 ppm [3]. Whereas according to the United States Environmental Protection Agency, the maximum contamination level for Chromium(VI) in domestic water supplies is 0.05 mg L^{-1}, while the permissible limit of Chromium(VI) for effluent discharge to inland surface water is 0.1 mg L^{-1} [4].

Long term release of such industrial wastewater may result in the accumulation of heavy metals in soil exerting a selection pressure on soil micro – biota [5]. So adsorption of Chromium(VI) in soil is significantly influenced by initial metal ion concentration. The initial concentration of metal ions in the solution plays a key role as a driving force to overcome the mass transfer resistance between the aqueous and solid phase [6]. It is generally agreed that the adsorption capacity increases as the initial metal ion concentration in the solution increases.

Conventional treatment processes for the removal of Chromium(VI) from industrial effluents include chemical precipitation, electrochemical process, ion exchange, reverse osmosis, and adsorption. Among these techniques, adsorption has been proven to be an attractive technique for the treatment of Chromium(VI)-laden wastewater due to its simplicity in operation and effectiveness [7]. Adsorption is a major process responsible for accumulation of heavy metals in soil. Therefore the study of adsorption processes is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase [8].

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [9]. pH of the solution is of greater importance in heavy metal adsorption [10]. This is because H^+ or OH^- ions influence the ionization capacity of the metal ions present in solution [11].

The pH value of the system controls the adsorption capacity due to its influence on the charge density of the adsorbent and the ionic form of the chrome ions in solutions. Hence, the pH value is one of the most important parameters while assesing the adsorption capacity of an adsorbent for metal ions sequestering from aqueous solution [12]. In the adsorption phenomenon, the pH value affects the two aspects: metal ion solubility and total charge of adsorbent surface, since protons can be adsorbed or released, the acidity of the medium affects the competition ability of hydrogen ions with metal ions to active sites on the adsorption surface [13-14].

The concentration, transport, and toxicity of Chromium(VI) in the soils and groundwater are controlled by numerous mechanisms including transformation reactions (i.e., chemical or biological reduction), adsorption, precipitation, or various combinations of these processes. These processes are governed by many factors including soil composition (electron donor availability, soil texture, soil mineralogy, competing ions, adsorption capabilities, etc.) and conditions in the soil (pH, Eh, moisture content, and the presence of vegetation) [15-20]. Hexavalent Chromium (i.e., Chromate) adsorption by soils is a multifaceted phenomenon due to the presence of many soil components (i.e., clays, Fe, Mn oxides and hydroxides, organic matter, carbonate, etc.), their unique surface configuration, the multi component nature of solute and soil interactions, and potential reduction of Chromium(VI) to Chromium(III), with subsequent precipitation or adsorption of Chromium(III) [21, 22]. Due to its anionic nature, Chromium(VI) is strongly adsorbed by clays and iron and manganese oxides and hydroxides, favorably in acidic media due to increase in positively charged adsorption sites at mineral surfaces [15, 23-26].

Retention of Chromium(VI) species (CrO_4^{2-}, $HCrO_4^-$, $Cr_2O_7^{2-}$) in these environments decreases with increasing pH, therefore these anionic species are weakly adsorbed into soils under alkaline to neutral conditions [27], resulting in increased mobility in the subsurface, especially in the presence of other competing anions such as SO_4^{2-}, HCO_3^{-}, and PO_4^{3-} [28].

On the other hand, the presence of competing cations in the soils may increase Chromium(VI) sorption. In alkaline soil, the presence of Ca^{2+} in the system favors greater retention and lesser mobility of Chromium(VI) compared to water [28]. cadmium, nickel, zinc, and especially copper, also favor the adsorption of Chromium(VI) in calcareous soils [22]. Chromium(VI) adsorption by manganese dioxide in aqueous solution is increased in the presence of cations such as cadmium, lead, and nickel by the accumulation of positive surface charges that attract anions more effectively [29, 30].

Adsorption is versatile and effective method for removing Chromium particularly when it is combined with appropriate regeneration step. This reduces the problem of sludge disposal and renders the system economically viable, especially when the adsorbents used are also of low cost. Adsorption process is used in a variety of important industrial applications and now it is increasingly used on large scale as an economical and efficient separation technique for metal ion removal from wastewater [31]. Various kinds of soils and clay materials have been tried by several investigators [32]. Retention of heavy metal cations in soils is due to their strong adsorption onto the negatively charged soil surfaces, their ability to form complex molecules with organic substances found in the soil and the formation of oxides, hydroxides and other insoluble minerals in soil [33].

Several types of crystalline clay minerals such as zeolites are also suitable due to their easy availability globally for the removal of heavy metal cations [34-37]. The metal adsorption efficiency of such clays is due to their chemical and mechanical stability, high surface area, permanent negative charge and a variety of surface and structural properties [38]. Fendorf et al (1994) concluded from experimental studies that Chromium(VI) is appreciably retained in soil colloids having net positive charge due to its anionic nature [39]. Chromium (VI) is adsorbed by a variety of soil phases with hydroxyl groups on their surfaces such as those present in kaolinite and montmorillonite [40]. Khan et al (1995) have reported that hydroxylated surfaces of oxides of Al, Ca, Mg, Si, etc. acquire charge when present in aqueous solution through amphoteric dissociation [41, 42].

Chromium, which is toxic to man and other living organism, presents potentially serious environmental problems throughout the world. When Chromium(VI) is discharged into water, soils or sediments, it would be distributed between soil/sediments and water [43]. Specially, Chromium(VI), in its high valence, is a relatively strong oxidant which can undergo redox reaction with soil constitutes, including minerals, aqueous inorganic ions, simple organic molecules and humic materials. So, not only does the adsorption process of Chromium(VI) but also its chemical reaction occur simultaneously when Chromium(VI) enters soil and sediments, which result in the study very complex. Therefore, it is very interesting to study the adsorption behavior of Chromium(VI) on minerals and soil so that its migration and conversion processes on soils could be further interpreted [44-46]. Study on the conversion between Chromium(VI) and Chromium(III) in minerals and soils showed that Chromium(VI) could be reduced by organic matter and metal ion in soil [47-49].

The soil type and composition plays an important role for heavy metal retention in soil. In general, coarse-grained soil exhibits lower tendency for heavy metal adsorption than fine grained soil. The fine-grained soil fraction content soil particles with large surface reactivities and large surface areas such as clay minerals, iron and manganese oxyhydroxides, humic acids, and others and displays enhanced adsorption properties. Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange as well as metal oxyhydroxides [50]. Soil organic matter exhibits a large number and variety of functional groups and high CEC values, which results in enhanced heavy metal retention ability mostly by surface complexation, ion exchange, and surface precipitation [51, 52].

Adsorption is the mechanism by which a constituent is partitioned between the aqueous and solid phases. Adsorption reactions have already been demonstrated to be significant in reducing the concentration and retarding the movement of contaminants in the subsurface. Many mathematical and theoretical constructs have been developed to describe the adsorption process. This is because adsorption is a function of solution conditions and surface parameters. These parameters include the chemical composition and ionic strength of the solution, the number and type of adsorbents present and their remaining adsorption capacity.

The ultimate goal of adsorption research on particular surfaces is the assumption that knowing what the adsorption parameters are for each individual component of a soil or aquifer, one could predict the adsorptive capacity of any soil mixture. B. D. Honeyman (1984) describes this assumption as "adsorptive additivity" [53]. In view of the need for these adsorption parameters, this research was undertaken.

3.2 Experimental

The soil samples were collected from RIICO industrial area, from two different depth. The soil samples were dried and sieved to get uniform particle size. A 100 mg L^{-1} stock solution of Chromium(VI) was prepared by weighing 0.2829 g $K_2Cr_2O_7$ and diluting with deionized water up to 1000 ml. To studied the effect of initial concentration of Chromium(VI) batch adsorption were carried out at different contact times (2, 4, 6, 8, 10, 12, 14, 16 & 20 min) for an initial Chromium(VI) concentration in the range of 0.5 mg to 5 mg. The soil amount was taken 2 g, solution pH, temperature, and particle size was kept constant at 8, 30^oC and 100 BSS mesh respectively. Stirring rate was also kept constant at 120 rpm. To studied the effect of amount of soil, Chromium(VI) batch adsorption were carried out at different contact times (2, 4, 6, 8, 10, 12, 14, 16 & 20 min) for amount of soil in the range of 2 g to 10 g soil. The initial Chromium(VI) concentration was taken 0.5 mg and solution pH, temperature, and particle size was kept constant at 8, 30^oC and 100 BSS mesh respectively. Stirring rate was also kept constant. For particle size variation the batch adsorption experiments were carried out by using various particle size of the soil i.e. 100 BSS mesh, 200 BSS mesh and 300 BSS mesh with varying initial Chromium(VI) concentration from 0.5 mg to 5 mg. 2 g amount of soil was used for each experiment, volume of sorption medium was 100 ml, temperature was 30^oC and stirring rate was kept constant. To investigate the effect of pH of the solution on the Chromium adsorption, studies were conducted at pH range of 2-10 for $[S_1]_{0-15}$ and $[S_2]_{15-30}$ into 250 ml of conical flask containing 100 ml 0.5 mg Chromium(VI) solution. The desired amount of 0.1N HCl and 0.1N NaOH added for maintaining the initial pH. The pH was measured by using Systronics digital pH meter. Batch experiments were also conducted to examine the influence of other ions such as sodium (Na^+), calcium (Ca^{2+}), lead (Pb^{2+}), magnesium (Mg^{2+}), zinc (Zn^{2+}), nitrate (NO_3^-), chloride (Cl^-), sulphate (SO_4^{-2}), and phosphate (PO_4^{3-}) that are present in the industrial effluent stream. These experiments are carried out by maintaining the initial Chromium(VI) concentration, pH of solution, and soil amount constant at 5 mg, 8 and 2 g respectively. Experiments are conducted for same concentration of other ions. For all the experiments sample were withdrawn from conical flasks after specified time interval and residual metal content analyzed by 1,5 diphenylcarbazide spectrophotometric method by using following equation. The detailed methodology was described in **Chapter 2** in **Section 2.6**.

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{3.1}$$

Q_t = adsorbed amount of Chromium(VI), C_o = initial concentration of Chromium(VI), C_t = Chromium(VI) concentration at time t, V = volume of the solution (L), M= mass of the soil (g).Graph between amount of adsorption versus initial Chromium(VI) concentration, amount of soil, pH of solution, particle size and coexisting ions was drawn.

3.3 Results and Discussion

Fundamental Parameters in Adsorption

3.3.1 Effect of Variation of Initial Chromium(VI) Concentration and Contact Time.

The effect of variation of initial Chromium(VI) concentration and contact time was studied on $[S_1]_{0-15}$ and $[S_2]_{15-30}$.

[A] Results for $[S_1]_{0-15}$:

It is apparent from **Table 3.1** and **Figure 3.4** and **3.5** that with an increase in the initial Chromium(VI) concentration from 0.5 mg to 5 mg the amount of adsorption of Chromium(VI) increases from 0.17 mg/g to 1.16 mg /g for $[S_1]_{0-15}$ while the percentage adsorption decreases (**Table 3.1 to 3.3** and **Figure 3.1 to**

3.3). It is clear from **Table 3.1** and **Figure 3.5** that percentage adsorption of Chromium(VI) from aqueous solution increases rapidly till 12 min and reaches up to 56% for 0.5 mg initial Chromium(VI) concentration and 46.2% for 5 mg initial Chromium(VI) concentration. After that the percentage adsorption increases slowly till 20 min and becomes constant thereafter.

[B] Results for $[S_2]_{15\text{-}30}$:

It is observed from the **Table 3.4** and **Figures 3.9** and **3.10** that with an increase in the initial Chromium(VI) concentration from 0.5 mg to 5 mg the amount of adsorption of Chromium(VI) increases from 0.18 mg/g to 1.190 mg/g for $[S_2]_{15\text{-}30}$ while percentage adsorption decreases (**Table 3.4 to 3.6** and **Figure 3.6** to **3.8**). It is apparent from **Table 3.4** and **Figure 3.10** that percentage adsorption of Chromium(VI) from aqueous solution increases rapidly till 12 min and reaches up to 64% for 0.5 mg initial Chromium (VI) concentration and 47% for 5 mg initial Chromium(VI) concentration respectively. After that the percentage adsorption increases slowly till 20 min and becomes constant thereafter.

At low initial Chromium(VI) concentration the ratio of available surface area of soil to initial Chromium(VI) concentration was large. However as initial Chromium(VI) concentration increases in the solution the ratio of surface area of soil to the available Chromium(VI) concentration decreases and therefore percentage adsorption slightly decreases.

In the process of adsorption, the adsorbed species concentration gradient acts as a driving force during the reaction. Accordingly, on increasing the initial Chromium(VI) concentration, the adsorption driving force was higher, hence increase in adsorption capacity was observed. Due to increased amount of Chromium(VI) the number of collisions between Chromium species and adsorbent get increased and a driving force to overcome all mass transfer resistances between the aqueous and solid phases was developed.

Initially, the rate of adsorption is fast. However it gradually slow down until reached equilibrium. This is due to the fact that a large number of vacant surface sites are available for adsorption during the initial stage.

Table 3.1: Influence of variation of initial Cr(VI) concentration $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^{o}C.

[Cr(VI)] mg	0.5			1			2			3			5		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	0.500	0.000	0.00	1.000	0.000	0.00	2.000	0.000	0.00	3.000	0.000	0.00	5.000	0.000	0.00
2	0.350	0.075	30.00	0.600	0.200	40.00	1.080	0.460	46.00	1.690	0.655	43.67	2.790	1.105	44.20
4	0.320	0.090	36.00	0.580	0.210	42.00	1.070	0.465	46.50	1.680	0.660	44.00	2.780	1.110	44.40
6	0.300	0.100	40.00	0.560	0.220	44.00	1.060	0.470	47.00	1.650	0.675	45.00	2.760	1.120	44.80
8	0.280	0.110	44.00	0.520	0.240	48.00	1.010	0.495	49.50	1.640	0.680	45.33	2.720	1.140	45.60
10	0.250	0.125	50.00	0.480	0.260	52.00	0.950	0.525	52.50	1.590	0.705	47.00	2.700	1.150	46.00
12	0.220	0.140	56.00	0.470	0.265	53.00	0.940	0.530	53.00	1.560	0.720	48.00	2.690	1.155	46.20
14	0.190	0.155	62.00	0.440	0.280	56.00	0.930	0.535	53.50	1.540	0.730	48.67	2.680	1.160	46.40
16	0.160	0.170	68.00	0.440	0.280	56.00	0.930	0.535	53.50	1.540	0.730	48.67	2.680	1.160	46.40
18	0.160	0.170	68.00	0.440	0.280	56.00	0.930	0.535	53.50	1.540	0.730	48.67	2.680	1.160	46.40
20	0.160	0.170	68.00	0.440	0.280	56.00	0.930	0.535	53.50	1.540	0.730	48.67	2.680	1.160	46.40
∞	0.160	0.170	68.00	0.440	0.280	56.00	0.930	0.535	53.50	1.540	0.730	48.67	2.680	1.160	46.40

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 3.2: Influence of variation of initial Cr(VI) concentration $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 200BSS mesh; temp. = 30°C.

[Cr(VI)] mg	0.5			1			2			3			5		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	0.500	0.000	0.00	1.000	0.000	0.00	2.000	0.000	0.00	3.000	0.000	0.00	5.000	0.000	0.00
2	0.330	0.085	34.00	0.580	0.210	42.00	1.075	0.463	46.25	1.670	0.665	44.33	2.785	1.108	44.30
4	0.310	0.095	38.00	0.540	0.230	46.00	1.060	0.470	47.00	1.655	0.673	44.83	2.750	1.125	45.00
6	0.290	0.105	42.00	0.510	0.245	49.00	1.040	0.480	48.00	1.620	0.690	46.00	2.710	1.145	45.80
8	0.260	0.120	48.00	0.470	0.265	53.00	0.980	0.510	51.00	1.570	0.715	47.67	2.680	1.160	46.40
10	0.230	0.135	54.00	0.440	0.280	56.00	0.930	0.535	53.50	1.520	0.740	49.33	2.640	1.180	47.20
12	0.190	0.155	62.00	0.420	0.290	58.00	0.890	0.555	55.50	1.470	0.765	51.00	2.600	1.200	48.00
14	0.160	0.170	68.00	0.400	0.300	60.00	0.860	0.570	57.00	1.440	0.780	52.00	2.500	1.250	50.00
16	0.140	0.180	72.00	0.400	0.300	60.00	0.860	0.570	57.00	1.440	0.780	52.00	2.500	1.250	50.00
18	0.140	0.180	72.00	0.400	0.300	60.00	0.860	0.570	57.00	1.440	0.780	52.00	2.500	1.250	50.00
20	0.140	0.180	72.00	0.400	0.300	60.00	0.860	0.570	57.00	1.440	0.780	52.00	2.500	1.250	50.00
∞	0.140	0.180	72.00	0.400	0.300	60.00	0.860	0.570	57.00	1.440	0.780	52.00	2.500	1.250	50.00

Unad- Unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 3.3: Influence of variation of initial Cr(VI) concentration $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; particle size = 300BSS mesh; temp. = 30^{o}C.

[Cr(VI)] mg	0.5			1			2			3			5		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	0.500	0.000	0.00	1.000	0.000	0.00	2.000	0.000	0.00	3.000	0.000	0.00	5.000	0.000	0.00
2	0.320	0.090	36.00	0.570	0.215	43.00	1.070	0.465	46.50	1.650	0.675	45.00	2.770	1.115	44.60
4	0.280	0.110	44.00	0.520	0.240	48.00	1.055	0.473	47.25	1.600	0.700	46.67	2.730	1.135	45.40
6	0.250	0.125	50.00	0.480	0.260	52.00	1.050	0.475	47.50	1.580	0.710	47.33	2.690	1.155	46.20
8	0.210	0.145	58.00	0.440	0.280	56.00	0.950	0.525	52.50	1.500	0.750	50.00	2.550	1.225	49.00
10	0.180	0.160	64.00	0.410	0.295	59.00	0.910	0.545	54.50	1.420	0.790	52.67	2.400	1.300	52.00
12	0.150	0.175	70.00	0.380	0.310	62.00	0.850	0.575	57.50	1.360	0.820	54.67	2.320	1.340	53.60
14	0.130	0.185	74.00	0.360	0.320	64.00	0.780	0.610	61.00	1.320	0.840	56.00	2.260	1.370	54.80
16	0.110	0.195	78.00	0.340	0.330	66.00	0.780	0.610	61.00	1.320	0.840	56.00	2.260	1.370	54.80
18	0.110	0.195	78.00	0.340	0.330	66.00	0.780	0.610	61.00	1.320	0.840	56.00	2.260	1.370	54.80
20	0.110	0.195	78.00	0.340	0.330	66.00	0.780	0.610	61.00	1.320	0.840	56.00	2.260	1.370	54.80
∞	0.110	0.195	78.00	0.340	0.330	66.00	0.780	0.610	61.00	1.320	0.840	56.00	2.260	1.370	54.80

Unad- Unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 3.4: Influence of variation of initial Cr(VI) concentration $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^{o}C.

[Cr(VI)] mg	0.5			1			2			3			5		
Time, min.	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad
0	0.500	0.000	0.00	1.000	0.000	0.00	2.000	0.000	0.00	3.000	0.000	0.00	5.000	0.000	0.00
2	0.320	0.090	36.00	0.560	0.220	44.00	1.030	0.485	48.50	1.650	0.675	45.00	2.760	1.120	44.80
4	0.310	0.095	38.00	0.550	0.225	45.00	1.020	0.490	49.00	1.640	0.680	45.33	2.750	1.125	45.00
6	0.290	0.105	42.00	0.520	0.240	48.00	1.000	0.500	50.00	1.620	0.690	46.00	2.730	1.135	45.40
8	0.260	0.120	48.00	0.480	0.260	52.00	0.950	0.525	52.50	1.590	0.705	47.00	2.700	1.150	46.00
10	0.220	0.140	56.00	0.450	0.275	55.00	0.930	0.535	53.50	1.550	0.725	48.33	2.680	1.160	46.40
12	0.180	0.160	64.00	0.440	0.280	56.00	0.920	0.540	54.00	1.530	0.735	49.00	2.650	1.175	47.00
14	0.140	0.180	72.00	0.410	0.295	59.00	0.900	0.550	55.00	1.510	0.745	49.67	2.620	1.190	47.60
16	0.140	0.180	72.00	0.410	0.295	59.00	0.900	0.550	55.00	1.510	0.745	49.67	2.620	1.190	47.60
18	0.140	0.180	72.00	0.410	0.295	59.00	0.900	0.550	55.00	1.510	0.745	49.67	2.620	1.190	47.60
20	0.140	0.180	72.00	0.410	0.295	59.00	0.900	0.550	55.00	1.510	0.745	49.67	2.620	1.190	47.60
∞	0.140	0.180	72.00	0.410	0.295	59.00	0.900	0.550	55.00	1.510	0.745	49.67	2.620	1.190	47.60

Unad- Unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 3.5: Influence of variation of initial Cr(VI) concentration $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 200BSS mesh; temp. = 30^{o}C.

[Cr(VI)] mg	0.5			1			2			3			5		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	0.500	0.000	0.00	1.00	0.00	0.00	2.000	0.000	0.00	3.000	0.000	0.00	5.000	0.000	0.00
2	0.300	0.100	40.00	0.55	0.23	45.00	1.025	0.488	48.75	1.640	0.680	45.33	2.750	1.125	45.00
4	0.280	0.110	44.00	0.52	0.24	48.00	1.010	0.495	49.50	1.630	0.685	45.67	2.720	1.140	45.60
6	0.250	0.125	50.00	0.48	0.26	52.00	0.980	0.510	51.00	1.600	0.700	46.67	2.700	1.150	46.00
8	0.220	0.140	56.00	0.45	0.28	55.00	0.940	0.530	53.00	1.570	0.715	47.67	2.670	1.165	46.60
10	0.180	0.160	64.00	0.41	0.30	59.00	0.910	0.545	54.50	1.520	0.740	49.33	2.610	1.195	47.80
12	0.150	0.175	70.00	0.38	0.31	62.00	0.880	0.560	56.00	1.430	0.785	52.33	2.550	1.225	49.00
14	0.120	0.190	76.00	0.37	0.32	63.00	0.820	0.590	59.00	1.400	0.800	53.33	2.420	1.290	51.60
16	0.120	0.190	76.00	0.37	0.32	63.00	0.820	0.590	59.00	1.400	0.800	53.33	2.420	1.290	51.60
18	0.120	0.190	76.00	0.37	0.32	63.00	0.820	0.590	59.00	1.400	0.800	53.33	2.420	1.290	51.60
20	0.120	0.190	76.00	0.37	0.32	63.00	0.820	0.590	59.00	1.400	0.800	53.33	2.420	1.290	51.60
∞	0.120	0.190	76.00	0.37	0.32	63.00	0.820	0.590	59.00	1.400	0.800	53.33	2.420	1.290	51.60

Unad- Unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 3.6: Influence of variation of initial Cr(VI) concentration $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 300BSS mesh; temp. = 30^{o}C.

[Cr(VI)] mg	0.5			1			2			3			5		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	0.500	0.000	0.00	1.00	0.00	0.00	2.000	0.000	0.00	3.000	0.000	0.00	5.000	0.000	0.00
2	0.310	0.095	38.00	0.54	0.23	46.00	1.020	0.490	49.00	1.630	0.685	45.67	2.740	1.130	45.20
4	0.270	0.115	46.00	0.50	0.25	50.00	1.000	0.500	50.00	1.610	0.695	46.33	2.700	1.150	46.00
6	0.220	0.140	56.00	0.46	0.27	54.00	0.940	0.530	53.00	1.580	0.710	47.33	2.620	1.190	47.60
8	0.180	0.160	64.00	0.41	0.30	59.00	0.870	0.565	56.50	1.520	0.740	49.33	2.560	1.220	48.80
10	0.140	0.180	72.00	0.38	0.31	62.00	0.810	0.595	59.50	1.400	0.800	53.33	2.420	1.290	51.60
12	0.110	0.195	78.00	0.35	0.33	65.00	0.780	0.610	61.00	1.320	0.840	56.00	2.360	1.320	52.80
14	0.090	0.205	82.00	0.33	0.34	67.00	0.750	0.625	62.50	1.280	0.860	57.33	2.240	1.380	55.20
16	0.090	0.205	82.00	0.33	0.34	67.00	0.750	0.625	62.50	1.280	0.860	57.33	2.240	1.380	55.20
18	0.090	0.205	82.00	0.33	0.34	67.00	0.750	0.625	62.50	1.280	0.860	57.33	2.240	1.380	55.20
20	0.090	0.205	82.00	0.33	0.34	67.00	0.750	0.625	62.50	1.280	0.860	57.33	2.240	1.380	55.20
∞	0.090	0.205	82.00	0.33	0.34	67.00	0.750	0.625	62.50	1.280	0.860	57.33	2.240	1.380	55.20

Unad- Unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

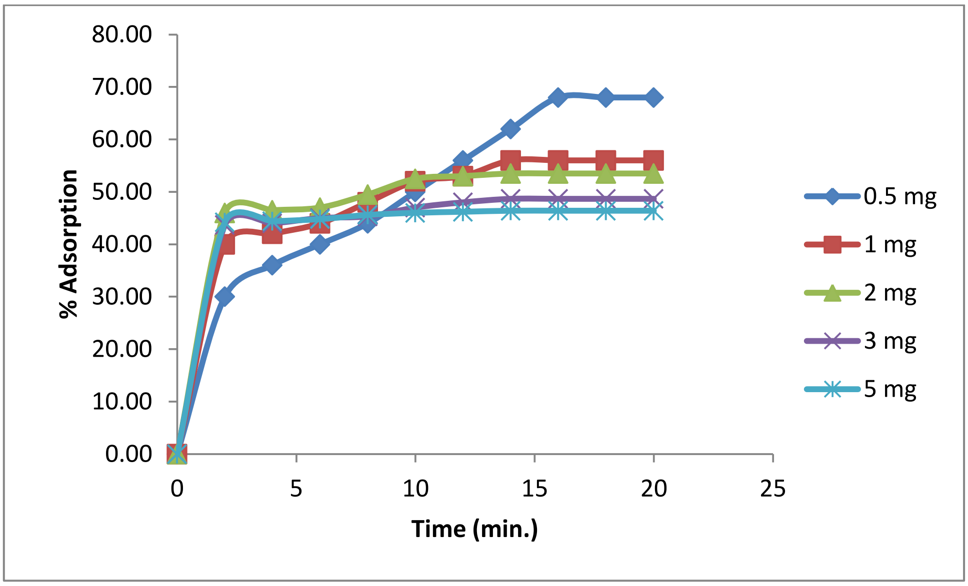

Figure 3.1: Change in % adsorption of Cr(VI) with time for different initial Cr(VI) concentration; $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh, temp. = 30^{o}C.

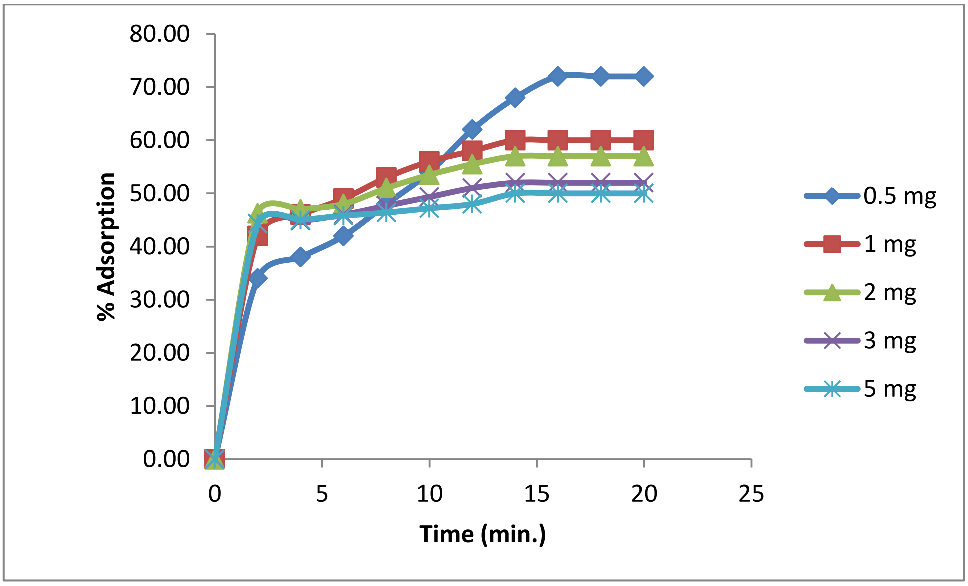

Figure 3.2: Change in % adsorption of Cr(VI) with time for different initial Cr(VI) concentration; $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 200BSS mesh; temp. = 30^{o}C.

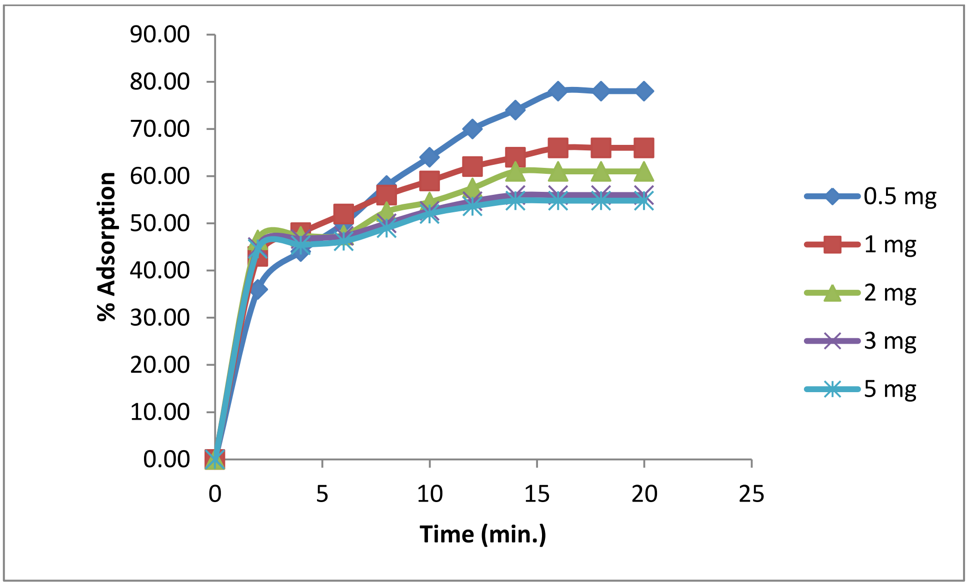

Figure 3.3: Change in % adsorption of Cr(VI) with time for different initial Cr(VI) concentration; $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; particle size = 300BSS mesh; temp. = 30°C.

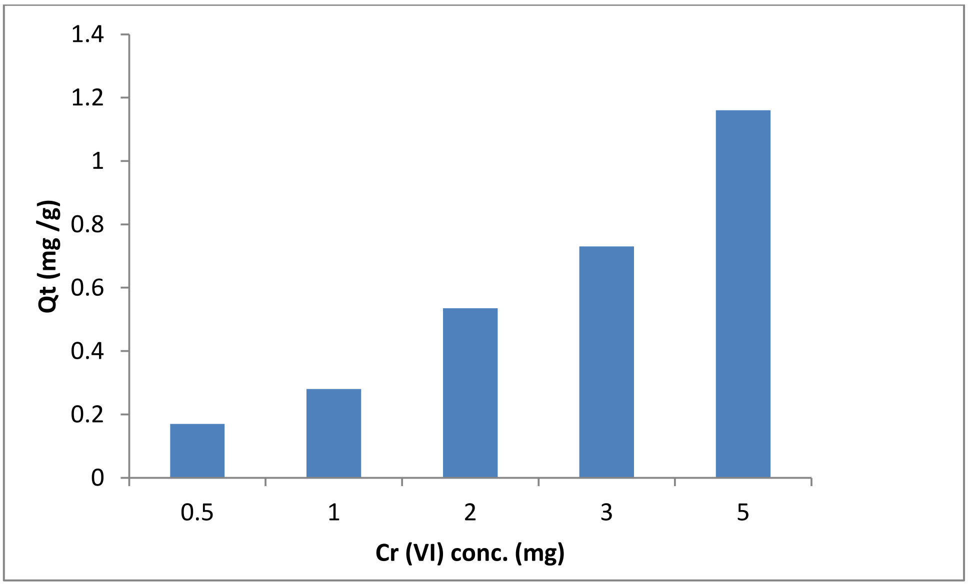

Figure 3.4: Change in amount of adsorption of Cr(VI) with different initial Cr(VI) concentration; $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

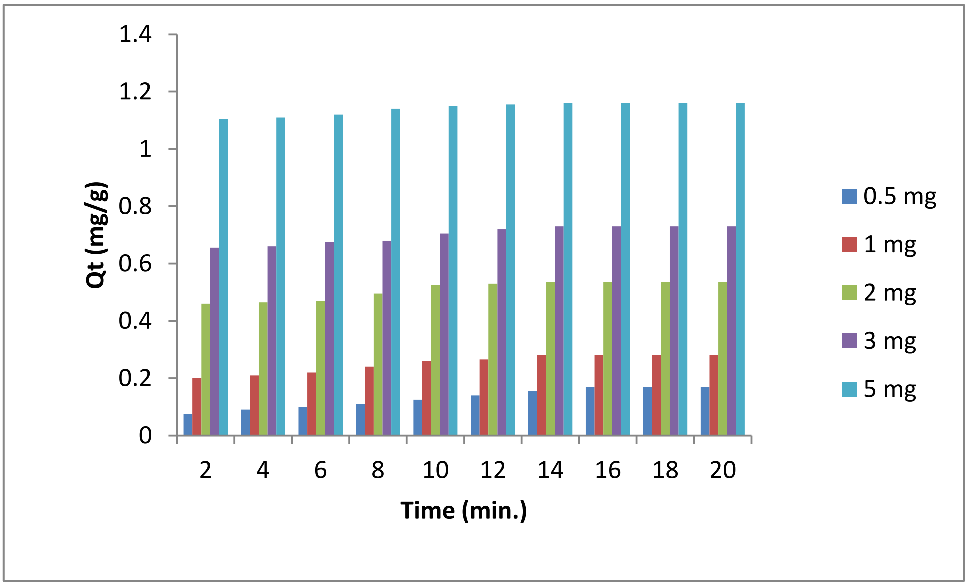

Figure 3.5: Change in amount of adsorption of Cr(VI) with time for different initial Cr(VI) concentration; $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

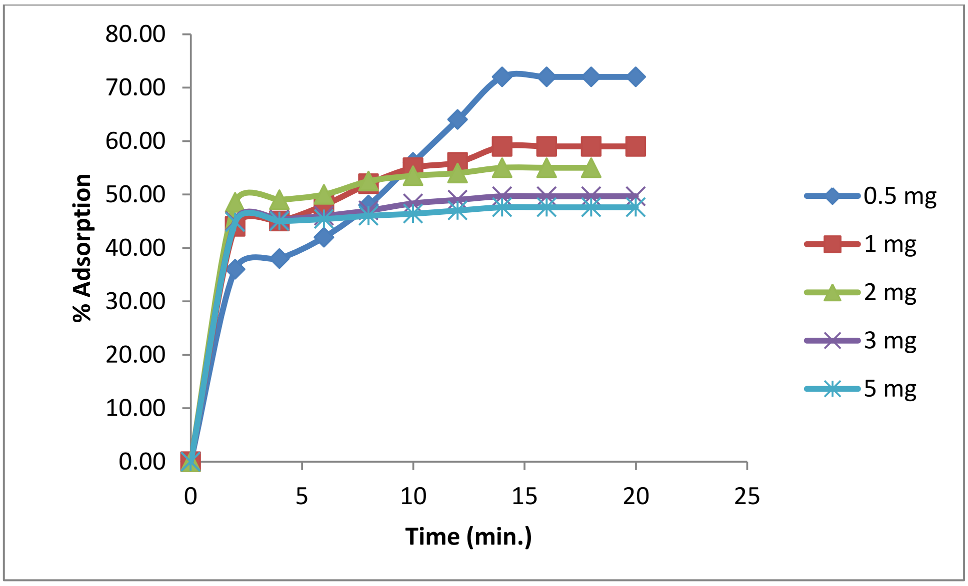

Figure 3.6: Change in % adsorption of Cr(VI) with time for different initial Cr(VI) concentration; $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

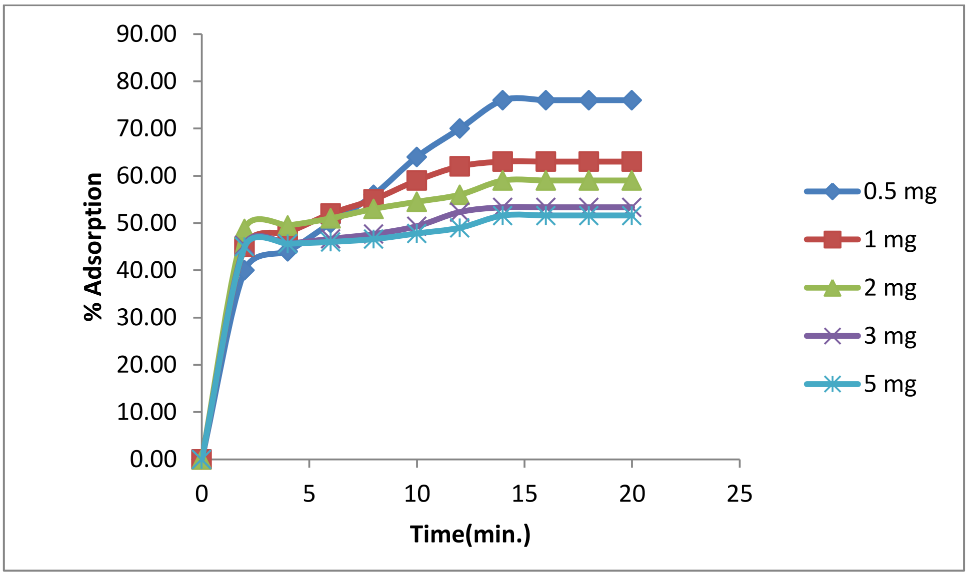

Figure 3.7: Change in % adsorption of Cr(VI) with time for different initial Cr(VI) concentration; $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 200BSS mesh; temp. = 30°C.

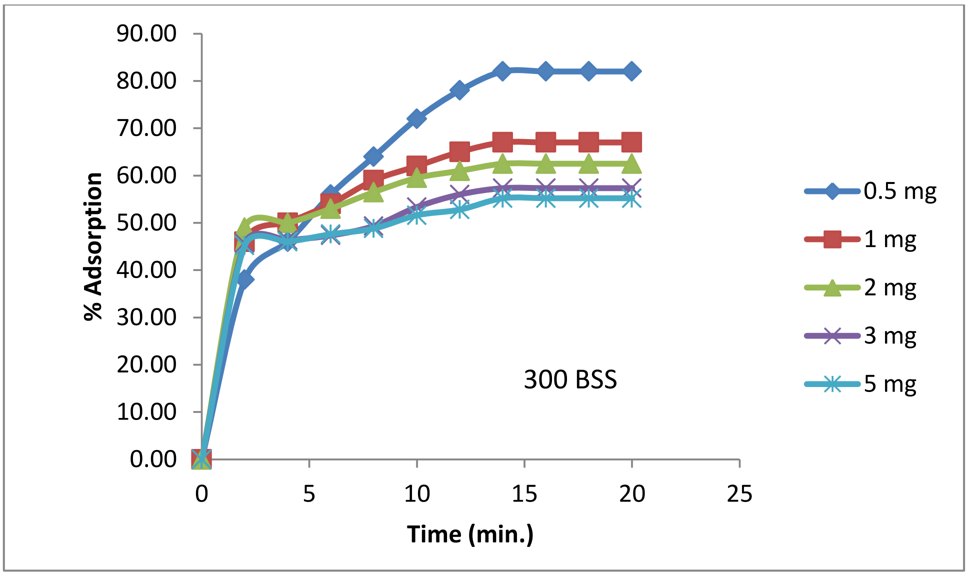

Figure 3.8: Change in % adsorption of Cr(VI) with time for different initial Cr(VI) concentration; $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 300BSS mesh; temp. = 30°C.

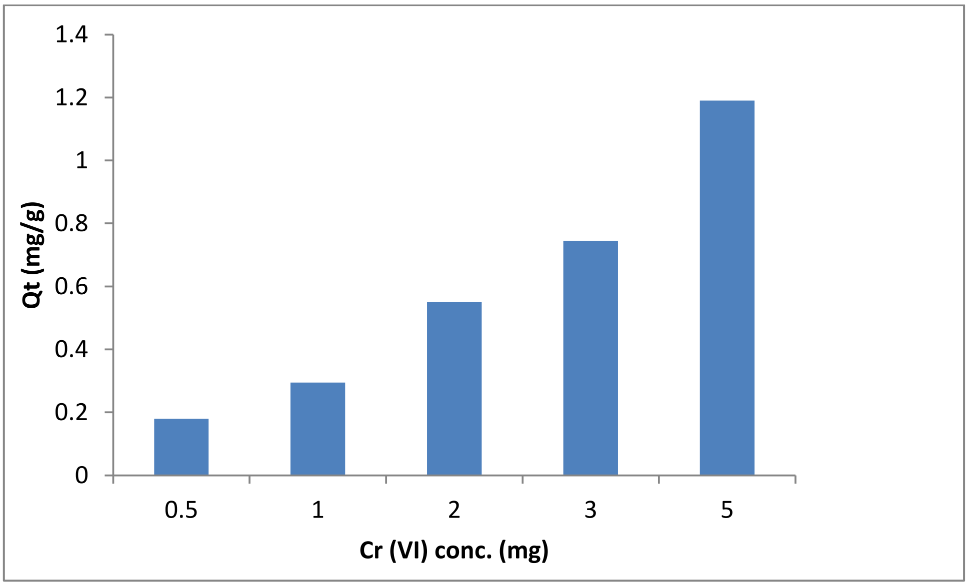

Figure 3.9: Change in amount of adsorption of Cr(VI) with different initial Cr(VI) concentration; $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

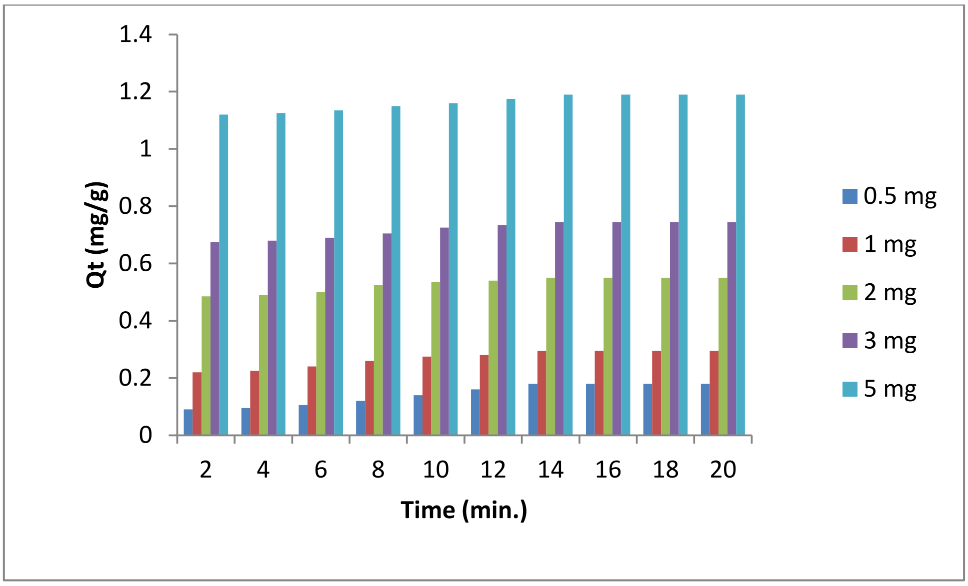

Figure 3.10: Change in amount of adsorption of Cr(VI) with time for different initial Cr(VI) concentration; $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

After a time interval, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules of the solid and bulk phases. On increases initial concentration, concentration difference increases and this difference provides an important driving force to overcome all mass transfer resistance of the Chromium ions between the aqueous and solid phases. Hence, a higher initial concentration of Chromium(VI) ions enhanced the adsorption process and the equilibrium adsorption capacity of soil was also increased with increase in initial metal ion concentration. Yet the percentage adsorption of total initial Chromium(VI) concentration was decreased.

Figure 3.1 and **3.6** and **Table 3.1** and **3.4** show that the contact time has significant influence on the adsorption process. The adsorption seemed to occur in two phases. The first phase involved rapid metal adsorption and more than 55 % of the adsorption occurred in first 12 min for 0.5 mg initial Chromium(VI) concentration. However, complete Chromium(VI) adsorption was achieved in 20 min and the curve was flattened. A further increase in contact time had negligible effect on the rate of adsorption of Chromium(VI). Hence the equilibrium time for adsorption was 20 min for both samples.

Results are in good agreement with the results of several earlier researchers [54-63].

So, amount of adsorption of Chromium(VI) slightly increases for $[S_2]_{15-30}$ as compare to adsorption of Chromium(VI) onto $[S_1]_{0-15}$. The reason is that due to the less contamination at the lower layer, the lower layers of soil have more vacant sites in comparison of upper layers of soil.

3.3.2 Effect of Variation of Particle Size

Particle size of adsorbent has a significant effect on Chromium(VI) adsorption. The effect of variation of particle size was studied on $[S_1]_{0-15}$ and $[S_2]_{15-30}$.

[A] Results for $[S_1]_{0-15}$:

It is apparent from the **Table 3.1** to **3.3** and **Figure 3.11** to **3.13**, that with a decrease in the particle size from 100 BSS mesh to 300 BSS mesh the amount of percentage adsorption increases from 68% to 78%, 56% to 66%, 53.50% to 61%, 48.66% to 56% and 46.40% to 54.80% for 0.5 mg, 1 mg, 2 mg, 3 mg and 5 mg added Chromium(VI) concentration respectively for $[S_1]_{0-15}$.

[B] Results for $[S_2]_{15-30}$:

It is observed from the **Table 3.4** to **3.6** and **Figure 3.14** to **3.16**, that amount of percentage adsorption increases from 72% to 82 %, 59% to 67%, 55% to 62.50%, 49.66% to 57.33% and 47.60% to 55.20% for 0.5 mg, 1 mg, 2 mg, 3 mg and 5 mg added Chromium(VI) concentration respectively on decreasing particle size from 100 BSS mesh to 300 BSS mesh for $[S_2]_{15-30.}$

Soil particle size has a significant influence on Chromium(VI) adsorption from aqueous solutions because of different distribution of active centers on the heterogeneous soil samples. It is clear from results that amount of Chromium(VI) adsorption increases on decreasing particle size from 100 BSS mesh to 300 BSS mesh (**Figure 3.13** and **3.16**). The relatively higher adsorption with smaller soil particles is attributed to the fact that smaller particles yield large surface areas for adsorption of Chromium(VI). The larger particle size of soil samples shows lesser Chromium(VI) adsorption as compared to the smaller particle size of soil samples. The reason is that surface area available for adsorption of Chromium(VI) onto soil samples decreases with the increase of particle size for the same dose of Chromium(VI), providing less active surface sites for adsorption.

Infact particle size is an important parameter to study the adsorption of toxic metals and pollutants onto different adsorbents. The reduction in Chromium(VI) adsorption capacity with increase in soil samples size gives an idea about the porosity of adsorbent i.e., if the adsorbent is highly porous then it would not have significant effect on Chromium(VI) adsorption at equilibrium. The results obtained are in accordance with adsorption, where smaller particles of adsorbents/ion the rate of metal uptake [66, 67]. The similar results were obtained in previous studies [68-71].

The amount of percentage adsorption for $[S_2]_{15-30}$ slightly increases as compare to the adsorption of Chromium(VI) onto $[S_1]_{0-15}$.

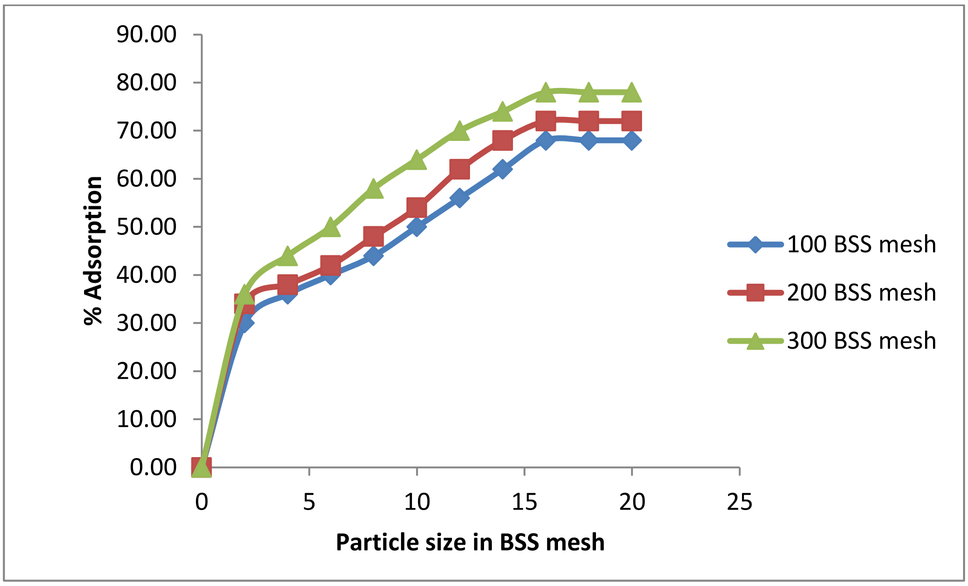

Figure 3.11: Change in % adsorption of Cr(VI) with time for variation of particle size; initial Cr(VI) concentration = 0.5 mg; $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; temp. = 30°C.

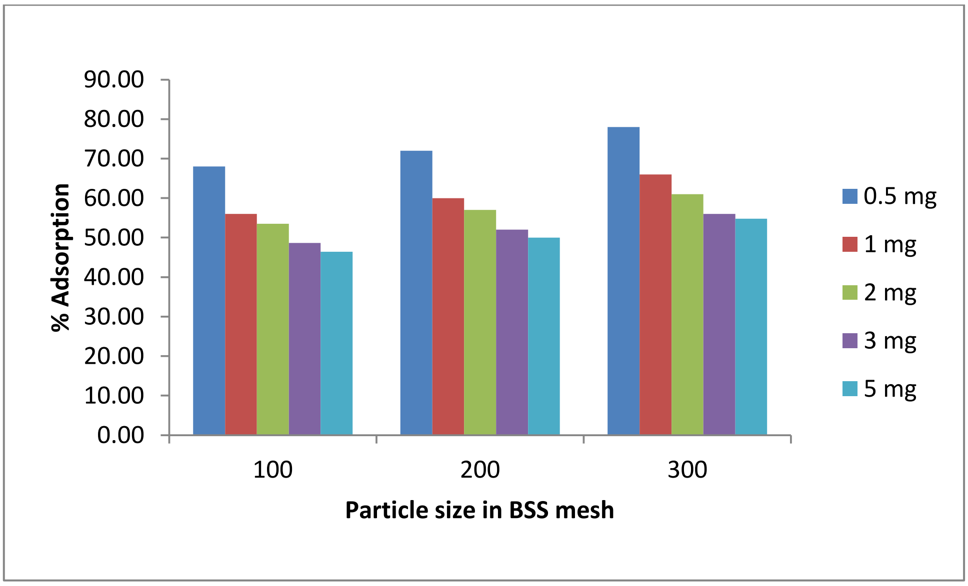

Figure 3.12: Change in % adsorption for variation of particle size at different initial Cr(VI) concentration, $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; temp. = 30°C.

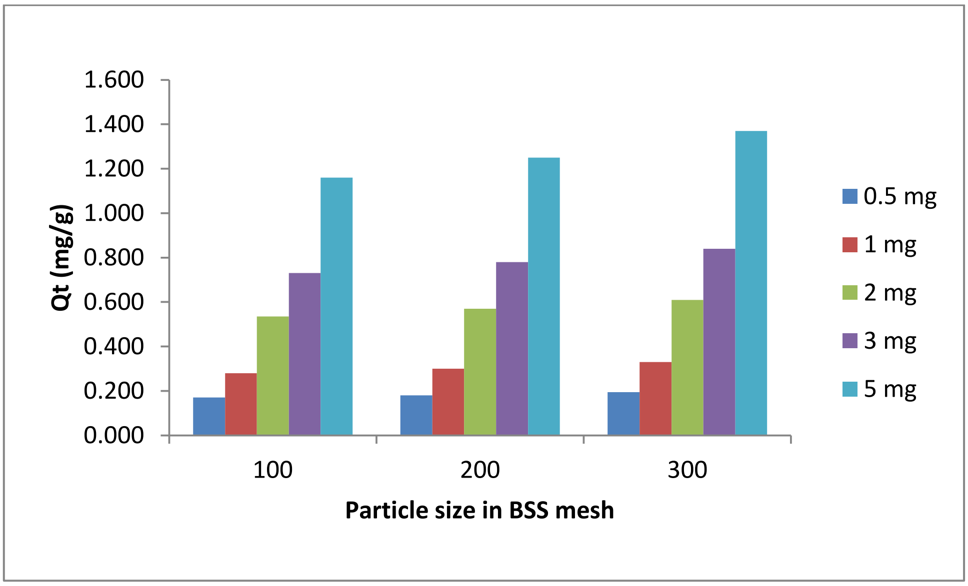

Figure 3.13: Change in amount of adsorption for variation of particle size at different initial Cr(VI) concentration $[S_1]_{0\text{-}15}$ = 2 g; pH= 8, temp. = 30°C.

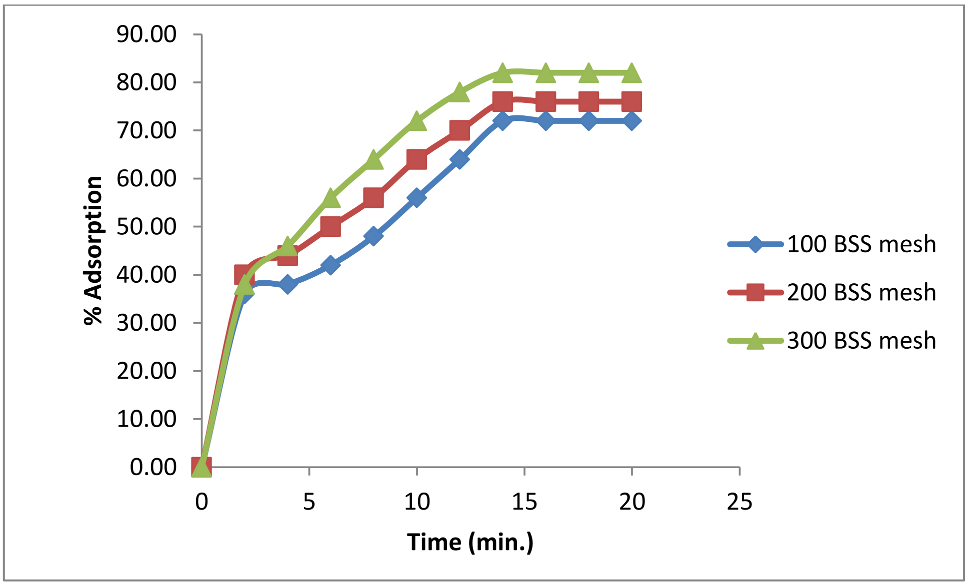

Figure 3.14: Change in % adsorption of Cr(VI) with time for variation of particle size; initial Cr(VI) concentration = 0.5 mg; $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; temp. = 30°C.

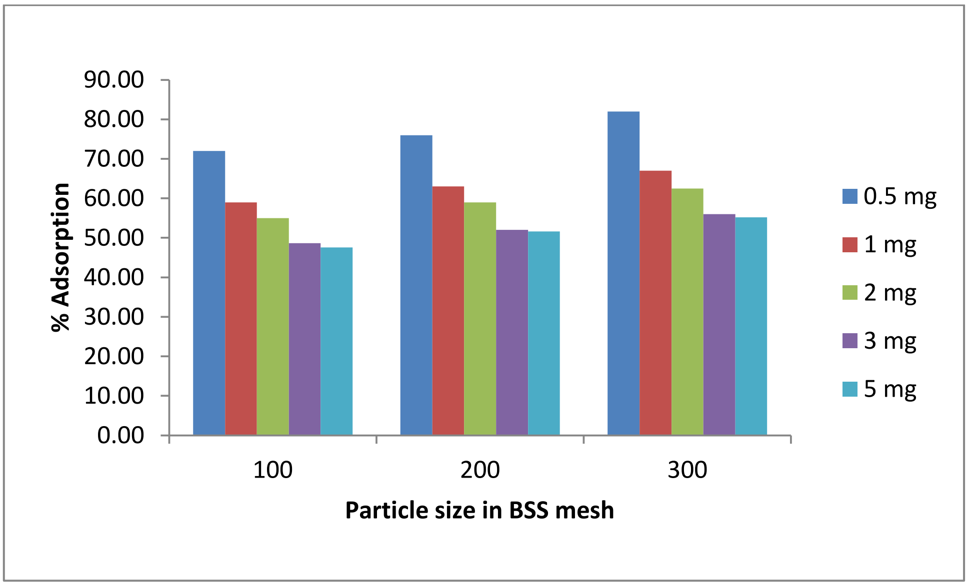

Figure 3.15: Change in % adsorption for variation of particle size at different initial Cr(VI) concentration, $[S_2]_{15-30}$ = 2 g; pH= 8; temp. = 30°C.

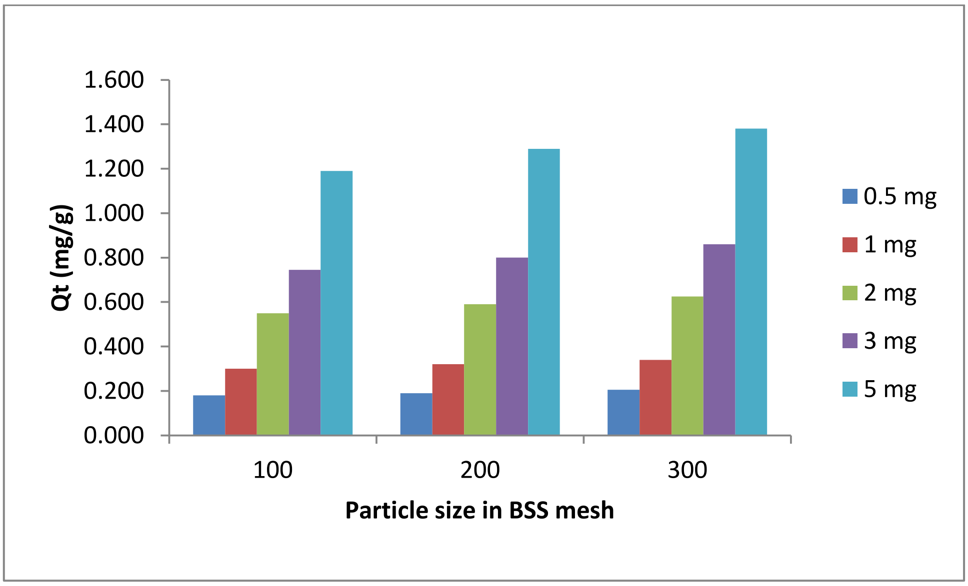

Figure 3.16: Change in amount of adsorption for variation of particle size at different initial Cr(VI) concentration $[S_2]_{15-30}$ = 2 g; pH= 8, temp. = 30°C.

3.3.3 Effect of Variation of Amount of Soil

The effect of variation of amount of soil was studied on $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30}$.

[A] Results for $[S_1]_{0\text{-}15}$:

It is apparent from the **Table 3.7** and **Figure 3.17**, that with an increase in the amount of soil from 2 g to 10 g the percentage adsorption increases from 68% to 82% , for $[S_1]_{0\text{-}15}$.

[B] Results for $[S_2]_{15\text{-}30}$:

It is observed from the **Table 3.8** and **Figure 3.18**, that percentage adsorption increases from 72% to 90% on increasing amount of soil from 2 g to 10 g for $[S_2]_{15\text{-}30.}$

There is an increase in adsorption of Chromium(VI) with increase of amount of soil as exhibited by both sample. It is inferred that the Chromium(VI) adsorption increases with increase in amount of soil due to greater availability of the exchangeable active sites or the surface area for adsorption onto soil samples. Moreover the percentage of metal ion adsorption on adsorbent is determined by adsorption capacity of the adsorbent. The maximum adsorption of 82% and 90 % is observed at the dosage of 10 g for both $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30}$ samples respectively among all five different amount of soil.

This revealed that on increased amount of soil, the number of sites available for adsorption was also increased, hence more surface area of soil samples was remained unsaturated and was available for adsorption of Chromium(VI). However slow increase in adsorption beyond an optimum dose was attributed to the attainment of equilibrium between adsorbate and adsorbent at the operating condition. This effect had been termed as “solid concentration effect” i.e. overcrowding by particles of pollutants [74]. Results are in good agreement with the results, reported by earlier researchers [62, 69, 72-73]. So, amount of adsorption of Chromium(VI) increases on increasing amount of soil for $[S_2]_{15\text{-}30}$ depth soil as compare to adsorption of Chromium(VI) onto $[S_1]_{0\text{-}15}$. This predicted that $[S_1]_{0\text{-}15}$ is comparatively more saturated than $[S_2]_{15\text{-}30}$.

Table 3.7: Influence of variation of amount of soil on Cr(VI) adsorption onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 0.5 mg; pH= 8; particle size = 100BSS mesh; temp. = 30^oC.

Amount of soil (g)	2			4			6			8			10		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00
2	0.350	0.075	30.00	0.320	0.045	36.00	0.300	0.033	40.00	0.280	0.028	44.00	0.250	0.025	50.00
4	0.320	0.090	36.00	0.280	0.055	44.00	0.270	0.038	46.00	0.240	0.033	52.00	0.200	0.030	60.00
6	0.300	0.100	40.00	0.250	0.063	50.00	0.240	0.043	52.00	0.210	0.036	58.00	0.150	0.035	70.00
8	0.280	0.110	44.00	0.240	0.065	52.00	0.220	0.047	56.00	0.170	0.041	66.00	0.130	0.037	74.00
10	0.250	0.125	50.00	0.210	0.073	58.00	0.180	0.053	64.00	0.130	0.046	74.00	0.110	0.039	78.00
12	0.220	0.140	56.00	0.190	0.078	62.00	0.160	0.057	68.00	0.120	0.048	76.00	0.090	0.041	82.00
14	0.190	0.155	62.00	0.140	0.090	72.00	0.130	0.062	74.00	0.110	0.049	78.00	0.090	0.041	82.00
16	0.160	0.170	68.00	0.140	0.090	72.00	0.130	0.062	74.00	0.110	0.049	78.00	0.090	0.041	82.00
18	0.160	0.170	68.00	0.140	0.090	72.00	0.130	0.062	74.00	0.110	0.049	78.00	0.090	0.041	82.00
20	0.160	0.170	68.00	0.140	0.090	72.00	0.130	0.062	74.00	0.110	0.049	78.00	0.090	0.041	82.00
∞	0.160	0.170	68.00	0.140	0.090	72.00	0.130	0.062	74.00	0.110	0.049	78.00	0.090	0.041	82.00

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption.

Table 3.8: Influence of variation of amount of soil on Cr(VI) adsorption onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.5 mg; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

Amount of soil (g)	**2**			**4**			**6**			**8**			**10**		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	**0.500**	**0.000**	**0.00**	**0.500**	**0.000**	**0.00**	**0.500**	**0.000**	**0.00**	**0.500**	**0.000**	**0.00**	**0.500**	**0.000**	**0.00**
2	**0.320**	**0.090**	**36.00**	**0.310**	**0.048**	**38.00**	**0.300**	**0.033**	**40.00**	**0.290**	**0.026**	**42.00**	**0.260**	**0.024**	**48.00**
4	**0.310**	**0.095**	**38.00**	**0.280**	**0.055**	**44.00**	**0.260**	**0.040**	**48.00**	**0.240**	**0.033**	**52.00**	**0.210**	**0.029**	**58.00**
6	**0.290**	**0.105**	**42.00**	**0.250**	**0.063**	**50.00**	**0.220**	**0.047**	**56.00**	**0.180**	**0.040**	**64.00**	**0.160**	**0.034**	**68.00**
8	**0.260**	**0.120**	**48.00**	**0.230**	**0.068**	**54.00**	**0.200**	**0.050**	**60.00**	**0.140**	**0.045**	**72.00**	**0.120**	**0.038**	**76.00**
10	**0.220**	**0.140**	**56.00**	**0.190**	**0.078**	**62.00**	**0.160**	**0.057**	**68.00**	**0.110**	**0.049**	**78.00**	**0.090**	**0.041**	**82.00**
12	**0.180**	**0.160**	**64.00**	**0.160**	**0.085**	**68.00**	**0.130**	**0.062**	**74.00**	**0.090**	**0.051**	**82.00**	**0.070**	**0.043**	**86.00**
14	**0.140**	**0.180**	**72.00**	**0.120**	**0.095**	**76.00**	**0.110**	**0.065**	**78.00**	**0.070**	**0.054**	**86.00**	**0.050**	**0.045**	**90.00**
16	**0.140**	**0.180**	**72.00**	**0.120**	**0.095**	**76.00**	**0.100**	**0.067**	**80.00**	**0.070**	**0.054**	**86.00**	**0.050**	**0.045**	**90.00**
18	**0.140**	**0.180**	**72.00**	**0.120**	**0.095**	**76.00**	**0.100**	**0.067**	**80.00**	**0.070**	**0.054**	**86.00**	**0.050**	**0.045**	**90.00**
20	**0.140**	**0.180**	**72.00**	**0.120**	**0.095**	**76.00**	**0.100**	**0.067**	**80.00**	**0.070**	**0.054**	**86.00**	**0.050**	**0.045**	**90.00**
∞	**0.140**	**0.180**	**72.00**	**0.120**	**0.095**	**76.00**	**0.100**	**0.067**	**80.00**	**0.070**	**0.054**	**86.00**	**0.050**	**0.045**	**90.00**

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption.

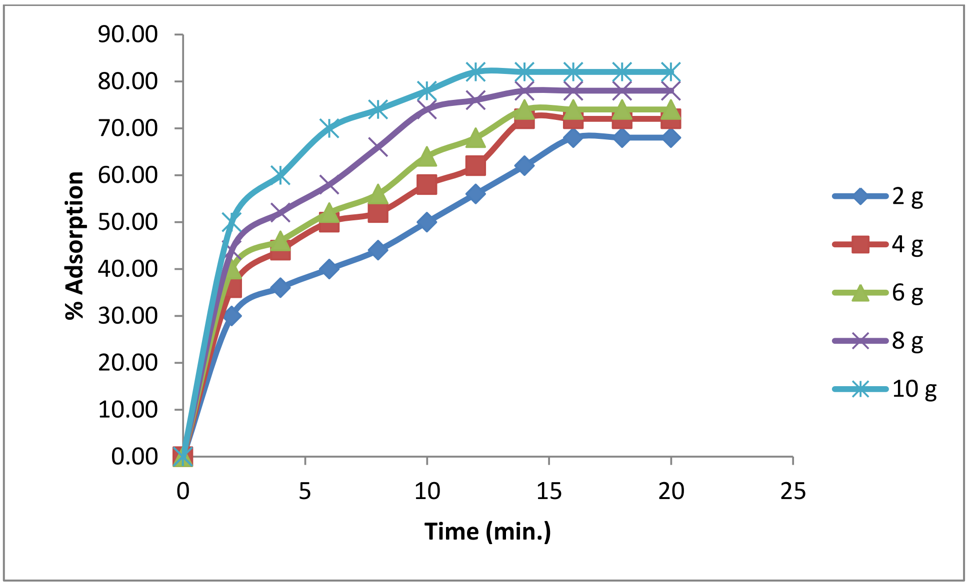

Figure 3.17: Change in % adsorption of Cr(VI) with time for different amount of soil on Cr(VI) adsorption onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 0.5 mg; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

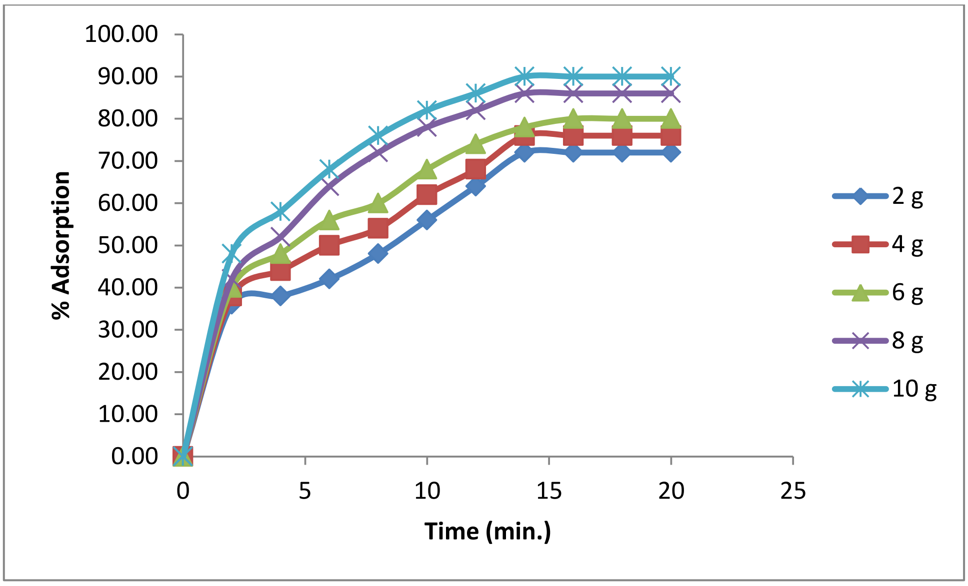

Figure 3.18: Change in % adsorption of Cr(VI) with time for different amount of soil on Cr(VI) adsorption onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.5 mg; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

3.3.4 Effect of Variation of pH of Solution

[A] Results $[S_1]_{0\text{-}15}$:

The results indicate that the adsorption capacity of soil decreases from 92% to 56% with increase in pH from 2 to 10 for $[S_1]_{0\text{-}15}$. The results are shown in **Figure 3.19** and **Table 3.9**.

[B] Results for $[S_2]_{15\text{-}30}$:

It is apparent from **Figure 3.20** and **Table 3.10** that with increase in pH from 2 to 10 adsorption of Chromium(VI) onto $[S_2]_{15\text{-}30}$ decreases from 96% to 58%.

The results are in accordance with previous study [75]. The state of metal ions in solution strongly depends on the pH of solution. The acidity and basicity of the solutions can influence the properties of the adsorbent surface and specification of metal ions. This is partly due to the fact that the hydrogen ion itself is a strong competing adsorbate, and partly due to the chemical specification of metal ions under the influence of the solution pH [76].

At acidic condition (pH 2-6), the predominant species of Chromium(VI) are $Cr_2O_7^{2-}$ and $HCrO_4^-$ [75]. Therefore, it can be inferred that Chromium(VI) adsorbed at pH 2 mainly in the form of $HCrO_4^-$ ions. The adsorption of metal ions depends upon both the nature of adsorbent surface and the species distribution of the metal ions in the aqueous solution [76]. The following reaction mechanism for adsorption of Chromium(VI) at different pH was proposed [77]:

$$2H^+ + HCrO_4^- \xleftrightarrow{2H^+} 2H_2CrO_4 \xleftrightarrow{2H^+} 2H_2O + Cr_2O_7^{2-} \longleftrightarrow 2CrO_3 + H_2O \qquad (3.1)$$

Within the acidic solution pH range of 2.0-6.0, chromium ions can exist in different forms, such as $Cr_2O_7^-$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ of which $HCrO_4^-$ predominant [78]. At lower solution pH value (2-3), the increase in Chromium(VI) adsorption is due to the electrostatic attraction between positively charged adsorbent surface and the $HCrO_4^-$. Another possible reason for the higher adsorption of Chromium(VI) on soil was the reduction of Chromium(VI) to

Chromium(III) in acidic medium. At low value of pH, the presence of H^+ ions in the solution is high which causes the reduction of Chromium(VI) to Chromium(III) ions due to high redox potential (1.3V at standard state) as shown in the reaction below [79].

$$HCrO_4^- + 7H^+ + 3e^- \longrightarrow Cr^{3+} + 4H_2O \qquad (3.2)$$

The oxidation product of this reaction is water. As the size of Chromium(III) ions is small, they can be easily replaced by the positively charged ions present on the soil surface [80]. Though in principle, there is a possibility of reduction of Chromium(VI) ion on to Chromium(III) at low pH, [81]. The mechanism of electrostatic attraction between soil surface and $HCrO_4^-$ is found more appropriate for explaining the Chromium(VI) adsorption onto the soil.

Similar results were obtained in a previous study related to adsorption of toxic metal Chromium(VI) on one step–steam pyrolysis corn cobs activated carbon [82]. The increases in Chromium(VI) adsorption with decrease in solution pH was also observed on peat [83], fungal biomass [84], bacterium biomass [85] banana pith [86], rice straw [87], green alga [88] and soil colloids [49].

It is observed that the Chromium(VI) adsorption efficiencies decreased with increasing pH. It is well established that Chromium(VI) exists as $HCrO_4^-$ and Cr_2O7^{2-} species at pH<6.0 and CrO_4^{2-} at pH>6.0 [89]. Increasing the pH value shifts the concentrating of $HCrO_4^-$ to other forms (CrO_4^{2-} and $Cr_2O_7^{2-}$). The decrease in adsorption of Chromium(VI) by increasing the value of pH may be due to the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates [76, 82].

This behavior also can be explained on the basis of zero point charge of the soil. At a higher pH above this zero point charge, the surface of the adsorbent gets negatively charged and at a lower pH below this, the surface of the adsorbent gets positively charged [90]. The pHpzc of soil in present study was found to be 9 (**Figure 2.10**) showing that surface was positively charged below pH 9, neutral at pH 9, and negatively charged above pH 9, and hence adsorption of Chromium(VI) was maximum at pH 2 due to electrostatic attraction between positively charged

Table 3.9: Influence of variation of pH of Cr(VI) solution on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50 mg $[S_1]_{0-15}$ = 2 g; particle size = 100BSS mesh; temp. = 30^{o} C.

$[pH]_{Cr\ (VI)\ sol.}$	**2**			**3**			**5**			**8**			**10**		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	**0.500**	**0.000**	**0.00**	**0.500**	**0.000**	**0.00**	**0.500**	**0.000**	**0.00**	**0.500**	**0.000**	**0.00**	**0.500**	**0.000**	**0.00**
2	**0.300**	**0.100**	**40.00**	**0.310**	**0.095**	**38.00**	**0.320**	**0.090**	**36.00**	**0.350**	**0.075**	**30.00**	**0.380**	**0.060**	**24.00**
4	**0.240**	**0.130**	**52.00**	**0.250**	**0.125**	**50.00**	**0.260**	**0.120**	**48.00**	**0.320**	**0.090**	**36.00**	**0.340**	**0.080**	**32.00**
6	**0.190**	**0.155**	**62.00**	**0.200**	**0.150**	**60.00**	**0.220**	**0.140**	**56.00**	**0.300**	**0.100**	**40.00**	**0.320**	**0.090**	**36.00**
8	**0.150**	**0.175**	**70.00**	**0.160**	**0.170**	**68.00**	**0.170**	**0.165**	**66.00**	**0.280**	**0.110**	**44.00**	**0.300**	**0.100**	**40.00**
10	**0.110**	**0.195**	**78.00**	**0.130**	**0.185**	**74.00**	**0.150**	**0.175**	**70.00**	**0.250**	**0.125**	**50.00**	**0.280**	**0.110**	**44.00**
12	**0.070**	**0.215**	**86.00**	**0.090**	**0.205**	**82.00**	**0.120**	**0.190**	**76.00**	**0.220**	**0.140**	**56.00**	**0.250**	**0.125**	**50.00**
14	**0.040**	**0.230**	**92.00**	**0.070**	**0.215**	**86.00**	**0.100**	**0.200**	**80.00**	**0.190**	**0.155**	**62.00**	**0.220**	**0.140**	**56.00**
16	**0.040**	**0.230**	**92.00**	**0.070**	**0.215**	**86.00**	**0.100**	**0.200**	**80.00**	**0.160**	**0.170**	**68.00**	**0.220**	**0.140**	**56.00**
18	**0.040**	**0.230**	**92.00**	**0.070**	**0.215**	**86.00**	**0.100**	**0.200**	**80.00**	**0.160**	**0.170**	**68.00**	**0.220**	**0.140**	**56.00**
20	**0.040**	**0.230**	**92.00**	**0.070**	**0.215**	**86.00**	**0.100**	**0.200**	**80.00**	**0.160**	**0.170**	**68.00**	**0.220**	**0.140**	**56.00**
∞	**0.040**	**0.230**	**92.00**	**0.070**	**0.215**	**86.00**	**0.100**	**0.200**	**80.00**	**0.160**	**0.170**	**68.00**	**0.220**	**0.140**	**56.00**

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption; $[pH]_{Cr\ (VI)\ sol.}$- pH of Cr(VI) solution

Table 3.10: Influence of variation of pH of Cr(VI) solution on Cr(VI) adsorption onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50 mg $[S_2]_{15-30}$ = 2 g; particle size = 100BSS mesh; temp. = 30^o C.

$[pH]_{Cr\ (VI)\ sol.}$	2			3			5			8			10		
Time, min.	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad
0	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00
2	0.270	0.115	46.00	0.290	0.105	42.00	0.300	0.100	40.00	0.320	0.090	36.00	0.340	0.080	32.00
4	0.240	0.130	52.00	0.260	0.120	48.00	0.280	0.110	44.00	0.310	0.095	38.00	0.330	0.085	34.00
6	0.210	0.145	58.00	0.230	0.135	54.00	0.240	0.130	52.00	0.290	0.105	42.00	0.320	0.090	36.00
8	0.180	0.160	64.00	0.190	0.155	62.00	0.210	0.145	58.00	0.260	0.120	48.00	0.310	0.095	38.00
10	0.120	0.190	76.00	0.160	0.170	68.00	0.180	0.160	64.00	0.220	0.140	56.00	0.280	0.110	44.00
12	0.080	0.210	84.00	0.100	0.200	80.00	0.130	0.185	74.00	0.180	0.160	64.00	0.240	0.130	52.00
14	0.030	0.235	94.00	0.050	0.225	90.00	0.090	0.205	82.00	0.140	0.180	72.00	0.210	0.145	58.00
16	0.020	0.240	96.00	0.050	0.225	90.00	0.090	0.205	82.00	0.140	0.180	72.00	0.210	0.145	58.00
18	0.020	0.240	96.00	0.050	0.225	90.00	0.090	0.205	82.00	0.140	0.180	72.00	0.210	0.145	58.00
20	0.020	0.240	96.00	0.050	0.225	90.00	0.090	0.205	82.00	0.140	0.180	72.00	0.210	0.145	58.00
∞	0.020	0.240	96.00	0.050	0.225	90.00	0.090	0.205	82.00	0.140	0.180	72.00	0.210	0.145	58.00

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption; $[pH]_{Cr\ (VI)\ sol.}$- pH of Cr(VI) solution

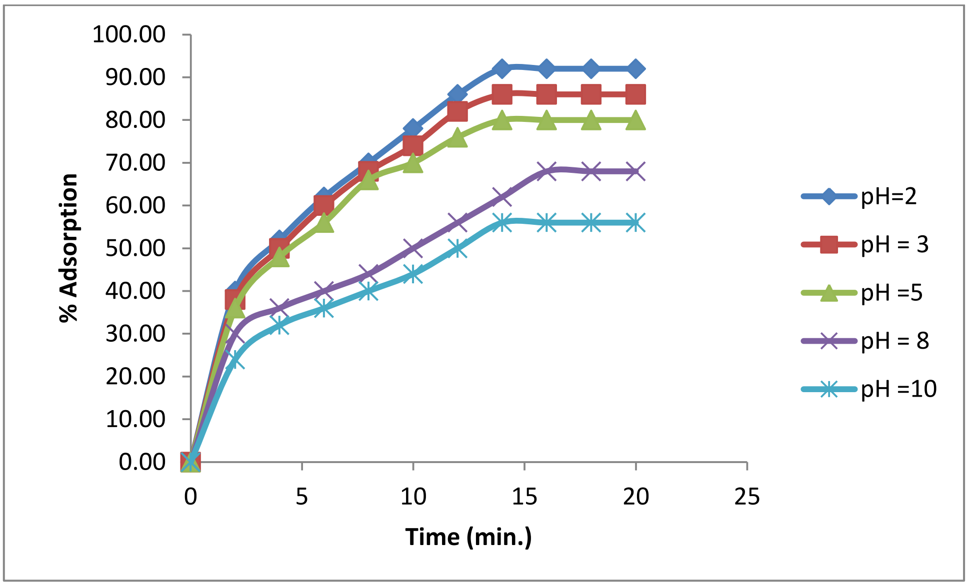

Figure 3.19: Change in % adsorption of Cr(VI) with time for different solution pH on Cr(VI) adsorption onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 0.50 mg $[S_1]_{0\text{-}15}$ = 2 g; particle size = 100BSS mesh; temp. = 30^{o}C.

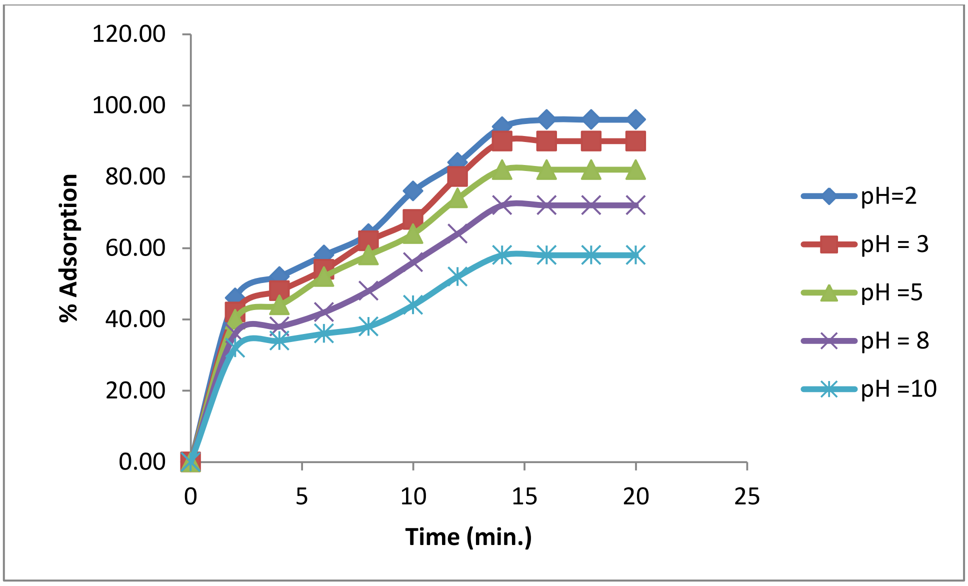

Figure 3.20: Change in % adsorption of Cr(VI) with time for different solution pH on Cr(VI) adsorption onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50 mg $[S_2]_{15\text{-}30}$ = 2 g; particle size = 100BSS mesh; temp. = 30^{o}C.

adsorbent surface and negatively charged Chromium(VI) and slowly decreased with increase in pH due to competition of OH^- ions.

A similar trend of result has been observed for the removal of Chromium(VI) by leaf mould [91], Fe(III)/ Cr(III) hydroxide [92], fly ash [93], polypyrrole coated oxidized multi walled carbon nanotubes [94] and Chromium(VI) adsorption on four typical soil colloids [49]. In general, the Chromium(VI) adsorption by different adsorbent have shown similar trend and the optimum pH 2 has been reported in several previous studies [95-100].

So, for both $[S_1]_{0-15}$ and $[S_2]_{15-30}$ adsorption of Chromium(VI) decreases on increasing pH from 2 to 10 and pH 2 was found optimum. The amount of Chromium(VI) adsorption by varying pH is slightly increases for $[S_2]_{15-30}$ as compared to $[S_1]_{0-15}$.

3.3.5 Effect of Co-Existing Ions

To understand the effect of different cations and anions on the adsorption of Chromium(VI) the values of their ionic radii are given in the **Table 3.11**:

Table 3.11: Ionic radii of cations and anions

Metal	Ionic radii nanometer
Na^+	0.102
Ca^{+2}	0.099
Mg^{+2}	0.072
Pb^{+2}	0.119
Zn^{+2}	0.007
Cl^-	0.181
NO_3^-	0.200
SO_4^{2-}	0.184
PO_4^{3-}	0.238
CrO_4^{2-}	0.240

[A] Results for effect of competitive co-ions:

Effect of existence of competitive cations was studied for Chromium(VI) adsorption and the results are summarized in **Table 3.11** and in **Figure 3.21** and **3.22**. The effects of competitive anions are presented in **Table 3.12** and in **Figure 3.23** and **3.24**. The anions taken for this study was phosphate, sulphate, nitrate and chloride. In addition to anions, metal ions (Na^+, Pb^{2+}, Zn^{2+}, Ca^{2+} and Mg^{2+}) were also investigated for their competitive effect in adsorption of Chromium(VI). The amounts of adsorption of Chromium(VI), without co-ions are given in **Table 3.4**.

According to previous study competing anions and metal ions are known to influence Chromium(VI) adsorption [101].

[B] Effect of Cations:

The percent adsorption of Chromium(VI) marginally decreased (47.6% to 44.6%) as shown in **Figure 3.21** and **3.22** by the presence of Na^+, Pb^{2+}, Zn^{2+}, Ca^{2+} and Mg^{2+} ions. Hence it can be inferred that the adsorption of Chromium(VI) was not significantly affected by the presence of Na^+, Pb^{2+}, Zn^{2+}, Ca^{2+} and Mg^{2+} ions. This was due to the higher ionic charge of the Chromium(VI) which dominates in the adsorption as compared to the other univalent ion Na^+ and divalent ions such as Pb^{2+}, Zn^{2+}, Ca^{2+} and Mg^{2+} ions present in the industrial effluent.

The binding forces between Chromium(VI) and soil fractions are dependent on pH and properties of ions like charge and ionic radius. The binding forces of Chromium(VI) ions to soils decrease with increasing pH of the environment. The ion with higher charge like Al^{3+} are stronger bound to soil particles than smaller charge such as Ca^{2+} [102]. When considering metal ions with the same charges the most important factors are ionic radius and rank of hydration. Ions which have bigger ionic radius emits the smaller electric field; consequently it is less hydrated than ions with smaller radius which emit stronger electrical fields [103]. This explains why ions of Chromium(VI) with higher ionic radius are preferably adsorbed from soil solution by soil particles.

[C] Effect of anions:

In case of anions the adsorption of Chromium(VI) by soil is decreased. As the adsorption sites were equivalent for all anions, different anions adsorbed/exchanged at different rates over these sites.

Table 3.12: Influence of variation of Co cation with initial Cr(VI) concentration $[Cr(VI)]_{ad1}$ = 5 mg; $[Cr(VI)]_{ad2}$ = 1.190 mg/g or 47.60%; $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

Cations	Ca^{2+}			Mg^{2+}			Zn^{2+}			Pb^{2+}			Na^{+}		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	5.000	0.000	0.00	5.000	0.000	0.00	5.000	0.000	0.00	5.000	0.000	0.000	5.000	0.000	0.000
2	2.780	1.110	44.40	2.800	1.100	44.00	2.770	1.115	44.60	2.790	1.105	44.20	2.900	1.050	42.00
4	2.770	1.115	44.60	2.780	1.110	44.40	2.750	1.125	45.00	2.770	1.115	44.60	2.880	1.060	42.40
6	2.750	1.125	45.00	2.770	1.115	44.60	2.730	1.135	45.40	2.750	1.125	45.00	2.870	1.065	42.60
8	2.730	1.135	45.40	2.750	1.125	45.00	2.720	1.140	45.60	2.740	1.130	45.20	2.850	1.075	43.00
10	2.710	1.145	45.80	2.740	1.130	45.20	2.700	1.150	46.00	2.730	1.135	45.40	2.820	1.090	43.60
12	2.690	1.155	46.20	2.730	1.135	45.40	2.680	1.160	46.40	2.710	1.145	45.80	2.790	1.105	44.20
14	2.680	1.160	46.40	2.720	1.140	45.60	2.660	1.170	46.80	2.700	1.150	46.00	2.770	1.115	44.60
16	2.680	1.160	46.40	2.720	1.140	45.60	2.660	1.170	46.80	2.700	1.150	46.00	2.770	1.115	44.60
18	2.680	1.160	46.40	2.720	1.140	45.60	2.660	1.170	46.80	2.700	1.150	46.00	2.770	1.115	44.60
20	2.680	1.160	46.40	2.720	1.140	45.60	2.660	1.170	46.80	2.700	1.150	46.00	2.770	1.115	44.60
∞	2.680	1.160	46.40	2.720	1.140	45.60	2.660	1.170	46.80	2.700	1.150	46.0	2.770	1.115	44.60

Unad- Unadsorbed amount of Cr (VI), Ad- Adsorbed amount of Cr (VI) (mg/g), %Ad-Percentage adsorption, $[r (VI)]_{ad1}$ = Added amount of Cr (VI); $[Cr (VI)]_{ad2}$ = adsorbed amount of Cr (VI) without Co cations.

Table 3.13: Influence of variation of Co anions with initial Cr(VI) concentration, $[Cr(VI)]_{ad1}$ = 5 mg; $[Cr(VI)]_{ad2}$ = 1.190 mg/g or 47.60%; $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

Anions	**SO_4^{2-}**			**NO_3^-**			**Cl^-**			**PO_4^{3-}**		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	**5.000**	**0.000**	**0.00**	**5.000**	**0.000**	**0.00**	**5.000**	**0.000**	**0.00**	**5.000**	**0.000**	**0.00**
2	**2.950**	**1.025**	**41.00**	**3.020**	**0.990**	**39.60**	**2.940**	**1.030**	**41.20**	**3.220**	**1.780**	**35.60**
4	**2.930**	**1.035**	**41.40**	**2.990**	**1.005**	**40.20**	**2.930**	**1.035**	**41.40**	**3.180**	**1.820**	**36.40**
6	**2.910**	**1.045**	**41.80**	**2.960**	**1.020**	**40.80**	**2.890**	**1.055**	**42.20**	**3.140**	**1.860**	**37.20**
8	**2.890**	**1.055**	**42.20**	**2.940**	**1.030**	**41.20**	**2.870**	**1.065**	**42.60**	**3.100**	**1.900**	**38.00**
10	**2.870**	**1.065**	**42.60**	**2.920**	**1.040**	**41.60**	**2.840**	**1.080**	**43.20**	**3.080**	**1.920**	**38.40**
12	**2.860**	**1.070**	**42.80**	**2.910**	**1.045**	**41.80**	**2.820**	**1.090**	**43.60**	**3.050**	**1.950**	**39.00**
14	**2.850**	**1.075**	**43.00**	**2.900**	**1.050**	**42.00**	**2.800**	**1.100**	**44.00**	**3.020**	**1.980**	**39.60**
16	**2.850**	**1.075**	**43.00**	**2.900**	**1.050**	**42.00**	**2.800**	**1.100**	**44.00**	**3.020**	**1.980**	**39.60**
18	**2.850**	**1.075**	**43.00**	**2.900**	**1.050**	**42.00**	**2.800**	**1.100**	**44.00**	**3.020**	**1.980**	**39.60**
20	**2.850**	**1.075**	**43.00**	**2.900**	**1.050**	**42.00**	**2.800**	**1.100**	**44.00**	**3.020**	**1.980**	**39.60**
∞	**2.850**	**1.075**	**43.00**	**2.900**	**1.050**	**42.00**	**2.800**	**1.100**	**44.00**	**3.020**	**1.980**	**39.60**

Unad- Unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption, $[Cr(VI)]_{ad1}$ = Added amount of Cr(VI); $[Cr(VI)]_{ad2}$ = adsorbed amount of Cr(VI) without Co anions.

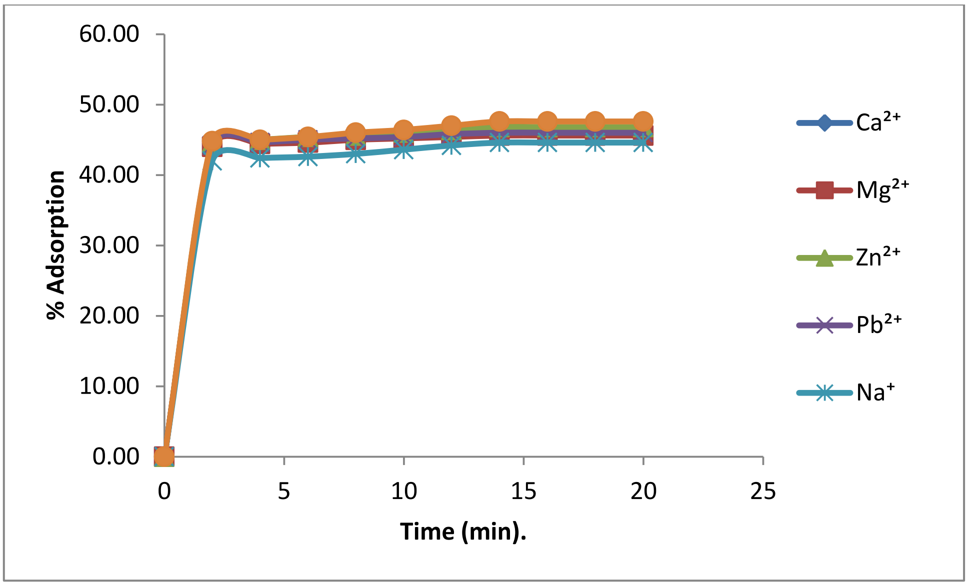

Figure 3.21: Influence of variation of co cations with initial Cr(VI) concentration, [Cr(VI)] = 2 mg; $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^{o}C.

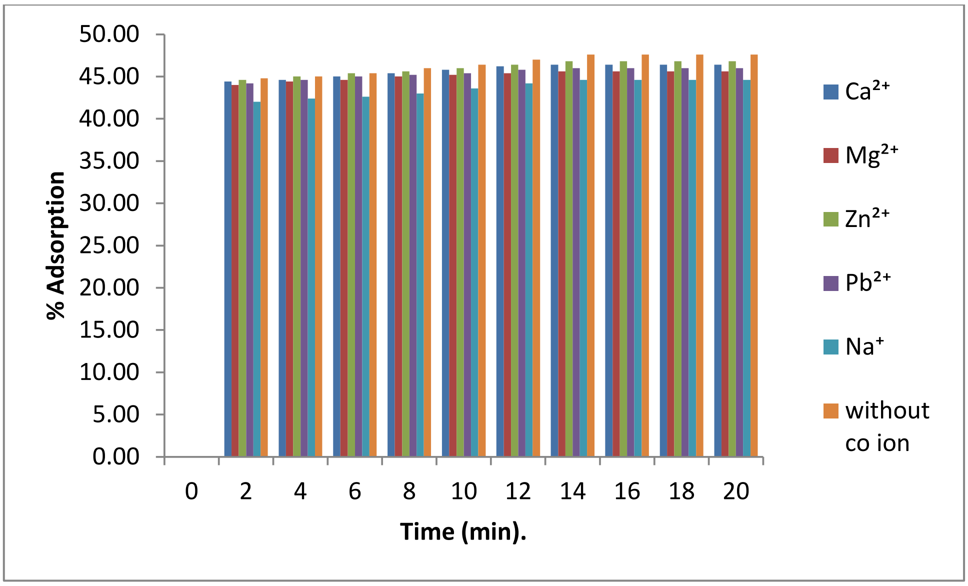

Figure 3.22: Influence of variation of co cations with initial Cr(VI) concentration, [Cr(VI)] = 2 mg; $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^{o}C.

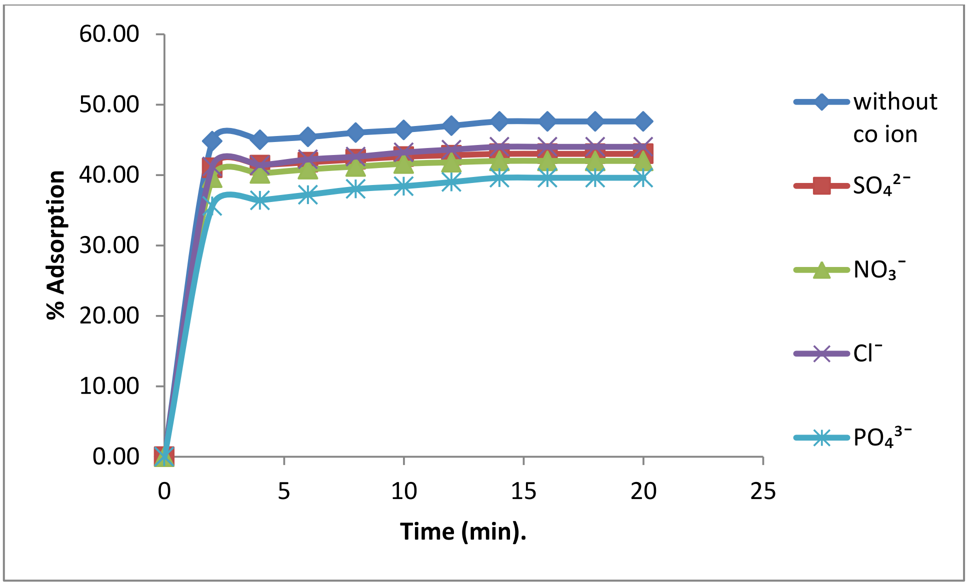

Figure 3.23: Influence of variation of Co anions with initial Cr(VI) concentration, [Cr(VI)] = 2 mg; $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^oC.

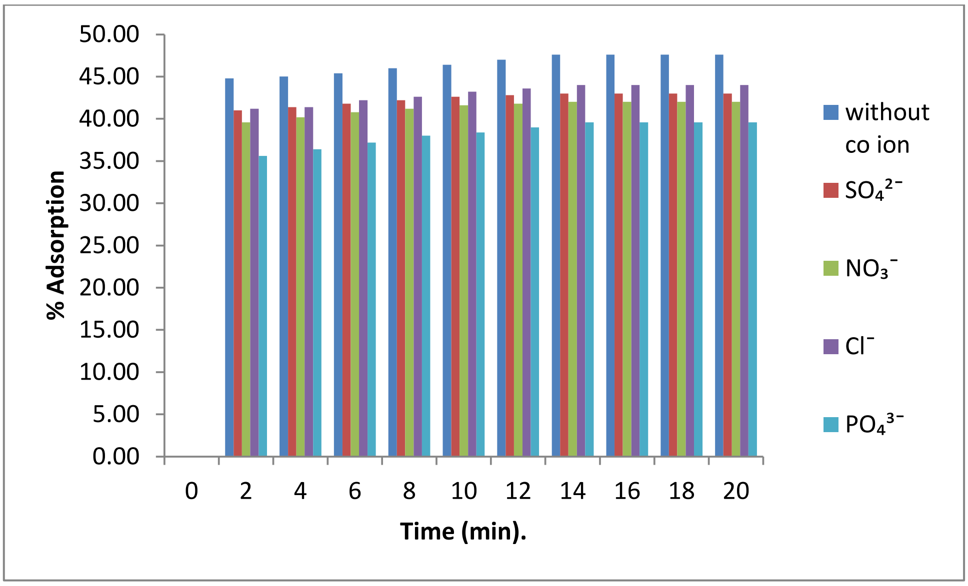

Figure 3.24: Influence of variation of Co anions with initial Cr(VI) concentration, [Cr(VI)] = 2 mg; $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^oC.

The results indicated (**Figure 3.23 and 3.24**) that the presence of phosphate anion highly influenced the uptake of Chromium while other anions like chloride and nitrate did not influence the uptake of Chromium significantly. In the case of sulphate the competition was relatively less. The reason is that, the ionic radii of divalent chromate and trivalent phosphate are almost identical (0.24 and 0.238 nm respectively), while ionic radii of mono-charged chloride and nitrate are low (0.181 and 0.200 nm respectively) thereby relatively ineffective competition in between chromate and these anions for adsorption. In case of the Cr(VI)/NO_3^- binary system, the selectivity of Chromium(VI) can be explained by the behavior of NO_3^- in adsorption processes. Nitrates (NO_3) are of low affinity ligands which are well known to form outer-sphere complexes with binding surfaces. Their low affinity nature thus implies weaker adsorption mechanism via outer-sphere complexation, and consequently, their competitive influence during Chromium(VI) adsorption was negligible.

The results are in accordance to previous studies [104-108].

3.4 Conclusion

On the basis of above results it is concluded that adsorbed amount of Chromium(VI) increases on increasing initial Chromium(VI) concentration for both soil samples, while percentage adsorption of Chromium(VI) decreases. On decreasing particle size adsorption of Chromium(VI) increases, for $[S_1]_{0-15}$ and $[S_2]_{15-30}$ because of different distribution of active centres. The percentage adsorption of Chromium(VI) increases on increasing amount of soil for both soil samples due to greater availability of the exchangeable active sites or the surface area for adsorption. Adsorption experiment results indicated that Chromium(VI) adsorption was strongly pH dependent. The maximum percentage adsorption was observed at pH 2. At acidic condition, the predominant species of Chromium(VI) are $Cr_2O_7^{2-}$ and $HCrO_4^-$. The higher adsorption in acidic medium is due to the positive surface charge on the soil surface attracting anionic Chromium(VI) species. The effect of Co existing cations was negligible due to higher ionic charge of Chromium(VI) species. Among the anions adsorption of Chromium(VI) was influenced by Phosphate anion due to similar ionic radii of both

Chromium(VI) and Phosphate ion. From all the adsorption experiment it is concluded that adsorption slightly increases for $[S_2]_{15-30}$ in comparison of $[S_1]_{0-15}$ due to more unsaturation in lower depth and adsorption process are governed by many factors including soil composition, initial metal ion concentration, Contact time, soil particle size, pH of solution and presence of different cations and anions in solution.

3.5 References

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Chapter – 4

Thermodynamic Consideration and Kinetic Modeling of Chromium(VI) Adsorption in Contaminated Alkaline Soil

ABSTRACT

The aim of this work was to study the adsorption of Chromium(VI) onto $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30}$ samples to give the best suited adsorption isotherm and to evaluate thermodynamic parameters, which are helpful to understand the interaction of Chromium with soil. The Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium studies on different temperatures ranging from 30^{o}C to 50^{o}C for both samples. On the basis of coefficient of determination (R^2) and standard error of estimation (σ), Freundlich isotherm best fits for both soil samples. The effect of temperature and calculation of ΔG^o ΔH^o ΔS^o for the adsorption of Chromium(VI) was also investigated in this chapter. The negative ΔG^o indicates that adsorption process is spontaneous. The Values of ΔH^o and ΔS^o were found positive indicates the adsorption process is endothermic for both soil samples. The experimental data of adsorption of Chromium(VI) onto $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30}$ were applied on the seven different Kinetic models and on the basis of coefficient of determination (R^2) and standard error of estimation (σ) , the pseudo second order model and intraparticle diffusion kinetic model were found best fitted for both soil samples.

4.1 Introduction

The problems of the ecosystem are increasing with developing technology; heavy metals pollution is one of the main problems [1]. Toxic metal compounds contaminate soil and water reservoirs. Heavy metals are non-biodegradable and can lead to accumulation in living organisms, causing various diseases and disorders [2]. It is well known that some metals are harmful to life, such as antimony, Chromium, copper, lead, manganese, mercury, cadmium, etc., and are significantly toxic to human beings and the ecological environment [3]. Therefore, studies on the removal of heavy metal pollution are increasingly challenging [1]. One of such methods is the use of adsorption technique.

Adsorption is the accumulation of a substance at the interface solid and liquid or solid and gas. Adsorbate is the substance that accumulates at the interface, and the solid on which adsorption occurs is known as adsorbent. The adsorption mainly occurs due to the unbalanced forces (Van der Waals, electrostatic) at the surface of the solids [4]. Chromium exists in more than one redox state, and its behavior in soil depends on different parameters such as pH and temperature. Temperature affects the vibrational energies of the adsorbed molecule, facilitates the diffusion in micropore system, that Chromium undergoes dehydration with increasing temperature [5, 6].

The adsorption mechanism (i.e., chemical or physical) is often an important indicator used to describe the type and level of interactions between the adsorbate and adsorbent. If adsorption decreases with increasing temperature, this may indicate a physical adsorption; the reverse is generally true for chemisorptions. However, there are a number of contradictory cases in the literature [7]. Nevertheless, only temperature is not sufficient to determine the type of adsorption. The type of adsorption may be determined through different thermodynamic quantities such as $\Delta H°$, $\Delta G°$ and $\Delta S°$ [8]. The adsorption process is composed of two contributions, enthalpy and entropy, which characterize whether the reaction is spontaneous or non spontaneous. Thus the feasibility of the adsorption process was evaluated by the thermodynamic parameters including free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°). So effect of temperature is an important parameter for adsorption study.

An adsorption isotherm was used to characterize the interactions of adsorbate molecule with the adsorbent material. The adsorption model assumes that the species are adsorbed at a fixed number of well defined sites, each of which is capable of holding only one molecule. These sites are also assumed to be energetically equivalent and distant from each other so that there are no interactions between molecules adsorbed on adjacent sites.

Adsorption equilibrium is known as adsorption isotherm and is obtained by plotting solute (adsorbate) concentration in the solid phase as a function of solute concentration in liquid phase at a given temperature [9]. The constant values derived from adsorption isotherm could express the surface properties and affinity of adsorbent. These constant values can also be useful to determine the adsorption capacity of the adsorbent [10].

Adsorption isotherms are important to describe the adsorption mechanism for the interaction of Chromium(VI) onto the soil surface. The equilibrium studies are useful to obtain the adsorption capacity onto soil for Chromium(VI) adsorption. The equilibrium data for the adsorption of Chromium(VI) using soil fits in various isotherm models which results in a suitable model that can be used for the design of an adsorption process. In the present study, three equilibrium models are analyzed to investigate the suitable adsorption isotherm [11].

Adsorption equilibrium provides fundamental physicochemical data for evaluating the applicability of adsorption process as a unit operation. Adsorption equilibrium is usually described by an isotherm equation whose parameter expresses the surface properties and affinity of the adsorbent at fixed temperature, pH and initial metal concentration. Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and solid phases, based on a set of assumptions that are related to heterogeneity or homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate species [12].

For adsorption of Chromium(VI) onto soil, it is important to explain the relationship between adsorbed metal ion per unit weight of adsorbent (q_e) and residual concentration of metal ion in solution (C_e) at equilibrium. The analysis of the adsorption isotherm data by fitting them to different adsorption isotherm models is an important step to find the suitable adsorption isotherm model that can be used for design purposes [13].

In the literature several isotherms are used for the determination of kinetic parameters of adsorption, with the most important being the Langmuir, Freundlich and Temkin [14-17]. The Langmuir model assumes monolayer adsorption on the solid surface, while Freundlich model is empirical in nature based on the adsorption of adsorbate onto heterogeneous surface [18], and Temkin isotherm describes the effect of indirect adsorbate-adsorbent interaction [19]. The most appropriate correlation of the experimental data to a theoretical model is necessary for the practical design and operation of an adsorption system. Therefore, the three most extensively used isotherm models namely Langmuir, Freundlich and Temkin models were applied to fit the isotherm data [20].

Adsorption kinetics was one of the most important characters representing the adsorption efficiency [18]. The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid solution interface [21]. Adsorption kinetics plays a vital role in the scale-up studies of soil remediation process design. These designs give a chance to pick the optimum operational conditions of Chromium(VI) and adsorbent to facilitate the effective adsorption process for removal of heavy metal at large scale processes [9]. The kinetic parameters are useful in predicting the adsorption rate which can be used as important information in designing and modeling of the adsorption and remedial operations [22].

Several researcher have been using these models in their study. The kinetics of adsorption of Chromium(VI) is explicitly explained in the literature using first order, pseudo first order, second order, intraparticle diffusion and Elovich kinetic models [23-25]. The kinetics of Chromium(VI) adsorption on the activated carbons were analysed using pseudo first order [26], pseudo second order [27], Elovich [28-29] and intraparticle diffusion [30-31] kinetic models in the literature [21]. Al-Ghouti et al (2009) [32] have carried out adsorption behavior of methylene blue onto Jordanian diatomite and the experimental results were also applied to the pseudo first and second order kinetic models. S. J. Allen et al (2005) [33], A. M. Kamash et al (2005) [34], L. Kumar et al (2008) [35] and A. Mittal et al (2008) [36] also applied their experimental data on different kinetic model in their study.

4.2 Experimental

Soil sample was collected from RIICO Industrial area, from two different depth, $[S_1]_{0-15}$ and $[S_2]_{15-30}$. Both samples were dried and sieved to get uniform particle size. A 100 mg L^{-1} stock solution of Chromium(VI) was prepared by weighing 0.2829 gm $K_2Cr_2O_7$ and diluting with deionized water up to 1000 ml. The effect of temperature on the adsorption of Chromium(VI) was investigated at different temperature 30^o, 35^o, 40^o, 45^o and 50^oC for $[S_1]_{0-15}$ and $[S_2]_{15-30}$ into 250 ml of conical flask containing 100 ml of 0.5 mg Chromium(VI) solution. The flasks were agitated in a thermostat shaker and batch adsorption were carried out at different contact times (2, 4, 6, 8, 10, 12, 14, 16 & 20 min). The soil amount was taken 2 g in 100 ml solution at pH 8, solution temperature 30^oC and stirring rate was kept constant at 120 rpm. The particle size was 100 BSS mesh. In order to construct adsorption isotherm for the adsorbent, experiments were carried out by varying the initial Chromium(VI) ion concentrations from 0.5 mg to 5 mg at different temperatures from 30^oC to 50^oC. From the experimental data it was possible to evaluate the adsorption capacity of the Chromium(VI) in solution. Experiments to determine the adsorption parameter were at operational conditions:

Conditions for $[S_1]_{0-15}$: initial Chromium(VI) concentration; 0.5, 1, 2, 3 and 5 mg, amount of soil; 2 g, pH; 8, and particle size = 100 BSS mesh, Volume of adsorption medium = 100 ml, temperature = $30\ ^o$, 35^o, 40^o, 45^o and 50^oC.

Conditions for $[S_2]_{15-30}$: initial Chromium(VI) concentration; 0.5, 1, 2, 3 and 5 mg, amount of soil; 2 g, pH; 8 and particle size = 100 BSS mesh, Volume of adsorption medium = 100 ml, temperature = $30\ ^o$, 35^o, 40^o, 45^o and 50^oC.

Sample was withdrawn from conical flasks after specified time interval and residual metal content was analyzed by 1, 5 diphenylcarbazide spectrophotometric method.

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{4.1}$$

Q_t = adsorbed amount of Chromium(VI), C_o = initial concentration of Chromium(VI), C_t = Chromium(VI) concentration at time t, V = volume of the solution (L), M= mass of soil (g).

Graph between amounts of adsorption versus temperature was draw. The linearized form of Freundlich, Langmuir and Temkin adsorption isotherms of Chromium(VI) by soil was obtained at the temperature of 30^o, 35^o, 40^o, 45^o and 50^oC, for $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30}$. The Kinetic models were applied on the results of variation of initial Chromium(VI) concentration, given in **Chapter 3**.

4.3 Thermodynamic Parameters

Thermodynamic parameter such as standard free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o), were calculated using the following relations [11, 37].

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{4.2}$$

The Gibbs energy change (ΔG^o) indicates the degree of spontaneity of an adsorption process. According to thermodynamic law, ΔG^o of adsorption was calculated from the following equation:

$$\Delta G^o = -RT \ln K_c \tag{4.3}$$

Where K_c is the thermodynamic equilibrium constant without units, T is the absolute temperature in Kelvin, and R is the gas constant.

K_c can be calculated by the following equation:

$$K_c = \frac{C_{Ad}}{C_e} \tag{4.4}$$

Where K_c is the equilibrium constant, and C_{Ad} and C_e are equilibrium concentrations of Chromium(VI) on the adsorbent and in the solution, respectively.

The values of ΔH^o and ΔS^o were calculated from the following Van’t Hoff equation

$$\ln K_c = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{4.5}$$

A plot of ln K_c v/s 1/T gave straight line, and ΔH^o and ΔS^o were calculated from the slope and intercept [13, 25].

These thermodynamic parameter estimates can offer insight into the type and mechanism of an adsorption process.

4.4 Isotherms

[A] Langmuir Isotherm:

A well known linear form of Langmuir equation can be expressed as:

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{Q_{\max} b} + \frac{C_{eq}}{Q_{\max}} \tag{4.6}$$

Where C_{eq} is the equilibrium concentration of the adsorbate (mg/L), Q_{eq} is the amount of adsorbate per unit mass of adsorbent (mg/g), Q_{max} is the maximum quantity of metal ions per unit weight of adsorbent to form a complete monolayer on the surface (mg g^{-1}) and b is a constant related to the affinity of binding sites with the metal ions (Lmg^{-1}) [38]. The essential feature of the Langmuir isotherm can be given in term of dimensionless separation factor R_L i. e. defined as:

$$R_L = \frac{1}{(1 + bC_0)} \tag{4.7}$$

Where C_o is the initial solute concentration and the value of R_L indicates the shape of the isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [39].

[B] Freundlich Isotherm:

The well known linear form of Freundlich model is expressed by:

$$\mathrm{n}\, q_e = \ln K_F + \left(\frac{1}{n_f}\right) \times \ln C_e \qquad [q_e = K_F C_e{}^{1/n}] \tag{4.8}$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L) and q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$) and n_f are Freundlich constants representing the adsorption capacity and intensity of adsorption, respectively [40-42].

K_F is the Freundlich constant which indicates the relative adsorption capacity of the adsorbent related to bonding energy and n_f is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient [42, 43].

If a value for n_f is equal to unity, the adsorption is linear. If the value of n_f is below unity, it implies that the adsorption process is unfavorable, but if the value of n_f is above unity, adsorption is favorable. n_f

[C] Temkin Isotherm:

The derivation of the Temkin isotherm is based on the assumption that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic, as implied in the Freundlich equation. It can be described as follow [44]:

$$q_e = \frac{RT}{b_T}\ln(a_T C_e) = \frac{RT}{b_T}\ln a_T + \frac{RT}{b_T}\ln C_e \tag{4.9}$$

where a_T is the equilibrium binding constant corresponding to the maximum binding energy (g L^{-1}), b_T is the Temkin constant related to the heat of sorption (kJ mol^{-1}), and R is the gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the absolute temperature (K). Thus, the constants can be obtained from the slope and intercept of a straight line plot of qe versus lnCe.

4.5 Kinetic Models

[A] Zero Order Kinetic Model:

This model utilizes the **Equation 4.10** as shown below as:

$$C_o - C_t = a - bt \tag{4.10}$$

The Zero Order plots were drawn with (C_o – C_t) and t. Zero order reaction have been applied to describe adsorption of potassium by A. F. Burns et al (1965) [45], Chromium by M. L. Amachar et al (1982) [46] and nitrogen reaction by D. R. Keeney et al (1973) in soils [47].

[B] First Order Kinetic Model:

To correlate the rate of reaction a simple first order model were used [48]. The first order rate constant was calculated using the **Equation (4.11)**:

$$\ln(C_o - C_t) = a - bt \tag{4.11}$$

The first order plot was drawn between ln (C_o – C_t) and t. The application of first order reaction for Chromium(VI) removal have been observed by N. K. Hamadia et al (2001) [48], T. Satish et al (2014) [9] and For Phosphorus soil chemical process have been applied by M. Vijay (2005) [49].

[C] Second Order Kinetic Model:

This model is based on the use of **Equation 4.12** or **4.13** given as;

$$\frac{1}{C_t} = \frac{1}{C_o} + kt \tag{4.12}$$

$$\frac{1}{C_t} = a - bt \tag{4.13}$$

Phosphate reaction on calcite by R. A. Griffin et al (1974) [50] and Al reaction in soil by P. M. Jardine et al (1986) [51] have been described by second order kinetic model.

[D] Pseudo First Order:

Lagergren showed that the rate of adsorption of solute on adsorbent is based on the adsorption capacity and followed a pseudo first-order equation [52, 53]. The non-linear form of the pseudo first-order equation is given by **Equation 4.14**:

$$\frac{dq_t}{d_t} = k_{ad}(q_e - q_t) \tag{4.14}$$

Where, q_e and q_t are the amounts of Chromium(VI) adsorbed (mg g^{-1}) at equilibrium time and at any instant of time, *t*, respectively, and k_{ad} (min^{-1}) is the rate constant of the pseudo first-order adsorption operation. The integrated rate law after application of the initial condition of q_t =0 at t = 0, becomes a linear equation as given by **Equation 4.15**:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_{ad}t}{2.303} \tag{4.15}$$

The plot of log ($q_e - q_t$) versus *t* gives a straight line for the pseudo first-order adsorption kinetics, from the slope adsorption rate constant, k_{ad}, is estimated.

The pseudo first order model have been applied to describe removal of Chromium(VI), from aqueous solution on seeds of Artimisia absinthium by R. A. K. Rao et al (2014) [13], from wastewater using sulfuric acid modified Avocado seed by M. Bhaumic et al (2014) [20] and from aqueous solution using divinylbenzene copolymer resin by S. Bajpai et al (2012) [54].

[E] Pseudo Second Order:

Pseudo-second-order rate equation [55] can be expressed in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4.16}$$

Where k_2 is the pseudo second-order adsorption rate constant (g mg^{-1} min^{-1}), and qe is the adsorption capacity calculated by the pseudo-second-order kinetic model (mg g^{-1}). The slope and intercept of plots of t/qt versus t are used to calculate K_2 and qe, respectively. The constant k_2 is used to calculate the initial sorption rate h (mg g^{-1} min^{-1}), at t→0 as follows [56]:

$$h = k_2 q_e^2 \tag{4.17}$$

The application of pseudo second order model for Chromium(VI) adsorption have been observed by D. J. L. Guerra et al (2014) using a modified and unmodified bentonite clay [57], by Xin-Jiang Hu et al (2011) using ethylenediamine modified cross-linked magnetic chitosan resin [58], by A. S. Kumar et al (2011) using cellulose-clay composite biosorbent [59].

[F] Intraparticle Diffusion Model:

Kinetic data was further analyzed using the intraparticle diffusion model based on the theory proposed by Weber and Morris [31]. The rate parameters for intraparticle diffusion (K_{id}) for Chromium(VI) removal were determined by using the following equation:

$$q_t = K_{id} t^{1/2} + C \tag{4.18}$$

Where K_{id} is the rate constant of intraparticle diffusion parameter (mg $g^{-1}min^{-1/2}$) and C is the intercept. The values of K_{id} and C can be determined from the slope and intercept of the plot qt versus $t^{1/2}$. Values of C give an idea about the thickness of boundary layer, i.e. the larger the intercept, the greater the contribution of the surface sorption in the rate controlling step [60].

This model have been used to study the removal of Chromium(VI); by A. Jyotikusum et al (2009) using activated carbon developed from Tamarind wood activated with zinc chloride [61], by M. Bhaumic (2011) using polypyrrole magnetic nanocomposite [62] and by V. Sarin et al (2006) using Eucalyptus bark [63].

[G] Elovich Equation:

The Elovich model equation is generally expressed as [28, 29]:

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_t) \times t^{1/2} + I \tag{4.19}$$

Where: α is the initial adsorption rate (mg·g^{-1}·min^{-1})

β is the desorption constant (g·mg^{-1}) during any one experiment

To simplify the Elovich equation, Chien and Clayton (1980) [28] assumed $\alpha\beta t >> t$ and by applying the boundary conditions $qt = 0$ at $t = 0$ and $qt = qt$ at $t = t$ **Equation 4.19** becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{4.20}$$

If Chromium(VI) adsorption fits the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(αβ). This equation have been used to describe the removal of Chromium(VI); by D. J. L. Guerra et al (2014) using a modified and unmodified bentonite clay [57], by M. Bhaumic et al (2014) using Sulfuric acid modified Avocado seed [20] and by E. Demirbas et al (2004) using activated carbons prepared from agricultural wastes [21].

4.6 Results and Discussion

Temperature Variation and Determination of Thermodynamics Quantities

4.6.1 Effect of Variation of Temperature

Temperature is an important parameter for study of Chromium(VI) adsorption. The effect of variation of temperature was studied on $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30}$.

[A] Results for $[S_1]_{0\text{-}15}$:

It is apparent from the **Table 4.1** to **4.5** and **Figure 4.1** to **4.5**, that with a increase in the temperature from 30^{o}C to 50^{o}C the amount of percentage adsorption increases from 68% to 78%, 56% to 68%, 53.50% to 65%, 48.67% to 62% and 46.40% to 58.20% for 0.5 mg, 1 mg, 2 mg, 3 mg and 5 mg initial Chromium(VI) concentration respectively for $[S_1]_{0\text{-}15}$.

[B] Results for $[S_2]_{15\text{-}30}$:

It is observed from the **Table 4.6** to **4.10** and **Figure 4.6** to **4.10**, that amount of percentage adsorption increases from 72% to 83%, 59% to 72 %, 55% to 67.50%, 49.67% to 63.67% and 47.60% to 59.20% for 0.5 mg, 1 mg, 2 mg, 3 mg and 5 mg initial Chromium(VI) concentration respectively on increasing from temperature from 30^{o}C to 50^{o}C for $[S_2]_{15\text{-}30.}$

The adsorption of Chromium(VI) at different temperature for $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30}$ was showed an increase in the adsorption capacity when the temperature was increased from 30^{o}C to 50^{o}C, indicates that the adsorption reaction is endothermic in nature. The increase in adsorption with increase in temperature was attributed to the formation of new active binding sites on and near the surface of soil as a result of breaking of some of internal bonds. Increase in the kinetic energy of Chromium(VI) was another reason for the increase in adsorption that facilitated diffusion of Chromium(VI) within pores of soil.

Diffusion was increased due to decrease in viscosity of solution as a consequence of increasing temperature and enlargement of pore size. Since diffusion is an endothermic process, it would be expected that an increased

Table 4.1: Influence of variation of temperature on Cr(VI) adsorption onto $[S_1]_{0-15,}$ [Cr(VI)] = 0.50 mg $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. ^{o}C	30			35			40			45			50		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00
2	0.350	0.075	30.00	0.330	0.085	34.00	0.320	0.090	36.00	0.310	0.095	38.00	0.280	0.110	44.00
4	0.320	0.090	36.00	0.290	0.105	42.00	0.280	0.110	44.00	0.270	0.115	46.00	0.250	0.125	50.00
6	0.300	0.100	40.00	0.270	0.115	46.00	0.240	0.130	52.00	0.230	0.135	54.00	0.210	0.145	58.00
8	0.280	0.110	44.00	0.240	0.130	52.00	0.220	0.140	56.00	0.210	0.145	58.00	0.190	0.155	62.00
10	0.250	0.125	50.00	0.200	0.150	60.00	0.190	0.155	62.00	0.180	0.160	64.00	0.150	0.175	70.00
12	0.220	0.140	56.00	0.180	0.160	64.00	0.160	0.170	68.00	0.140	0.180	72.00	0.110	0.195	78.00
14	0.190	0.155	62.00	0.150	0.175	70.00	0.130	0.185	74.00	0.120	0.190	76.00	0.110	0.195	78.00
16	0.160	0.170	68.00	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.110	0.195	78.00
18	0.160	0.170	68.00	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.110	0.195	78.00
20	0.160	0.170	68.00	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.110	0.195	78.00
∞	0.160	0.170	68.00	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.110	0.195	78.00

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.2: Influence of variation of temperature on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 1 mg $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. °C	30			35			40			45			50		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	1.000	0.000	0.00	1.000	0.000	0.00	1.000	0.000	0.00	1.000	0.000	0.00	1.000	0.000	0.00
2	0.600	0.200	40.00	0.580	0.210	42.00	0.550	0.225	45.00	0.520	0.240	48.00	0.490	0.255	51.00
4	0.580	0.210	42.00	0.520	0.240	48.00	0.510	0.245	49.00	0.480	0.260	52.00	0.460	0.270	54.00
6	0.560	0.220	44.00	0.510	0.245	49.00	0.480	0.260	52.00	0.450	0.275	55.00	0.420	0.290	58.00
8	0.520	0.240	48.00	0.480	0.260	52.00	0.440	0.280	56.00	0.410	0.295	59.00	0.380	0.310	62.00
10	0.490	0.255	51.00	0.450	0.275	55.00	0.410	0.295	59.00	0.380	0.310	62.00	0.350	0.325	65.00
12	0.470	0.265	53.00	0.420	0.290	58.00	0.390	0.305	61.00	0.360	0.320	64.00	0.320	0.340	68.00
14	0.440	0.280	56.00	0.400	0.300	60.00	0.370	0.315	63.00	0.350	0.325	65.00	0.320	0.340	68.00
16	0.440	0.280	56.00	0.400	0.300	60.00	0.370	0.315	63.00	0.350	0.325	65.00	0.320	0.340	68.00
18	0.440	0.280	56.00	0.400	0.300	60.00	0.370	0.315	63.00	0.350	0.325	65.00	0.320	0.340	68.00
20	0.440	0.280	56.00	0.400	0.300	60.00	0.370	0.315	63.00	0.350	0.325	65.00	0.320	0.340	68.00
∞	0.440	0.280	56.00	0.400	0.300	60.00	0.370	0.315	63.00	0.350	0.325	65.00	0.320	0.340	68.00

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.3: Influence of variation of temperature on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 2 mg $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. °C	30			35			40			45			50		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	2.000	0.000	0.00	2.000	0.000	0.00	2.000	0.000	0.00	2.000	0.000	0.00	2.000	0.000	0.00
2	1.080	0.460	46.00	1.040	0.480	48.00	1.020	0.490	49.00	1.000	0.500	50.00	0.970	0.515	51.50
4	1.070	0.465	46.50	1.020	0.490	49.00	0.980	0.510	51.00	0.970	0.515	51.50	0.910	0.545	54.50
6	1.060	0.470	47.00	0.980	0.510	51.00	0.940	0.530	53.00	0.920	0.540	54.00	0.880	0.560	56.00
8	1.010	0.495	49.50	0.950	0.525	52.50	0.900	0.550	55.00	0.860	0.570	57.00	0.820	0.590	59.00
10	0.970	0.515	51.50	0.910	0.545	54.50	0.880	0.560	56.00	0.810	0.595	59.50	0.760	0.620	62.00
12	0.940	0.530	53.00	0.890	0.555	55.50	0.840	0.580	58.00	0.780	0.610	61.00	0.720	0.640	64.00
14	0.930	0.535	53.50	0.870	0.565	56.50	0.820	0.590	59.00	0.760	0.620	62.00	0.700	0.650	65.00
16	0.930	0.535	53.50	0.870	0.565	56.50	0.820	0.590	59.00	0.760	0.620	62.00	0.700	0.650	65.00
18	0.930	0.535	53.50	0.870	0.565	56.50	0.820	0.590	59.00	0.760	0.620	62.00	0.700	0.650	65.00
20	0.930	0.535	53.50	0.870	0.565	56.50	0.820	0.590	59.00	0.760	0.620	62.00	0.700	0.650	65.00
∞	0.930	0.535	53.50	0.870	0.565	56.50	0.820	0.590	59.00	0.760	0.620	62.00	0.700	0.650	65.00

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.4: Influence of variation of temperature on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 3 mg $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. °C	30			35			40			45			50		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	3.000	0.000	0.00	3.000	0.000	0.00	3.000	0.000	0.00	3.000	0.000	0.000	3.000	0.000	0.00
2	1.690	0.655	43.67	1.600	0.700	46.67	1.540	0.730	48.67	1.510	0.745	49.67	1.410	0.795	53.00
4	1.680	0.660	44.00	1.570	0.715	47.67	1.490	0.755	50.33	1.460	0.770	51.33	1.360	0.820	54.67
6	1.650	0.675	45.00	1.520	0.740	49.33	1.440	0.780	52.00	1.400	0.800	53.33	1.320	0.840	56.00
8	1.640	0.680	45.33	1.480	0.760	50.67	1.410	0.795	53.00	1.350	0.825	55.00	1.270	0.865	57.67
10	1.590	0.705	47.00	1.470	0.765	51.00	1.400	0.800	53.33	1.320	0.840	56.00	1.220	0.890	59.33
12	1.560	0.720	48.00	1.470	0.765	51.00	1.390	0.805	53.67	1.300	0.850	56.67	1.180	0.910	60.67
14	1.540	0.730	48.67	1.460	0.770	51.33	1.380	0.810	54.00	1.300	0.850	56.67	1.160	0.920	61.33
16	1.540	0.730	48.67	1.460	0.770	51.33	1.380	0.810	54.00	1.300	0.850	56.67	1.140	0.930	62.00
18	1.540	0.730	48.67	1.460	0.770	51.33	1.380	0.810	54.00	1.300	0.850	56.67	1.140	0.930	62.00
20	1.540	0.730	48.67	1.460	0.770	51.33	1.380	0.810	54.00	1.300	0.850	56.67	1.140	0.930	62.00
∞	1.540	0.730	48.67	1.460	0.770	51.33	1.380	0.810	54.00	1.300	0.850	56.67	1.140	0.930	62.00

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.5: Influence of variation of temperature on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 5 mg $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. ^{o}C	30			35			40			45			50		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	5.000	0.000	0.00	5.000	0.000	0.00	5.000	0.000	0.00	5.000	0.000	0.00	5.000	0.000	0.00
2	2.790	1.105	44.20	2.710	1.145	45.80	2.660	1.170	46.80	2.610	1.195	47.80	2.350	1.325	53.00
4	2.780	1.110	44.40	2.680	1.160	46.40	2.620	1.190	47.60	2.540	1.230	49.20	2.290	1.355	54.20
6	2.760	1.120	44.80	2.650	1.175	47.00	2.560	1.220	48.80	2.480	1.260	50.40	2.240	1.380	55.20
8	2.720	1.140	45.60	2.620	1.190	47.60	2.510	1.245	49.80	2.410	1.295	51.80	2.190	1.405	56.20
10	2.700	1.150	46.00	2.580	1.210	48.40	2.440	1.280	51.20	2.350	1.325	53.00	2.130	1.435	57.40
12	2.690	1.155	46.20	2.560	1.220	48.80	2.390	1.305	52.20	2.290	1.355	54.20	2.090	1.455	58.20
14	2.680	1.160	46.40	2.550	1.225	49.00	2.360	1.320	52.80	2.260	1.370	54.80	2.090	1.455	58.20
16	2.680	1.160	46.40	2.550	1.225	49.00	2.340	1.330	53.20	2.250	1.375	55.00	2.090	1.455	58.20
18	2.680	1.160	46.40	2.550	1.225	49.00	2.340	1.330	53.20	2.250	1.375	55.00	2.090	1.455	58.20
20	2.680	1.160	46.40	2.550	1.225	49.00	2.340	1.330	53.20	2.250	1.375	55.00	2.090	1.455	58.20
∞	2.680	1.160	46.40	2.550	1.225	49.00	2.340	1.330	53.20	2.250	1.375	55.00	2.090	1.455	58.20

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.6: Influence of variation of temperature on Cr(VI) adsorption onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50 mg $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. ^{o}C	30			35			40			45			50		
Time, min.	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad
0	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00	0.500	0.000	0.00
2	0.330	0.085	34.00	0.315	0.093	37.00	0.305	0.098	39.00	0.295	0.103	41.00	0.280	0.110	44.00
4	0.310	0.095	38.00	0.290	0.105	42.00	0.270	0.115	46.00	0.260	0.120	48.00	0.240	0.130	52.00
6	0.290	0.105	42.00	0.270	0.115	46.00	0.240	0.130	52.00	0.220	0.140	56.00	0.200	0.150	60.00
8	0.260	0.120	48.00	0.230	0.135	54.00	0.200	0.150	60.00	0.180	0.160	64.00	0.165	0.168	67.00
10	0.220	0.140	56.00	0.200	0.150	60.00	0.160	0.170	68.00	0.145	0.178	71.00	0.125	0.188	75.00
12	0.180	0.160	64.00	0.160	0.170	68.00	0.140	0.180	72.00	0.120	0.190	76.00	0.095	0.203	81.00
14	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.100	0.200	80.00	0.085	0.208	83.00
16	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.100	0.200	80.00	0.085	0.208	83.00
18	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.100	0.200	80.00	0.085	0.208	83.00
20	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.100	0.200	80.00	0.085	0.208	83.00
∞	0.140	0.180	72.00	0.130	0.185	74.00	0.120	0.190	76.00	0.100	0.200	80.00	0.085	0.208	83.00

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.7: Influence of variation of temperature on Cr(VI) adsorption onto [S$_2$]$_{15-30}$, [Cr(VI)] = 1 mg [S$_2$]$_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. °C	30			35			40			45			50		
Time, min.	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad	Ad	% Ad
0	1.000	0.000	0.00	1.000	0.000	0.00	1.000	0.000	0.00	1.000	0.000	0.00	1.000	0.000	0.00
2	0.560	0.220	44.00	0.540	0.230	46.00	0.500	0.250	50.00	0.480	0.260	52.00	0.470	0.265	53.00
4	0.550	0.225	45.00	0.510	0.245	49.00	0.470	0.265	53.00	0.440	0.280	56.00	0.420	0.290	58.00
6	0.520	0.240	48.00	0.470	0.265	53.00	0.440	0.280	56.00	0.410	0.295	59.00	0.390	0.305	61.00
8	0.480	0.260	52.00	0.440	0.280	56.00	0.400	0.300	60.00	0.370	0.315	63.00	0.340	0.330	66.00
10	0.450	0.275	55.00	0.420	0.290	58.00	0.370	0.315	63.00	0.340	0.330	66.00	0.320	0.340	68.00
12	0.440	0.280	56.00	0.400	0.300	60.00	0.360	0.320	64.00	0.320	0.340	68.00	0.290	0.355	71.00
14	0.410	0.295	59.00	0.380	0.310	62.00	0.340	0.330	66.00	0.310	0.345	69.00	0.280	0.360	72.00
16	0.410	0.295	59.00	0.380	0.310	62.00	0.340	0.330	66.00	0.310	0.345	69.00	0.280	0.360	72.00
18	0.410	0.295	59.00	0.380	0.310	62.00	0.340	0.330	66.00	0.310	0.345	69.00	0.280	0.360	72.00
20	0.410	0.295	59.00	0.380	0.310	62.00	0.340	0.330	66.00	0.310	0.345	69.00	0.280	0.360	72.00
∞	0.410	0.295	59.00	0.380	0.310	62.00	0.340	0.330	66.00	0.310	0.345	69.00	0.280	0.360	72.00

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.8: Influence of variation of temperature on Cr(VI) adsorption onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 2 mg $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. °C	30			35			40			45			50		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	2.000	0.000	0.00	2.000	0.000	0.00	2.000	0.000	0.00	2.000	0.000	0.00	2.000	0.000	0.00
2	1.030	0.485	48.50	1.031	0.485	48.45	0.950	0.525	52.50	0.950	0.525	52.50	0.930	0.535	53.50
4	1.025	0.488	48.75	1.000	0.500	50.00	0.940	0.530	53.00	0.900	0.550	55.00	0.860	0.570	57.00
6	1.005	0.498	49.75	0.960	0.520	52.00	0.910	0.545	54.50	0.840	0.580	58.00	0.800	0.600	60.00
8	0.970	0.515	51.50	0.910	0.545	54.50	0.840	0.580	58.00	0.790	0.605	60.50	0.740	0.630	63.00
10	0.930	0.535	53.50	0.860	0.570	57.00	0.800	0.600	60.00	0.750	0.625	62.50	0.680	0.660	66.00
12	0.920	0.540	54.00	0.820	0.590	59.00	0.760	0.620	62.00	0.720	0.640	64.00	0.650	0.675	67.50
14	0.900	0.550	55.00	0.810	0.595	59.50	0.760	0.620	62.00	0.710	0.645	64.50	0.650	0.675	67.50
16	0.900	0.550	55.00	0.810	0.595	59.50	0.760	0.620	62.00	0.710	0.645	64.50	0.650	0.675	67.50
18	0.900	0.550	55.00	0.810	0.595	59.50	0.760	0.620	62.00	0.710	0.645	64.50	0.650	0.675	67.50
20	0.900	0.550	55.00	0.810	0.595	59.50	0.760	0.620	62.00	0.710	0.645	64.50	0.650	0.675	67.50
∞	0.900	0.550	55.00	0.810	0.595	59.50	0.760	0.620	62.00	0.710	0.645	64.50	0.650	0.675	67.50

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.9: Influence of variation of temperature on Cr(VI) adsorption onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 3 mg $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. °C	30			35			40			45			50		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	3.000	0.000	0.00	3.000	0.000	0.00	3.000	0.000	0.00	3.000	0.000	0.00	3.000	0.000	0.00
2	1.650	0.675	45.00	1.580	0.710	47.33	1.540	0.730	48.67	1.470	0.765	51.00	1.400	0.800	53.33
4	1.640	0.680	45.33	1.520	0.740	49.33	1.460	0.770	51.33	1.440	0.780	52.00	1.350	0.825	55.00
6	1.620	0.690	46.00	1.500	0.750	50.00	1.410	0.795	53.00	1.360	0.820	54.67	1.280	0.860	57.33
8	1.590	0.705	47.00	1.480	0.760	50.67	1.370	0.815	54.33	1.300	0.850	56.67	1.220	0.890	59.33
10	1.550	0.725	48.33	1.440	0.780	52.00	1.320	0.840	56.00	1.240	0.880	58.67	1.160	0.920	61.33
12	1.530	0.735	49.00	1.410	0.795	53.00	1.300	0.850	56.67	1.200	0.900	60.00	1.120	0.940	62.67
14	1.510	0.745	49.67	1.380	0.810	54.00	1.290	0.855	57.00	1.170	0.915	61.00	1.090	0.955	63.67
16	1.510	0.745	49.67	1.380	0.810	54.00	1.290	0.855	57.00	1.170	0.915	61.00	1.090	0.955	63.67
18	1.510	0.745	49.67	1.380	0.810	54.00	1.290	0.855	57.00	1.170	0.915	61.00	1.090	0.955	63.67
20	1.510	0.745	49.67	1.380	0.810	54.00	1.290	0.855	57.00	1.170	0.915	61.00	1.090	0.955	63.67
∞	1.510	0.745	49.67	1.380	0.810	54.00	1.290	0.855	57.00	1.170	0.915	61.00	1.090	0.955	63.67

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

Table 4.10: Influence of variation of temperature on Cr(VI) adsorption onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 5 mg $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temp. ^{o}C	30			35			40			45			50		
Time, min.	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**	**Unad**	**Ad**	**% Ad**
0	5.000	0.000	0.00	5.000	0.000	0.00	5.000	0.000	0.00	5.000	0.000	0.00	5.000	0.000	0.00
2	2.760	1.120	44.80	2.680	1.160	46.40	2.620	1.190	47.60	2.590	1.205	48.20	2.300	1.350	54.00
4	2.750	1.125	45.00	2.640	1.180	47.20	2.550	1.225	49.00	2.520	1.240	49.60	2.260	1.370	54.80
6	2.730	1.135	45.40	2.600	1.200	48.00	2.510	1.245	49.80	2.450	1.275	51.00	2.180	1.410	56.40
8	2.700	1.150	46.00	2.570	1.215	48.60	2.460	1.270	50.80	2.360	1.320	52.80	2.140	1.430	57.20
10	2.680	1.160	46.40	2.530	1.235	49.40	2.400	1.300	52.00	2.280	1.360	54.40	2.060	1.470	58.80
12	2.650	1.175	47.00	2.500	1.250	50.00	2.380	1.310	52.40	2.240	1.380	55.20	2.040	1.480	59.20
14	2.620	1.190	47.60	2.500	1.250	50.00	2.360	1.320	52.80	2.200	1.400	56.00	2.040	1.480	59.20
16	2.620	1.190	47.60	2.500	1.250	50.00	2.350	1.325	53.00	2.200	1.400	56.00	2.040	1.480	59.20
18	2.620	1.190	47.60	2.500	1.250	50.00	2.350	1.325	53.00	2.200	1.400	56.00	2.040	1.480	59.20
20	2.620	1.190	47.60	2.500	1.250	50.00	2.350	1.325	53.00	2.200	1.400	56.00	2.040	1.480	59.20
∞	2.620	1.190	47.60	2.500	1.250	50.00	2.350	1.325	53.00	2.200	1.400	56.00	2.040	1.480	59.20

Unad- unadsorbed amount of Cr(VI), Ad- Adsorbed amount of Cr(VI) (mg/g), %Ad-Percentage adsorption

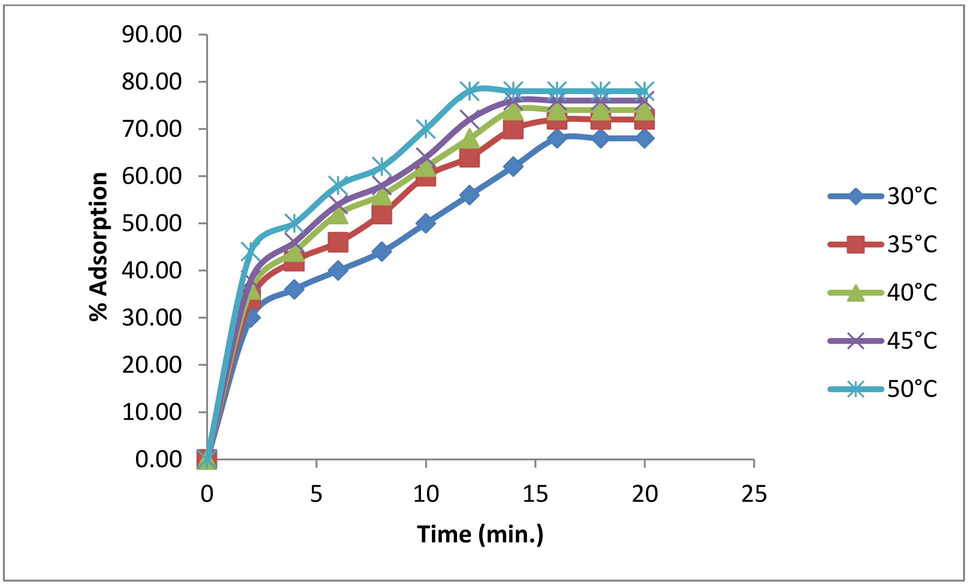

Figure 4.1: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 0.5 mg; $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

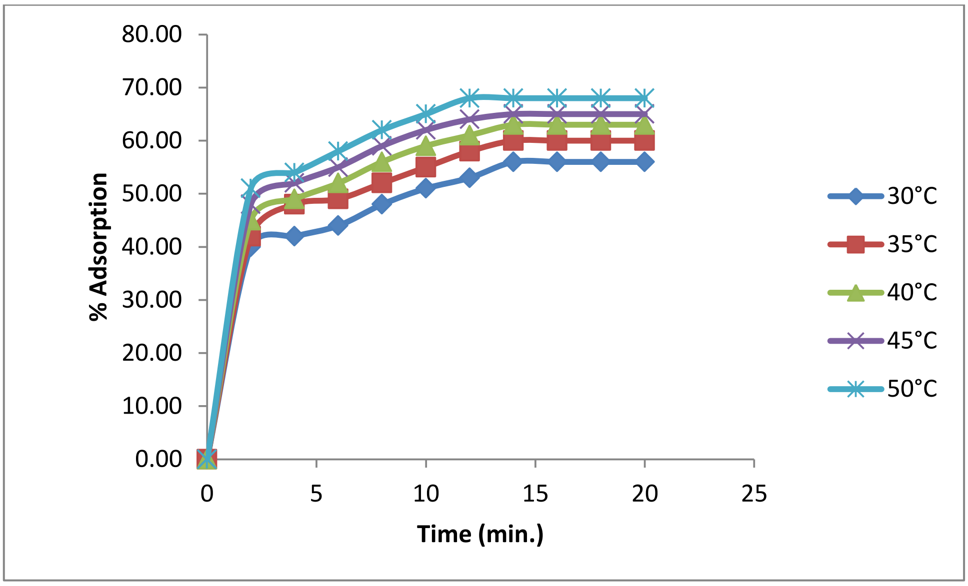

Figure 4.2: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 1 mg; $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

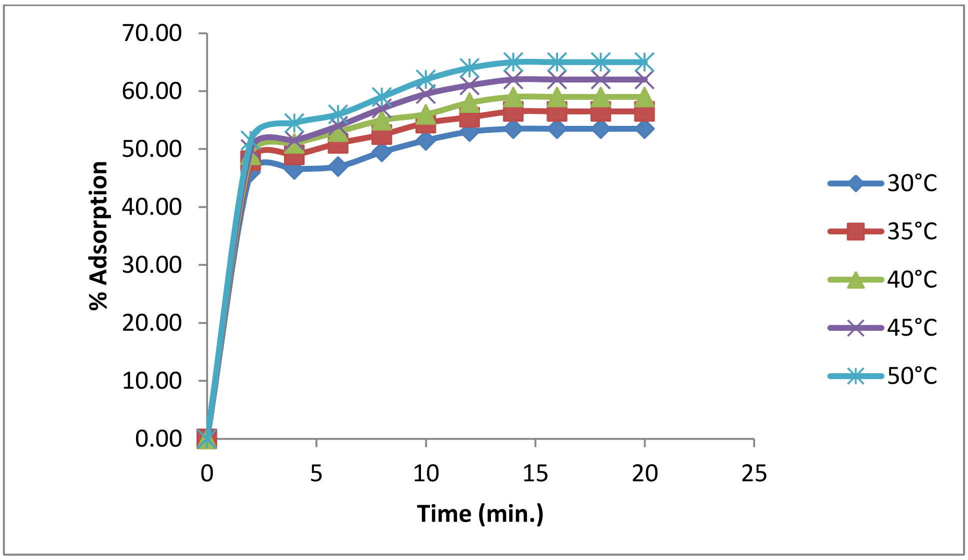

Figure 4.3: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 2 mg; $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

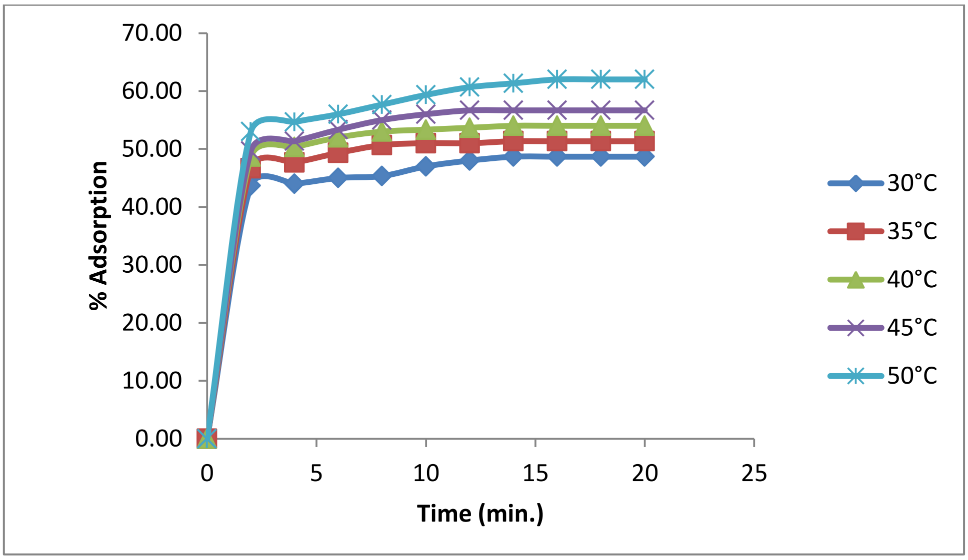

Figure 4.4: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 3 mg; $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

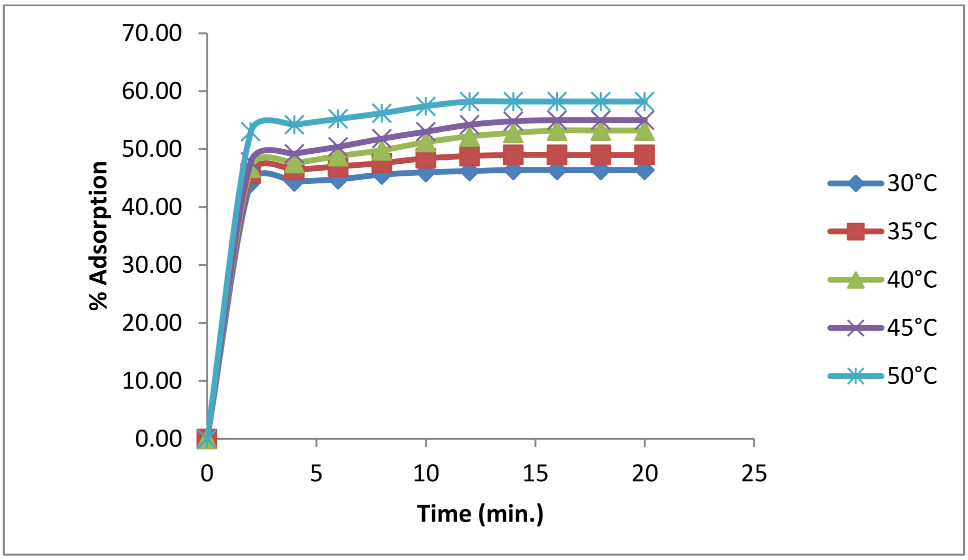

Figure 4.5: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 5 mg; $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

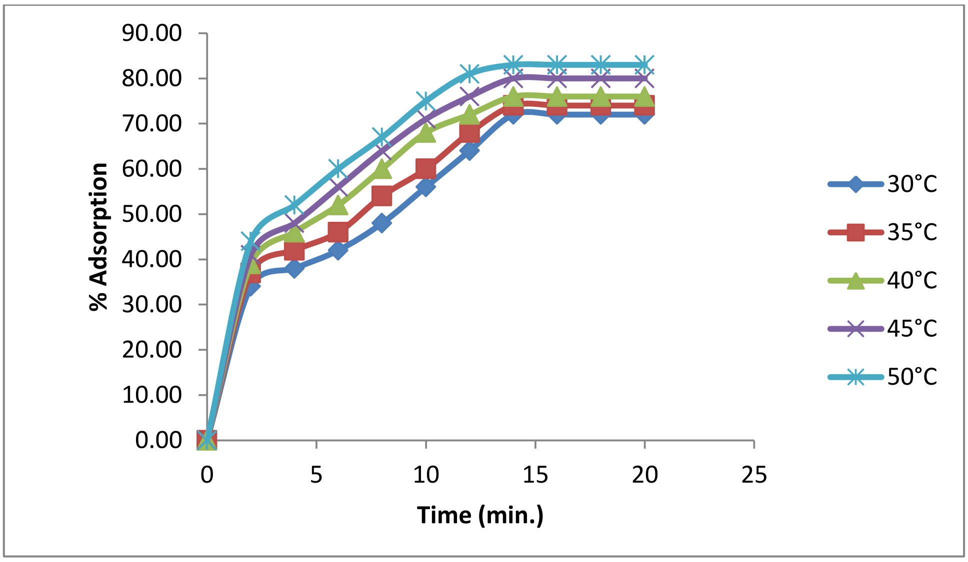

Figure 4.6: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_2]_{15-30}$, [Cr(VI)] = 0.5 mg; $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

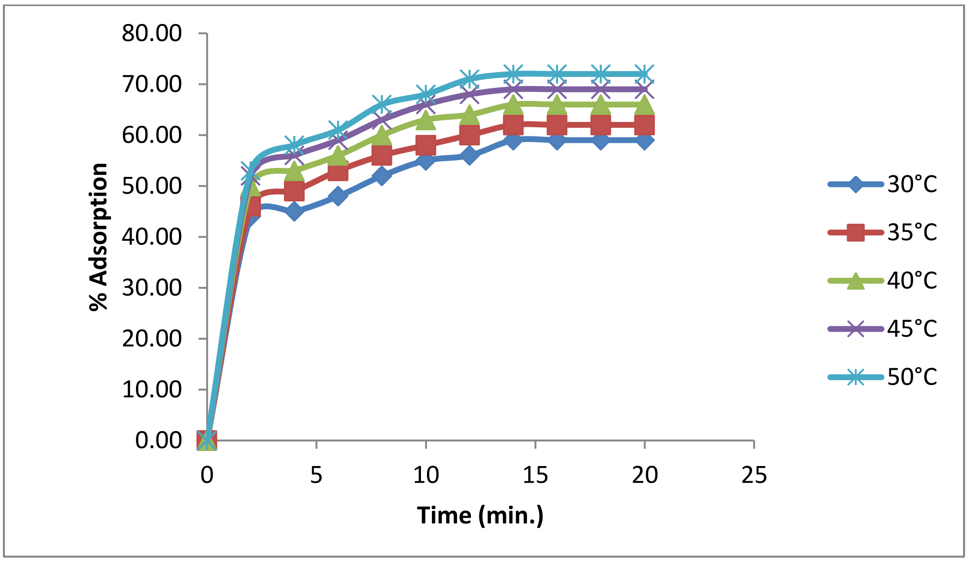

Figure 4.7: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_2]_{15-30}$, [Cr(VI)] = 1 mg; $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

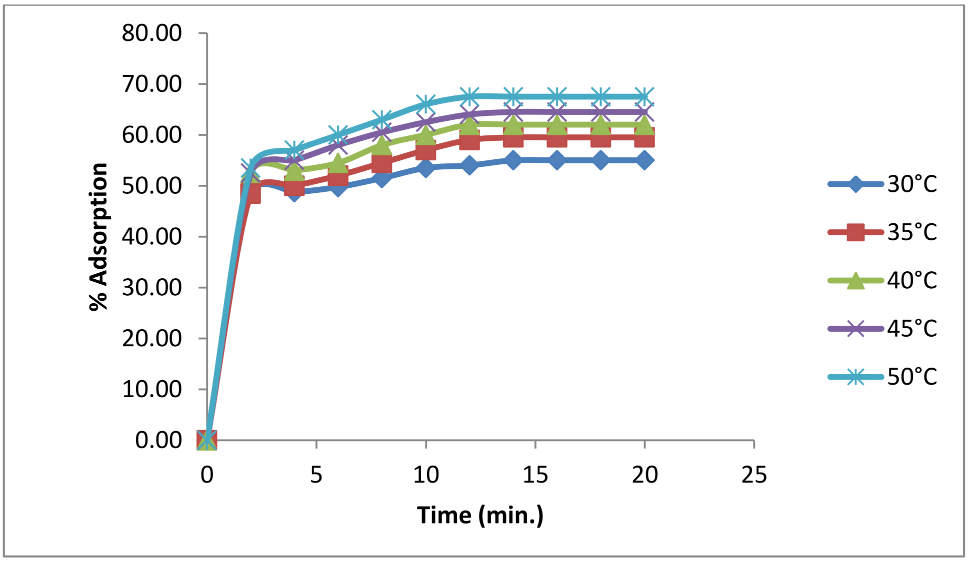

Figure 4.8: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_2]_{15-30}$, [Cr(VI)] = 2 mg; $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

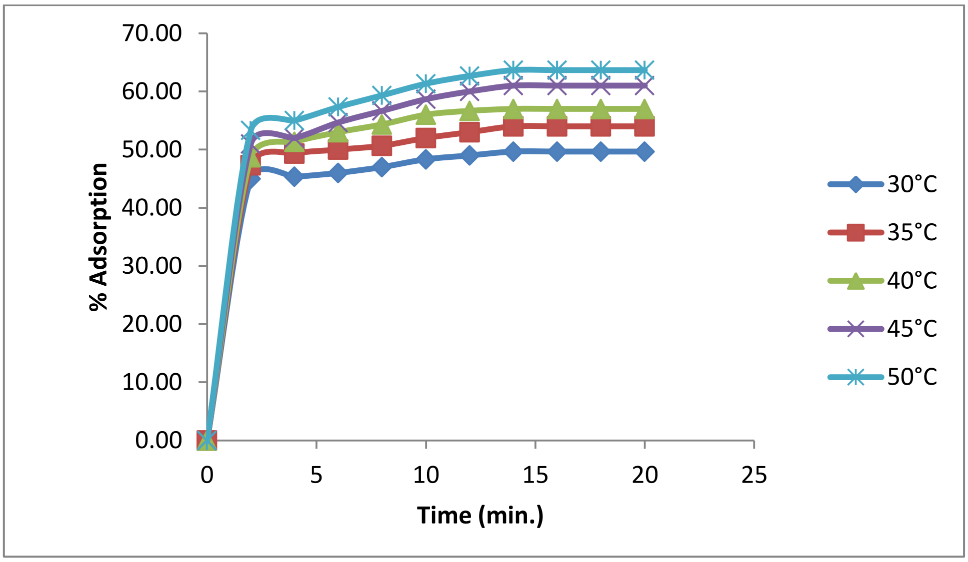

Figure 4.9: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_2]_{15-30}$, [Cr(VI)] = 3 mg; $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

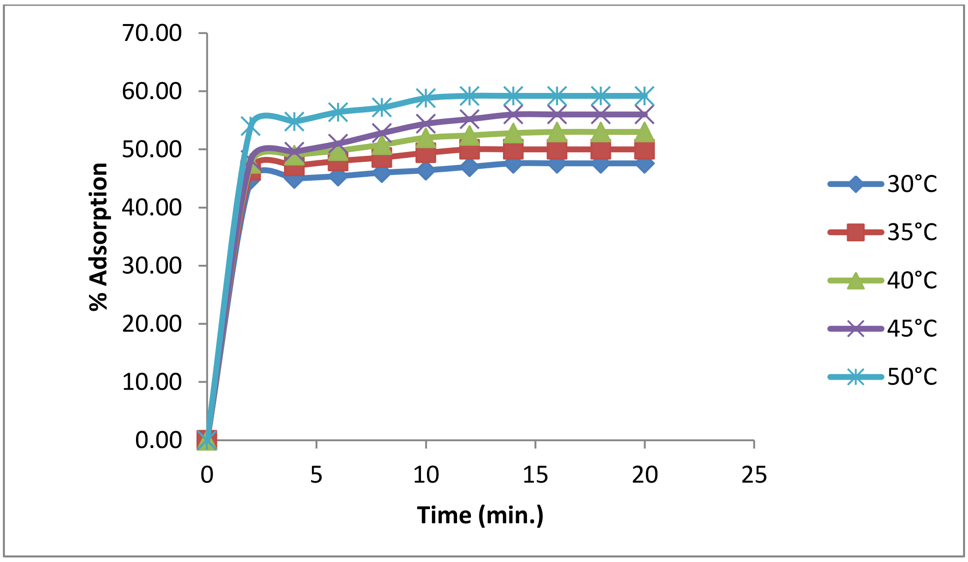

Figure 4.10: Change in % adsorption of Cr(VI) with time for different temperatures on Cr(VI) adsorption onto $[S_2]_{15-30}$, [Cr(VI)] = 5 mg; $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

solution temperature would result in increased adsorption capacity. Hence, the enhanced mobility of Chromium(VI) from the bulk solution towards the soil surface was also played an important role in increasing the rate of adsorption.

Adsorption interaction in the present study involves some type of specific interaction at higher temperature i.e. probable bond cleavage (endo process) in smaller entities feasible to certain pore size. Alternatively such behavior is reported as “activated” adsorption which accelerates diffusion into certain pores in the adsorbent [64]. The results of the present investigation support the conclusion that Chromium(VI) adsorption is controlled by pore diffusion as the most suited model is intraparticle diffusion model (**Figure 4.48 and 4.55**).

Results are in good agreement with the results reported in previous studies [65-69].

So, for both $[S_1]_{0-15}$ and $[S_2]_{15-30}$ adsorption of Chromium(VI) increases on increasing temperature, and the 50^{o}C temperature was thus optimized for the adsorption. The amount of Chromium(VI) adsorption by varying temperature is slightly increased for $[S_2]_{15-30}$ as compared to $[S_1]_{0-15}$.

4.6.2 Thermodynamic Parameters

[A] Thermodynamic parameters (ΔG^o, ΔS^o and ΔH^o) for $[S_1]_{0-15}$:

The estimation of standard Gibb’s free energy of adsorption at different temperature for $[S_1]_{0-15}$ is shown in **Table 4.11**. It is apparent from **Table 4.11** that the values of ΔG^o was found to be -0.153, -0.644, -0.918, -1.215 and -1.537 kJ/mol for the temperature 30^o, 35^o, 40^o, 45^o and 50^{o}C respectively.

The ΔG^o was observed to be more negative with increase in temperature. The negative values of ΔG^o confirm the feasibility of the process and the spontaneous nature of adsorption with a high preference for Chromium(VI) onto $[S_1]_{0-15.}$ The results were in accordance with the earlier study where ΔG^o obtained was negative during adsorption of Chromium(VI) by polypyrrole magnetic nanocomposite [62].

From the **Figure 4.11** the value of ln K_c was found to decrease linearly with increase in value of 1/T. The line had equation $y = -2415x + 8.061$ with slope 2415 and intercept 8.061. The data of line was found to fit satisfactory as coefficient of determination (R^2) was 0.986. The slope of line and intercept was used in Van't Hoff equation to calculate ΔH^o and ΔS^o in given **Table 4.12** The value of ΔH^o and ΔS^o was found to be 20.155 kJ mol^{-1} and 0.0668 kJ mol^{-1} K^{-1} respectively.

Both ΔH^o and ΔS^o were found to be positive for the adsorption. The positive value of ΔH^o and ΔS^o predict that the adsorption reaction was unfavorable for enthalpy but favorable for entropy. The positive value of ΔS^o reveal increased randomness at the solid/solution interface during adsorption and the system became more disordered through adsorption process.

The similar finding (positive ΔH^o and positive ΔS^o) was reported in the study of the adsorption of nitrate from aqueous solutions by activated carbons prepared from sugar beet bagasse activated chemically with $ZnCl_2$ [70], and in the study of adsorbing copper from aqueous solutions using watermelon shell, positive ΔH^o and positive ΔS^o was also observed [71].

[B] Themodynamic Parameters (ΔG^o, ΔS^o and ΔH^o) for $[S_2]_{15-30}$:

The thermodynamic parameters calculated for $[S_2]_{15-30}$ at different temperature 30°, 35°, 40°, 45° and 50° are shown in **Table 4.13**. It is apparent from **Table 4.13** that values of ΔG^o was found to be -0.633, -0.903, -1.196, -1.833 and -2.397 kJ/mol for the temperature 30°, 35°, 40°, 45° and 50°C respectively.

The negative values of ΔG^o indicated spontaneous nature of the adsorption process and more negative values with increased in temperature showed that an increase in temperature favored the adsorption process.

The magnitude of ΔG^o values increased on increasing temperature revealed that the degree of spontaneity increased when performed at higher temperature. The negative values of ΔG^o indicated feasibility and spontaneous nature of Chromium(VI) adsorption onto soil. The value of enthalpy of a adsorption process may be used to distinguish between chemical and physical sorption. For chemical adsorption enthalpy values range from 83 to 830 kJ mol^{-1}, while for physical adsorption they range from 8 to 25 kJ mol^{-1} [72].

Table 4.11: Values of standard Gibb’s free energy of Cr(VI) adsorption onto $[S_1]_{0-15}$ at different temperatures, [Cr(VI)] = 0.50 mg $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temperature (^oC)	Temperature T (K)	1/T	(C_e) (mg/L)	C_{Ad} (mg/L)	$K_c = C_{Ad}/C_e$	$\ln K_c$	$\Delta G^o = -RT \ln K_c$ (kJ mol^{-1})
30	303 K	0.00330	0.160	0.170	1.063	0.061	-0.153
35	308 K	0.00324	0.140	0.180	1.286	0.251	-0.644
40	313 K	0.00319	0.130	0.185	1.423	0.353	-0.918
45	318 K	0.00314	0.120	0.190	1.583	0.460	-1.215
50	323 K	0.00309	0.110	0.195	1.773	0.573	-1.537

C_e = Equilibrium Concentration of Cr(VI) ; C_{Ad} =Adsorbed concentration of Cr(VI); ΔG^o = Gibb’s free energy

Table 4.12: Van’t Hoff equation and calculated values of ΔH^o and ΔS^o of Cr(VI) adsorption onto $[S_1]_{0-15}$ at different temperatures.

Van’t Hoff Equation	Equation of line with correlation coefficient	Slope	Intercept	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})
$\ln K_c = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	y = -2415.x + 8.061 R^2 = 0.986	-2415	8.061	20.155	0.0668

Table 4.13: Values of standard Gibb's free energy of Cr(VI) adsorption onto $[S_2]_{15-30}$ at different temperatures, [Cr(VI)] = 0.50 mg $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Temperature (^oC)	Temperature T (K)	1/T	(C_e) (mg/L)	C_{Ad} (mg/L)	$K_c = C_{Ad}/C_e$	$\ln K_c$	$\Delta G^o = -RT \ln K_c$ (kJ mol^{-1})
30	**303 K**	**0.00330**	**0.140**	**0.180**	**1.286**	**0.251**	**-0.633**
35	**308 K**	**0.00324**	**0.130**	**0.185**	**1.423**	**0.353**	**-0.903**
40	**313 K**	**0.00319**	**0.120**	**0.190**	**1.583**	**0.460**	**-1.196**
45	**318 K**	**0.00314**	**0.100**	**0.200**	**2.000**	**0.693**	**-1.833**
50	**323 K**	**0.00309**	**0.085**	**0.208**	**2.441**	**0.892**	**-2.397**

C_e = Equilibrium Concentration of Cr(VI) ; C_{Ad} =Adsorbed concentration of Cr(VI); ΔG^o = Gibb's free energy

Table 4.14: Van't Hoff equation and calculated values of ΔH^o and ΔS^o of Cr(VI) adsorption onto $[S_2]_{15-30}$ at different temperatures.

Van,t Hoff Equation	Equation of line with correlation coefficient	Slope	Intercept	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})
$\ln K_c = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	**y = -3165.x + 10.64** **R^2 = 0.961**	**-3165**	**10.64**	**26.191**	**0.0889**

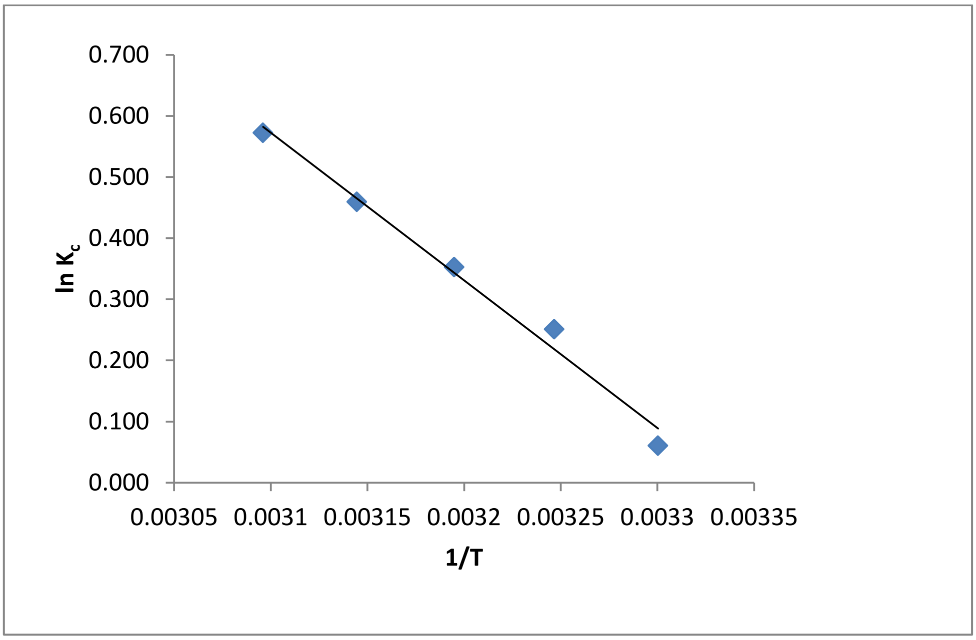

Figure 4.11: Plot of ln K_c vs. 1/T for Chromium(VI) adsorption onto $[S_1]_{0\text{-}15}$.

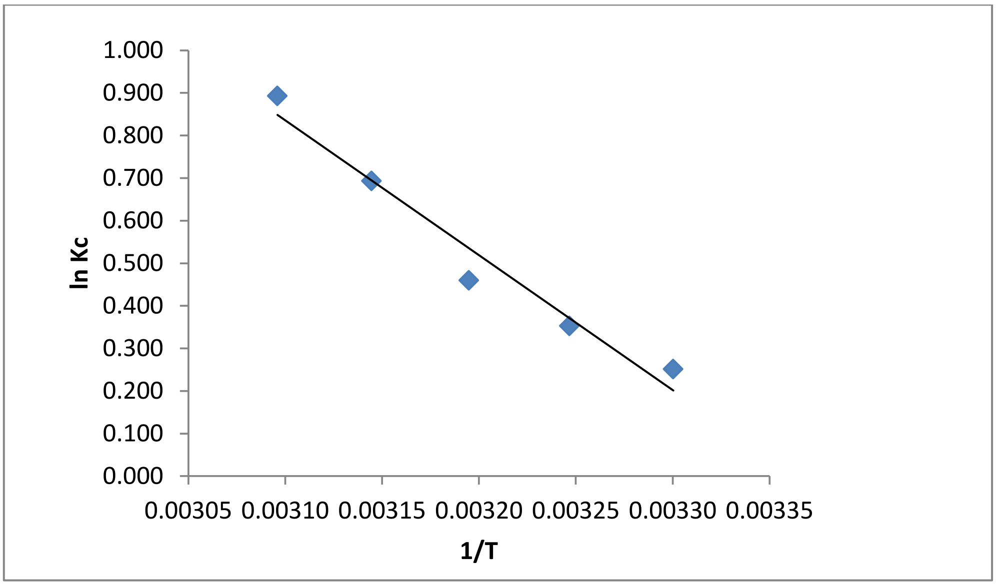

Figure 4.12: Plot of ln K_c vs. 1/T for Chromium(VI) adsorption onto $[S_2]_{15\text{-}30}$.

From the **Figure 4.12** the value of ln K_c was found to decrease linearly with increase in value of 1/T. The line had equation y = -3165.x + 10.64 with slope 3165 and y intercept 10.64. The data of line was found to fit satisfactory as coefficient of determination (R^2) was 0.961. The slope of line and intercept was used in Van’t Hoff equation to calculate ΔH^o and ΔS^o in given **Table 4.14** The value of ΔH^o and ΔS^o was found to be 26.191 kJ mol^{-1} and 0.0889 kJ mol^{-1} K^{-1} respectively.

The enthalpy change values were found to be positive and less than 30 kJ/mol, which indicated that the nature of adsorption process is endothermic and physiosorption together with chemisorption [73, 74]. The positive values of ΔS^o reflected a increased degree of disorderness at the solid/liquid interface during the adsorption of Chromium(VI) onto soil. In this study ΔS^o value is positive (i.e. entropy increases as a result of adsorption). This occurs as a result of redistribution energy between the adsorbate and the adsorbent [11].

Adsorption is thus likely to occur spontaneously at normal and high temperatures because $\Delta H^o > 0$, and $\Delta S^o > 0$ also as shown from **Table 4.14** numerically the higher value of ΔH^o (26.191 kJ/mol) obtained in the studied system than usually reported [75] for physical adsorption or ion exchange adsorption (having the ΔH^o value of 8.4 ± 12.6 kJ mol^{-1}) clearly suggests to us that the overall process of adsorption of Chromium(VI) does not proceed only via ion exchange mechanism. This indicates the possibility of surface complex formation in the system (i.e. chemisorptions), which is in agreement with the results reported earlier [76]. Positive value of ΔG^o was also reported in literature [77].

So, it is clear from the results that for $[S_1]_{0-15}$ and $[S_2]_{15-30}$, adsorption process is spontaneous on increasing temperature from 30°C to 50°C. Other parameters i.e. ΔH^o and ΔS^o shows almost similar trends for both $[S_1]_{0-15}$ and $[S_2]_{15-30}$. On increasing temperature adsorption of Chromium(VI) increases for both depth soil, However for $[S_2]_{15-30}$ adsorption of Chromium(VI) increases more in comparision of $[S_1]_{0-15}$.

4.6.3 Application of Equilibrium Adsorption Data to Langmuir, Freundlich and Temkin Adsorption Isotherms

[A] Results for $[S_1]_{0\text{-}15}$:

In the study, the adsorption data of Chromium(VI) were fitted to Freundlich, Langmuir and Temkin isotherm models. The Langmuir, Freundlich and Temkin isotherms at different temperatures from 30°C to 50°C are shown in the **Figure 4.13** to **4.17**, **4.18** to **4.22** and **4.23** to **4.27** respectively. Values of correlation coefficients for Chromium (VI) – $[S_1]_{0\text{-}15}$ soil system using Langmuir, Freundlich and Temkin isotherm, the values of q_{max} and b obtained from slope and intercept of the Langmuir isotherms plots, the values of K_F and n_f for Freundlich isotherms and the values of a_T and b_T for Temkin isotherms are presented in **Table 4.15**.

[B] Results for $[S_2]_{15\text{-}30}$:

The Langmuir, Freundlich and Temkin isotherms at different temperatures from 30°C to 50°C are shown in the **Figure 4.28** to **4.32**, **4.33** to **4.37** and **4.38** to **4.42** respectively. The observed correlation coefficients for Langmuir, Freundlich and Temkin isotherm, at different temperatures from 30°C to 50°C for $[S_2]_{15\text{-}30}$, the values of q_{max} and b obtained from slope and intercept of the Langmuir isotherms plots, the values of K_F and n_f for Freundlich isotherms and the values of a_T and b_T for Temkin isotherms are shown in **Table 4.16**.

Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecule at one site will not affect the adsorption of molecules at an adjacent site [38].

The dimensionless factor (R_L) values for $[S_1]_{0\text{-}15}$ shown in **Table 4.15** and for $[S_2]_{15\text{-}30}$ shown in **Table 4.16**, lies in between 0 and 1. This suggested the favorable adsorption of Chromium(VI) onto soil samples.

Freundlich isotherm assumes that uptake of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration [41].

The n_f values are given in **Table 4.15** and **4.16** for $[S_1]_{0-15}$ and $[S_2]_{15-30}$ respectively. The values of n_f for Freundlich equation were found to be greater than one for both $[S_1]_{0-15}$ and $[S_2]_{15-30}$. The situation $n_f > 1$ is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent adsorbate interaction with increasing surface intensity [41], and the values of n_f within the range 1-10 represent good adsorption [78, 79]. The value of n_f is greater than unity, indicating the Chromium(VI) ions were favorably adsorbed on the soil investigated.

The values of K_F are presented in **Table 4.15** for $[S_1]_{0-15}$ and in **Table 4.16** for $[S_2]_{15-30}$ and was found to be 0.259, 0.330, 0.418, 0.501 and 0.611 for $[S_1]_{0-15}$ and 0.299, 0.387, 0.488, 0.624 and 0.785 for $[S_2]_{15-30}$ which indicates that soil has a high adsorption capacity for Chromium(VI) solution.

Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [80]. Temkin constants are given in **Table 4.15** for $[S_1]_{0-15}$ and in **Table 4.16** for $[S_2]_{15-30.}$ Typical bonding energy range for ion-exchange mechanism is reported to be in the range of 8–16 kJ mol^{-1} while physisorption processes are reported to have adsorption energies less than -40 kJ mol^{-1} [58, 81]. Values of b_T for $[S_1]_{0-15}$ and for $[S_2]_{15-30}$, obtained in the present study indicates that the adsorption process seems to involve chemisorption and physisorption.

In this study, better regression coefficient (R^2) and low standard error of estimation (σ) (**Table 4.15 and 4.16**) for Freundlich model, for both $[S_1]_{0-15}$ and $[S_2]_{15-30}$ suggests the multilayer adsorption, process. The fact that Freundlich model fits the experimental data very well suggests physical adsorption as well as heterogeneous distribution of active site on the soil surface.

Several studies perform on various adsorbent for adsorption of Chromium(VI) supports our results [82-87].

Table 4.15: Isotherm model constant and correlation coefficient for Cr(VI) adsorption onto $[S_1]_{0\text{-}15}$, at different temperatures, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Model	Constants	Temperature (^oC)				
		30^o	35^o	40^o	45^o	50^o
Langmuir	Q_{max} (mg/g)	2.092	2.066	2.320	2.370	2.375
	b (L/mg)	0.404	0.484	0.474	0.517	0.589
	R_L	0.832	0.805	0.809	0.795	0.773
	R^2	0.818	0.830	0.783	0.811	0.801
	σ	0.262	0.243	0.232	0.200	0.198
Freundlich	K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$)	0.259	0.330	0.418	0.501	0.611
	n_f	1.451	1.504	1.473	1.477	1.488
	R^2	0.989	0.990	0.989	0.989	0.988
	σ	0.090	0.088	0.094	0.091	0.100
Temkin	b_T (kJ/mol)	7.497	7.487	7.033	6.921	6.764
	a_T (g/L)	7.170	8.327	8.640	9.324	10.222
	R^2	0.886	0.882	0.866	0.875	0.872
	σ	0.154	0.164	0.192	0.191	0.208

Table 4.16: Isotherm model constant and correlation coefficient for Cr(VI) adsorption onto $[S_2]_{15-30}$, at different temperatures, [Cr(VI)] = 0.50, 1, 2, 3 and 5, $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh.

Model	Constants	Temperature (^oC)				
		30^o	35^o	40^o	45^o	50^o
Langmuir	Q_{max} (mg/g)	1.942	2.053	2.15	2.217	2.278
	b (L/mg)	0.500	0.547	0.595	0.679	0.772
	R_L	0.800	0.785	0.771	0.746	0.772
	R^2	0.820	0.873	0.889	0.875	0.862
	σ	0.275	0.203	0.169	0.164	0.158
Freundlich	K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$)	0.299	0.387	0.488	0.624	0.785
	n_f	1.546	1.520	1.515	1.563	1.597
	R^2	0.987	0.990	0.995	0.992	0.990
	σ	0.097	0.085	0.061	0.079	0.088
Temkin	b_T (kJ/mol)	7.727	7.337	7.091	7.050	6.993
	a_T (g/L)	8.428	9.027	9.806	11.499	13.304
	R^2	0.875	0.899	0.902	0.892	0.882
	σ	0.163	0.155	0.162	0.181	0.201

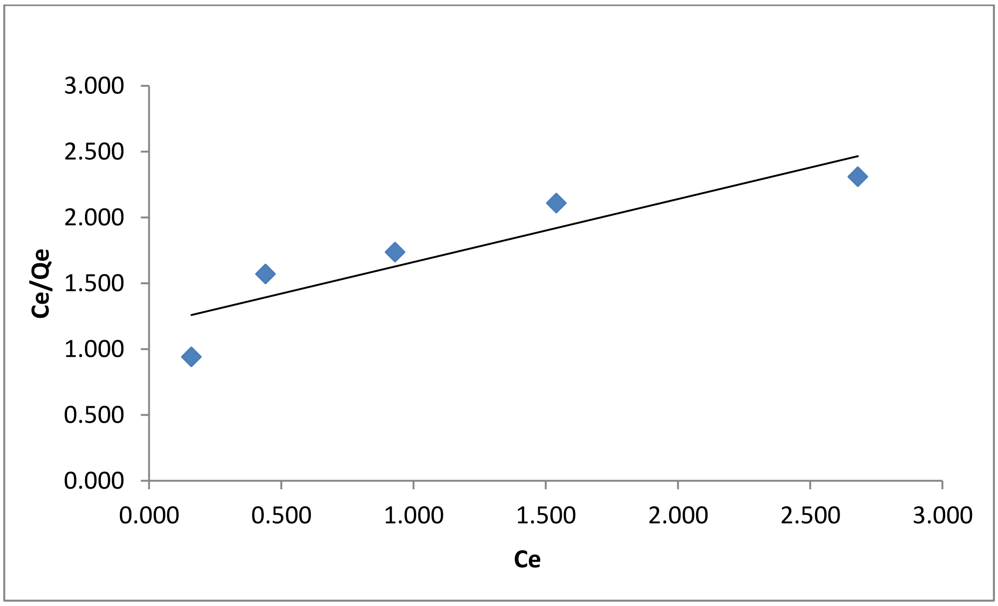

Figure 4.13: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 30°C; pH= 8; particle size = 100BSS mesh.

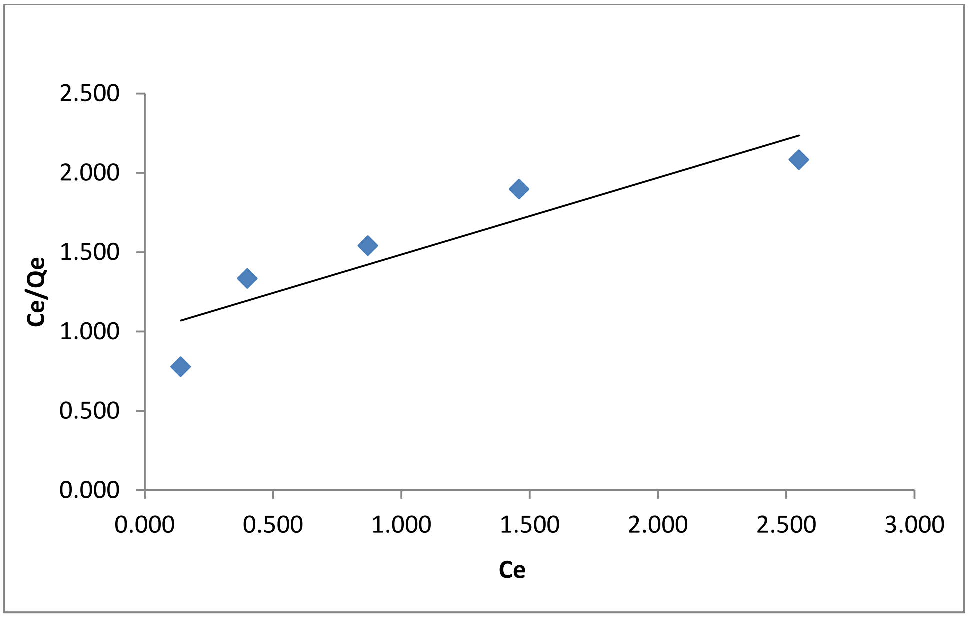

Figure 4.14: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 35°C; pH= 8; particle size = 100BSS mesh.

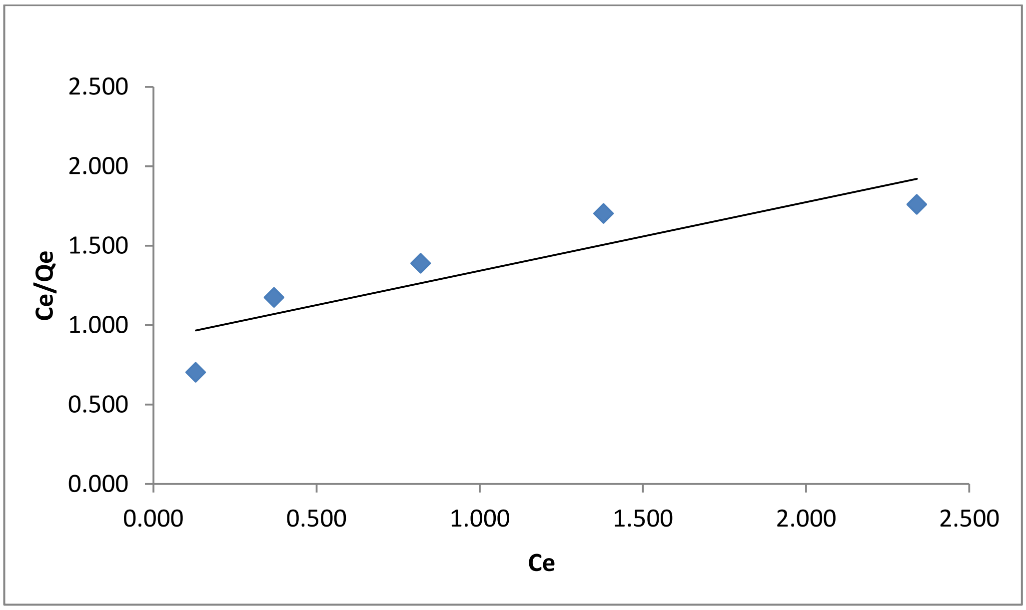

Figure 4.15: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 40°C; pH= 8; particle size = 100BSS mesh.

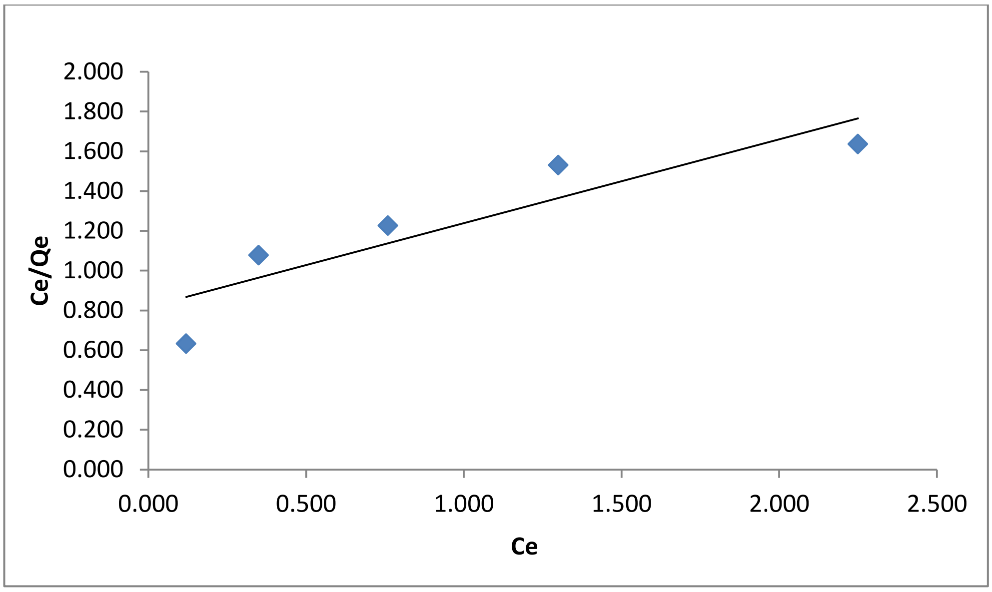

Figure 4.16: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 45°C; pH= 8; particle size = 100BSS mesh.

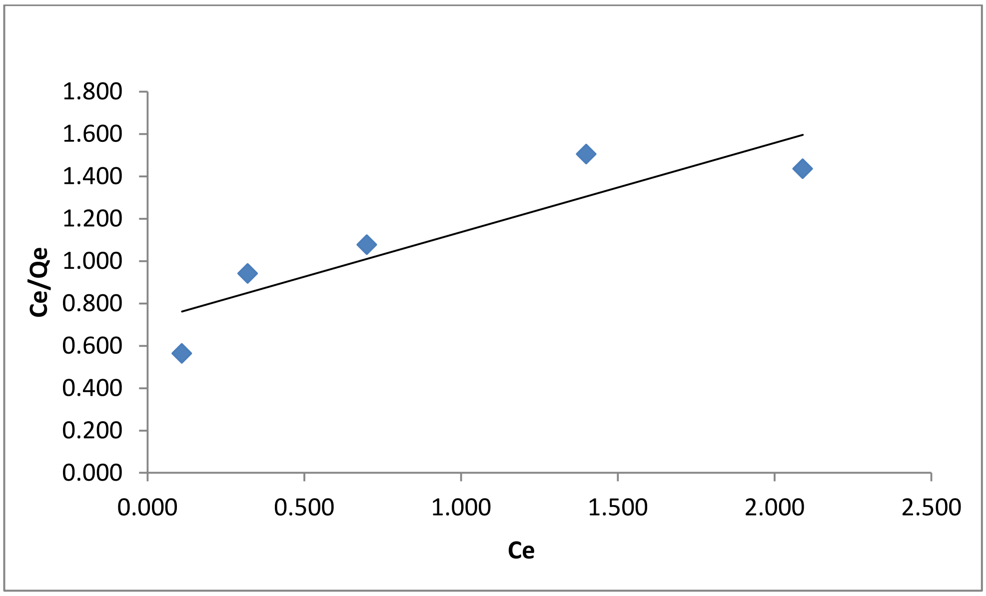

Figure 4.17: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0\text{-}15}$ = 2 g; temp. = 50^oC; pH= 8; particle size = 100BSS mesh.

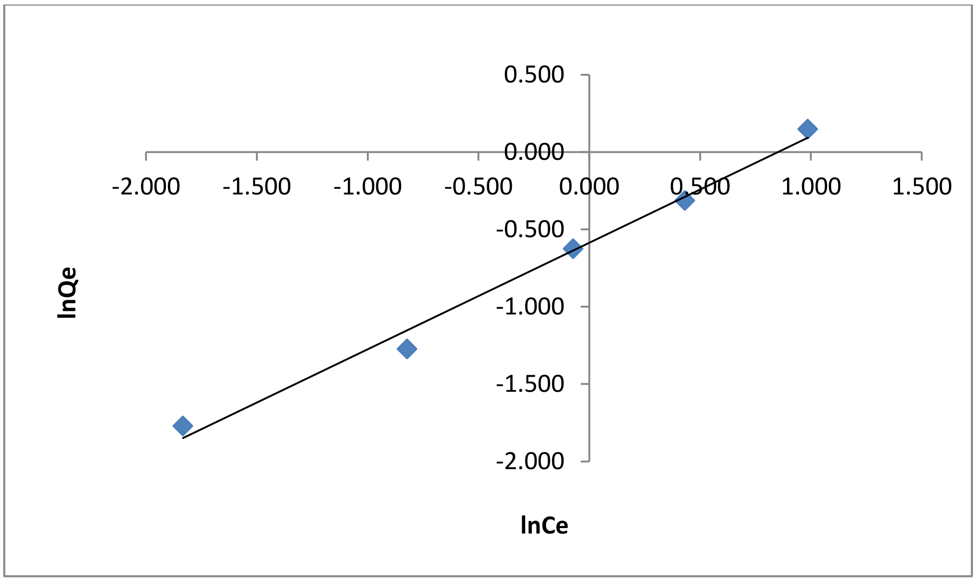

Figure 4.18: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0\text{-}15}$ = 2 g; temp. = 30^oC; pH= 8; particle size = 100BSS mesh.

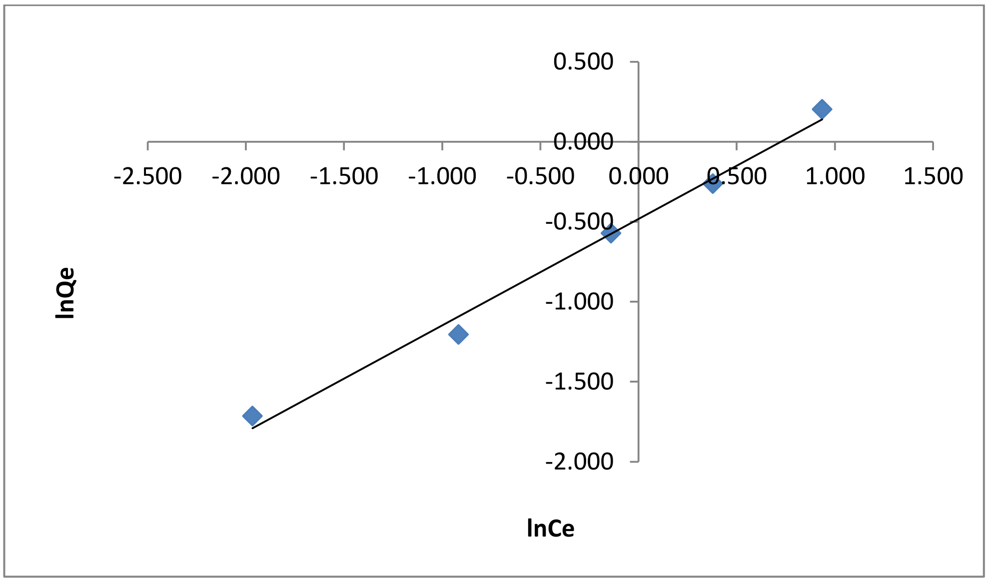

Figure 4.19: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 35°C; pH= 8; particle size = 100BSS mesh.

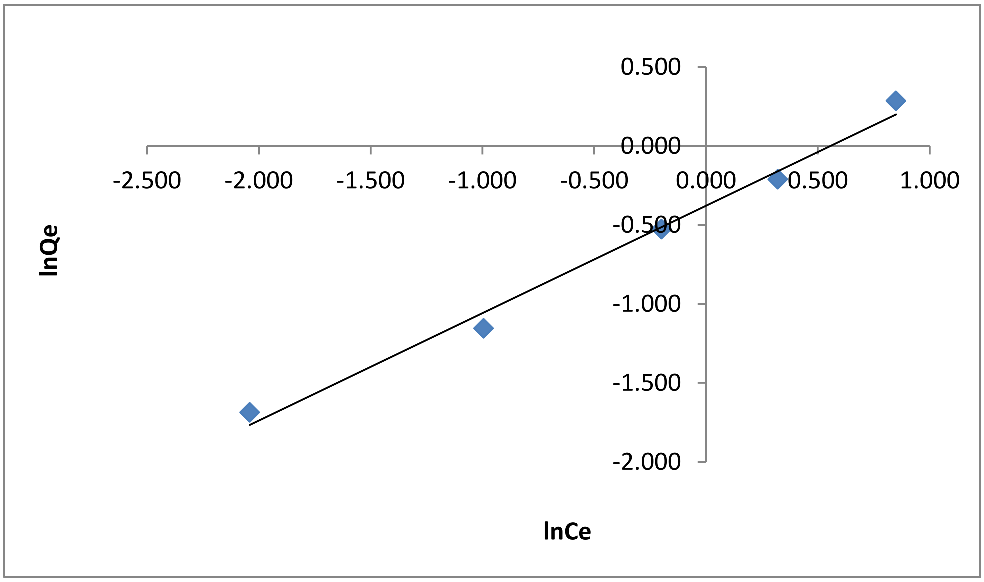

Figure 4.20: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 40°C; pH= 8; particle size = 100BSS mesh.

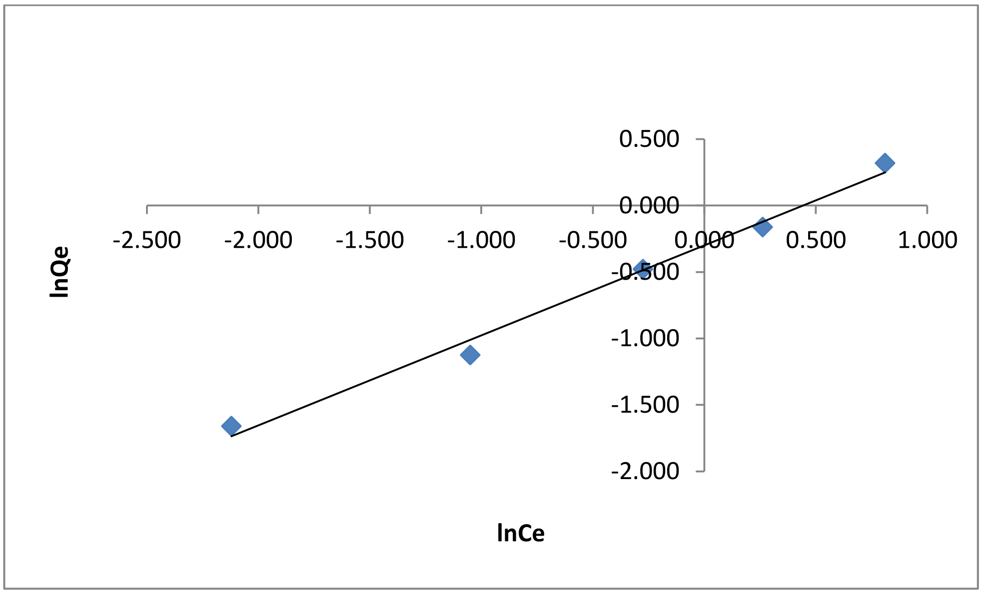

Figure 4.21: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 45°C; pH= 8; particle size = 100BSS mesh.

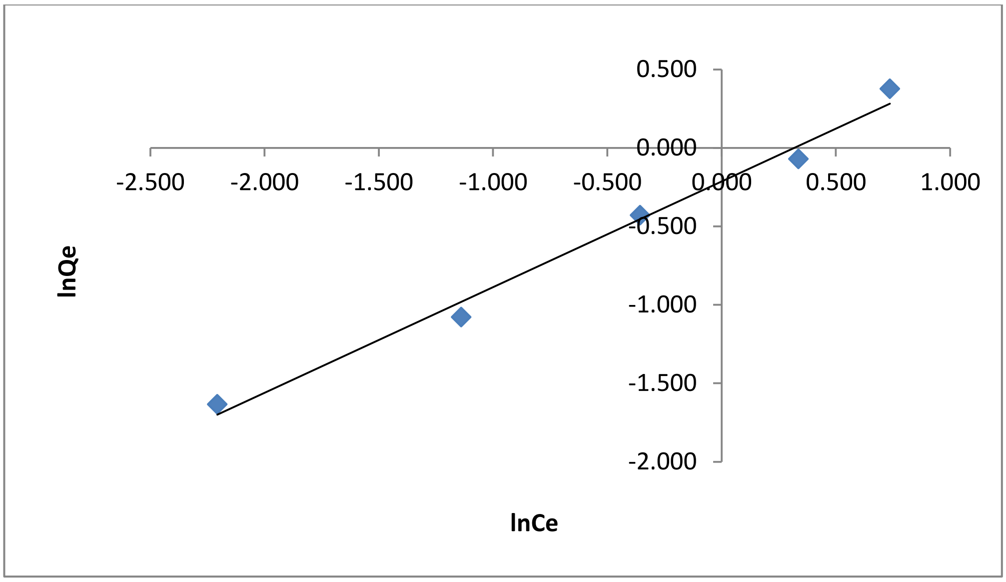

Figure 4.22: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 50°C; pH= 8; particle size = 100BSS mesh.

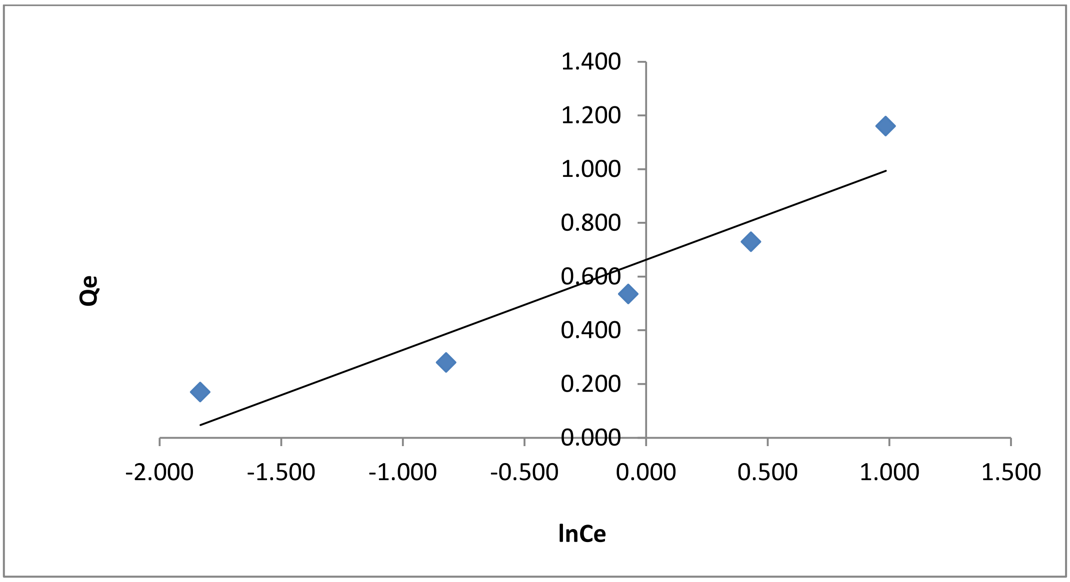

Figure 4.23: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 30°C; pH= 8; particle size = 100BSS mesh.

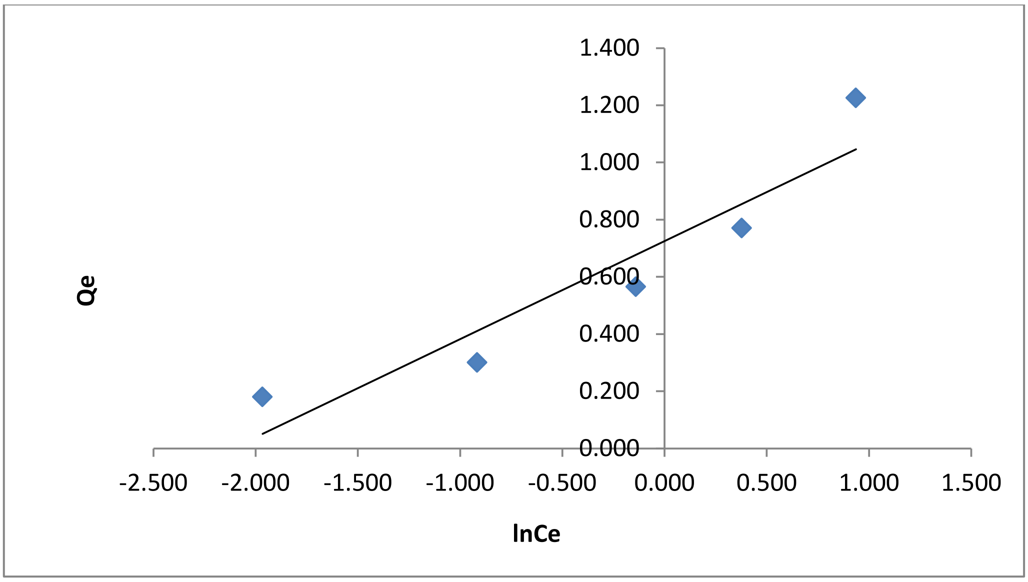

Figure 4.24: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 35°C; pH= 8; particle size = 100BSS mesh.

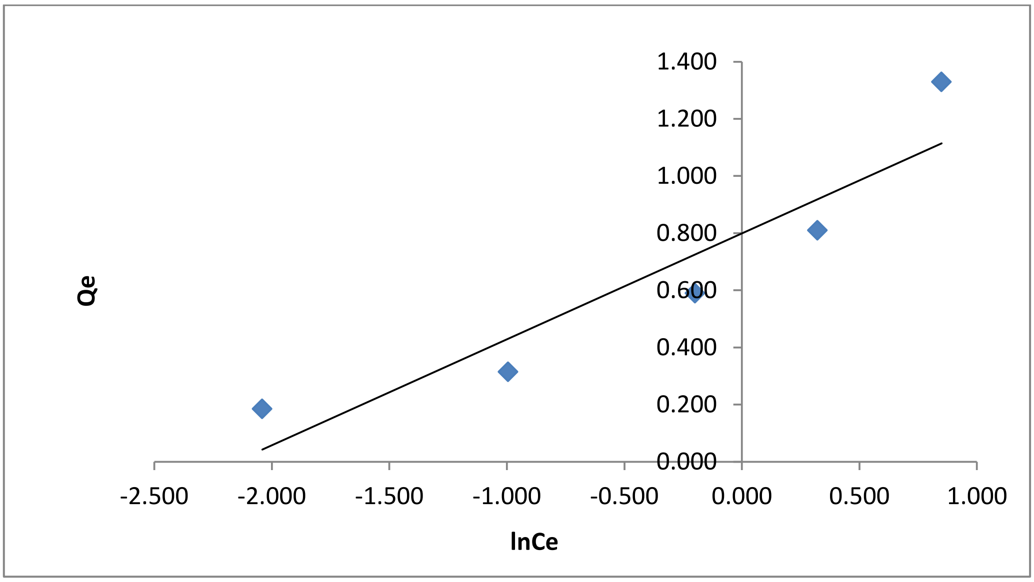

Figure 4.25: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0\text{-}15}$ = 2 g; temp. = 40°C; pH= 8; particle size = 100BSS mesh.

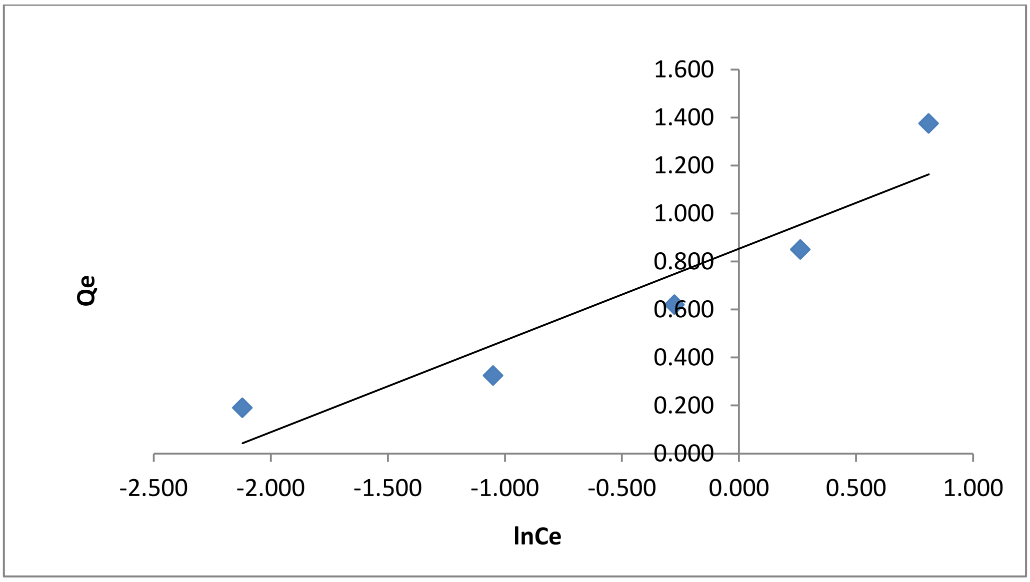

Figure 4.26: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0\text{-}15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0\text{-}15}$ = 2 g; temp. = 45°C; pH= 8; particle size = 100BSS mesh.

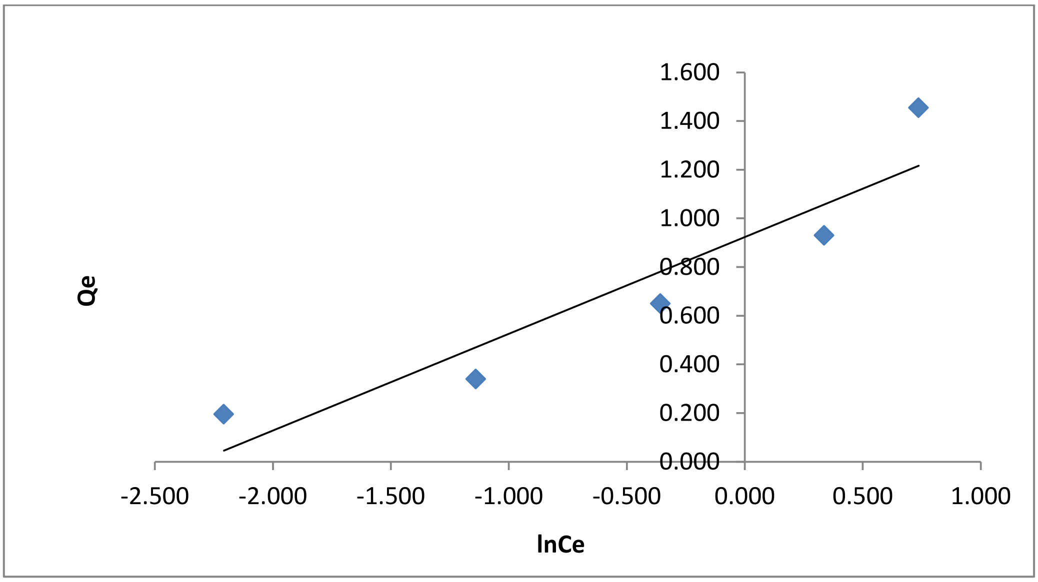

Figure 4.27: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_1]_{0-15}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; temp. = 50°C; pH= 8; particle size = 100BSS mesh.

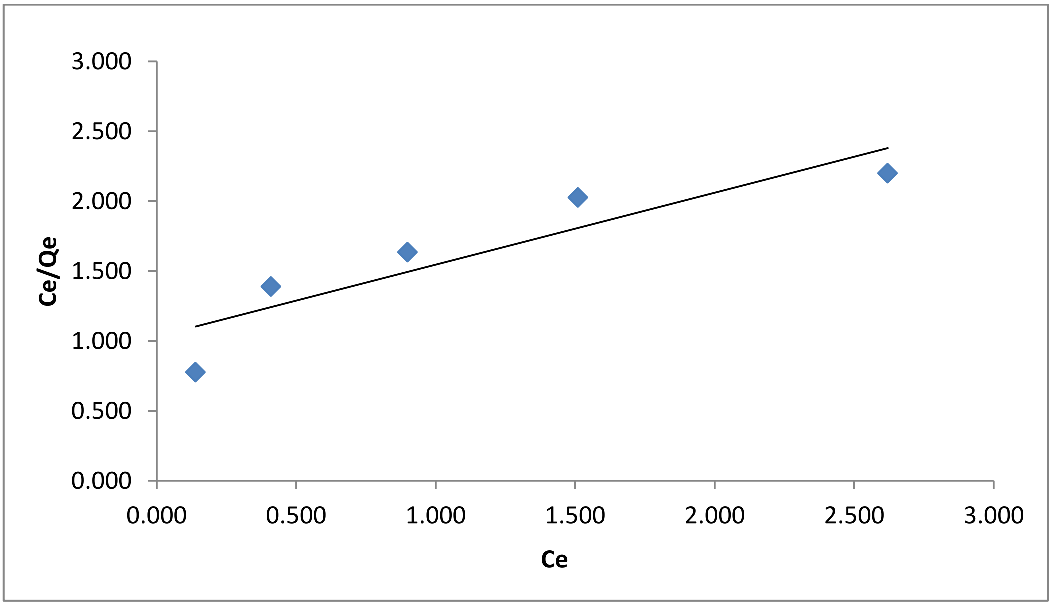

Figure 4.28: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; temp. = 30°C; pH= 8; particle size = 100BSS mesh.

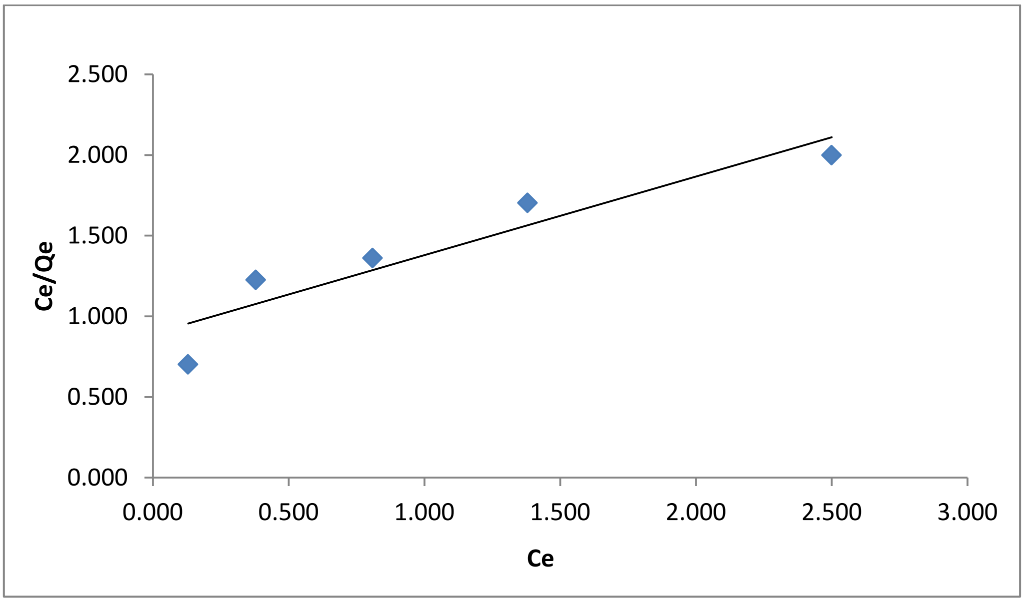

Figure 4.29: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; temp. = 35°C; pH= 8; particle size = 100BSS mesh.

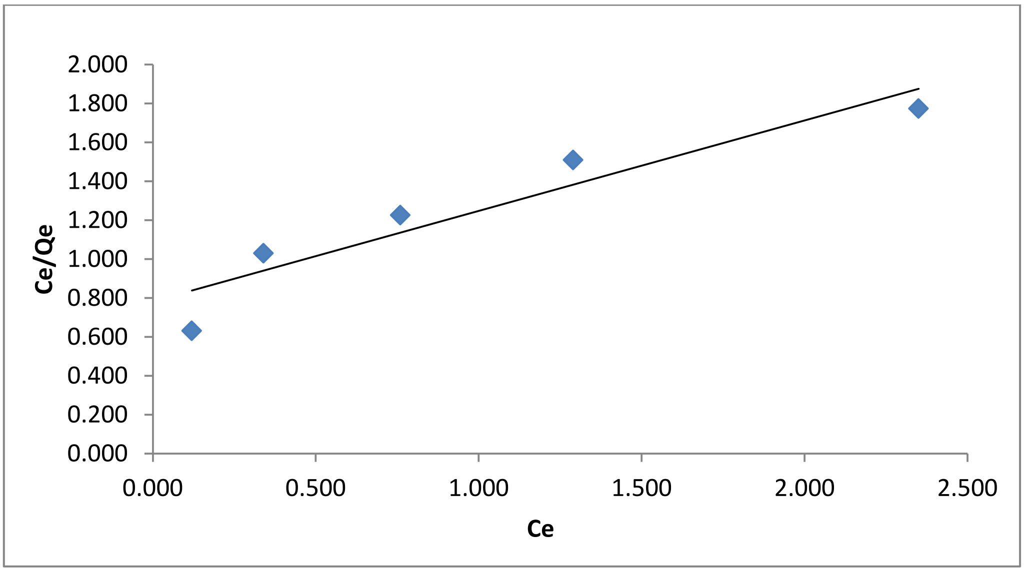

Figure 4.30: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; temp. = 40°C; pH= 8; particle size = 100BSS mesh.

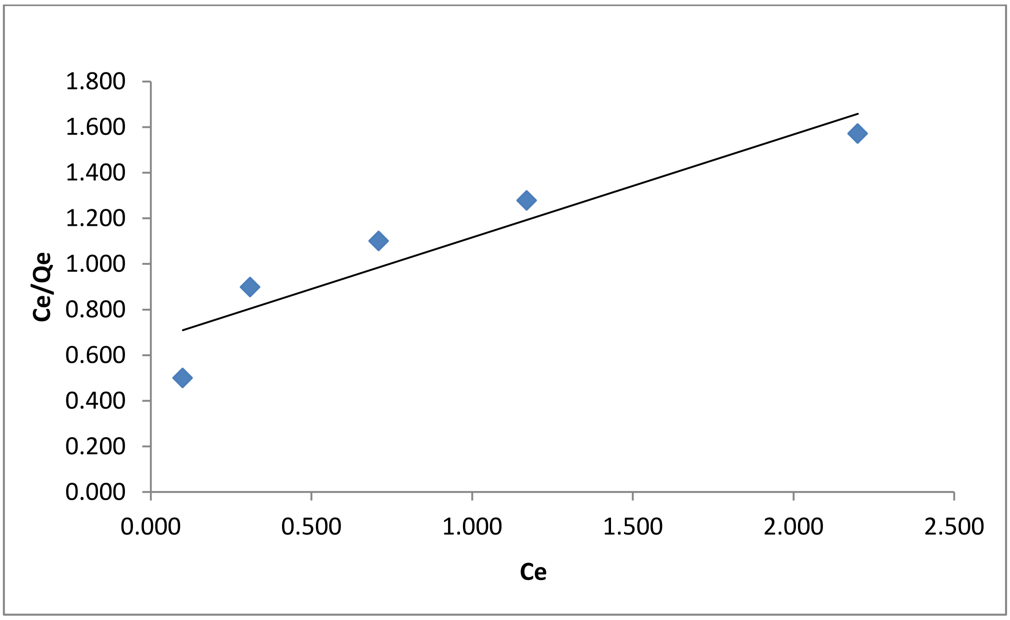

Figure 4.31: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; temp. = 45°C; pH= 8; particle size = 100BSS mesh.

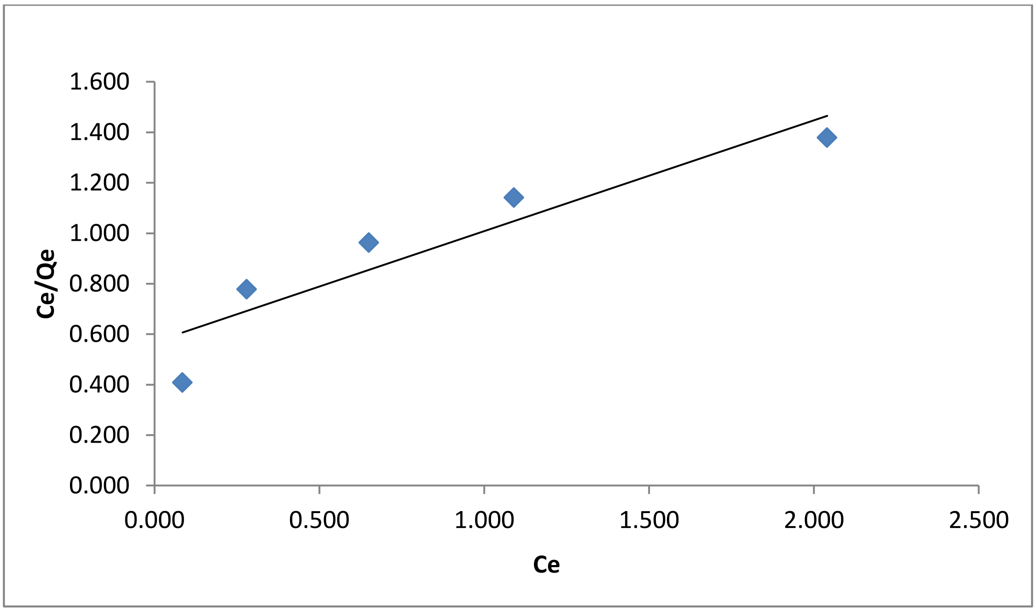

Figure 4.32: The linear Langmuir isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; temp. = 50°C; pH= 8; particle size = 100BSS mesh.

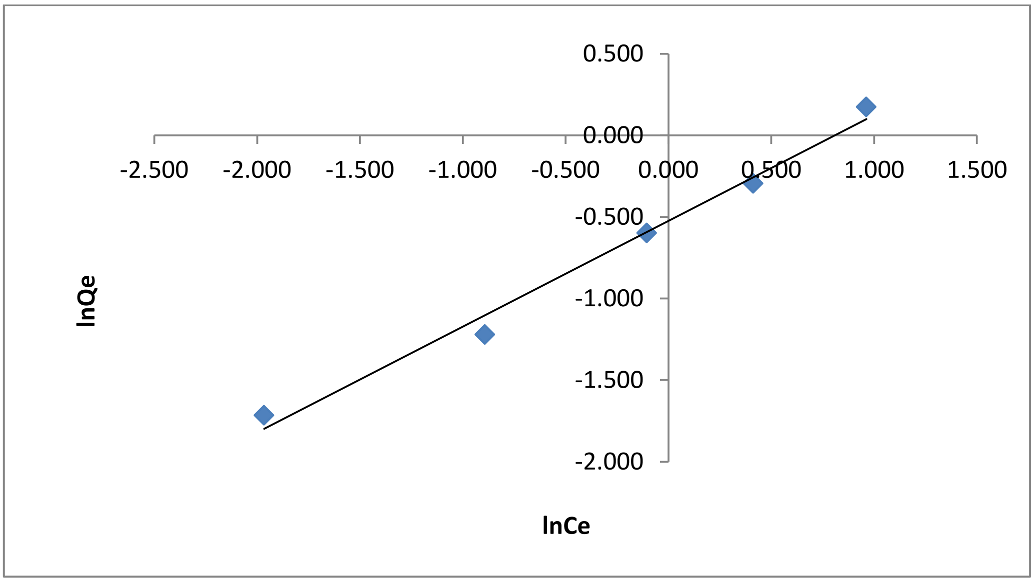

Figure 4.33: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; temp. = 30°C; pH= 8; particle size = 100BSS mesh.

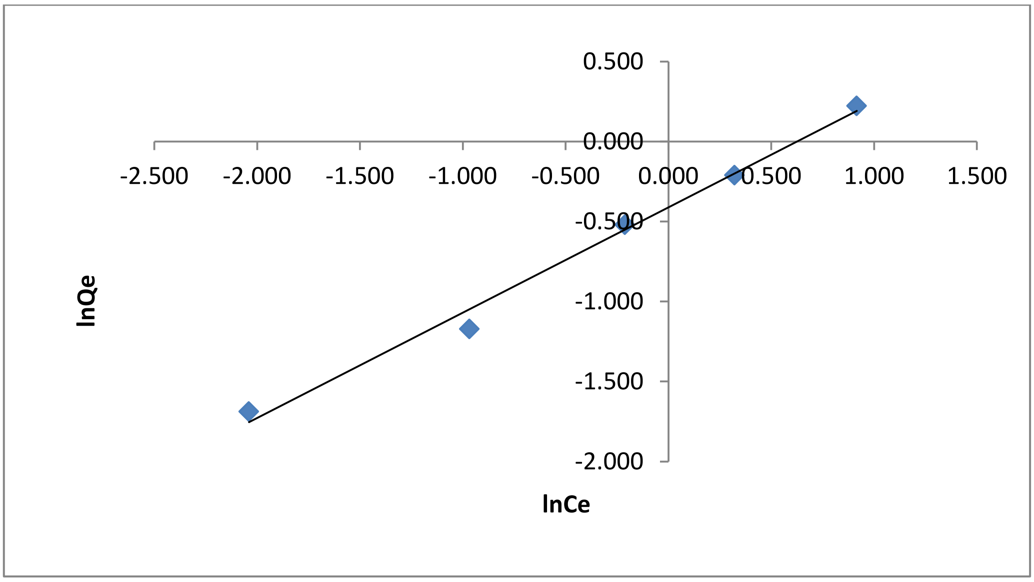

Figure 4.34: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_1]_{15\text{-}30}$ = 2 g; temp. = 35°C; pH= 8; particle size = 100BSS mesh.

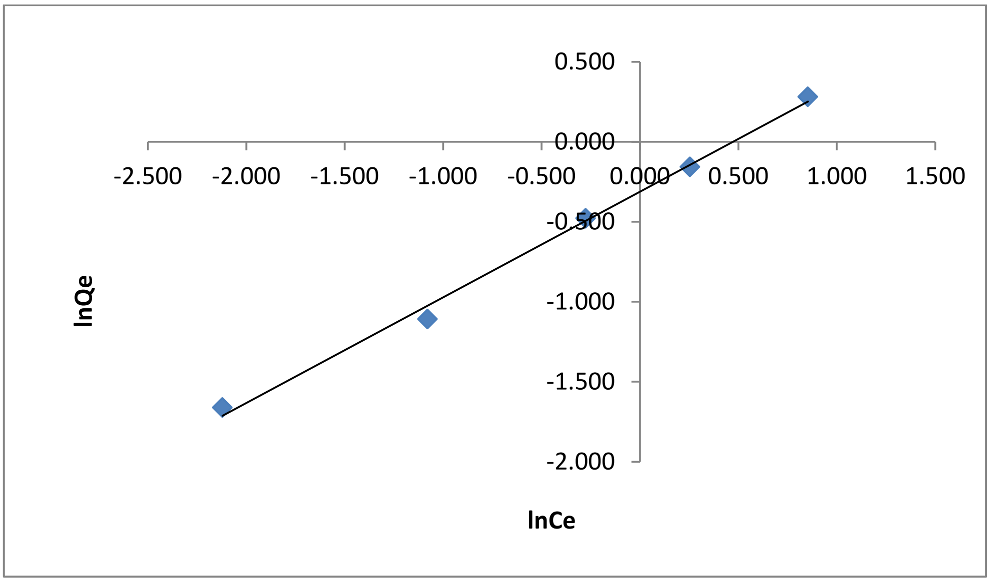

Figure 4.35: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; temp. = 40°C; pH= 8; particle size = 100BSS mesh.

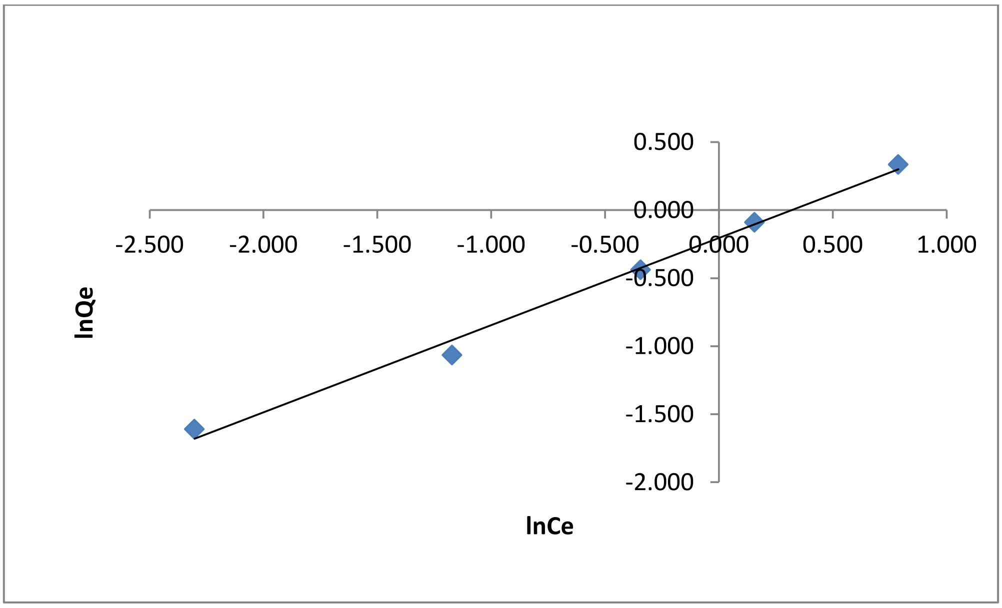

Figure 4.36: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; temp. = 45°C; pH= 8; particle size = 100BSS mesh.

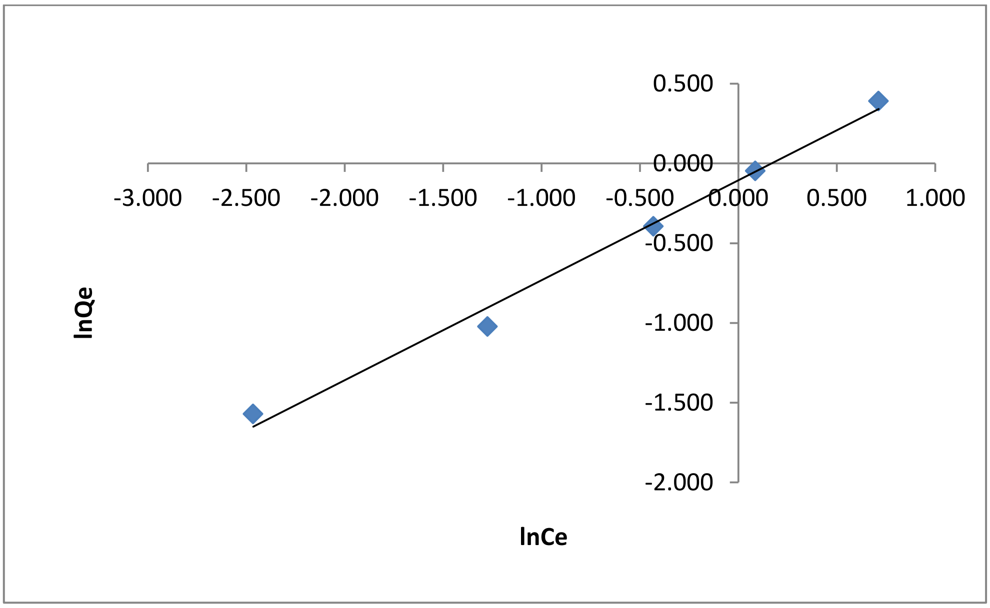

Figure 4.37: The linear Freundlich isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; temp. = 50°C; pH= 8; particle size = 100BSS mesh.

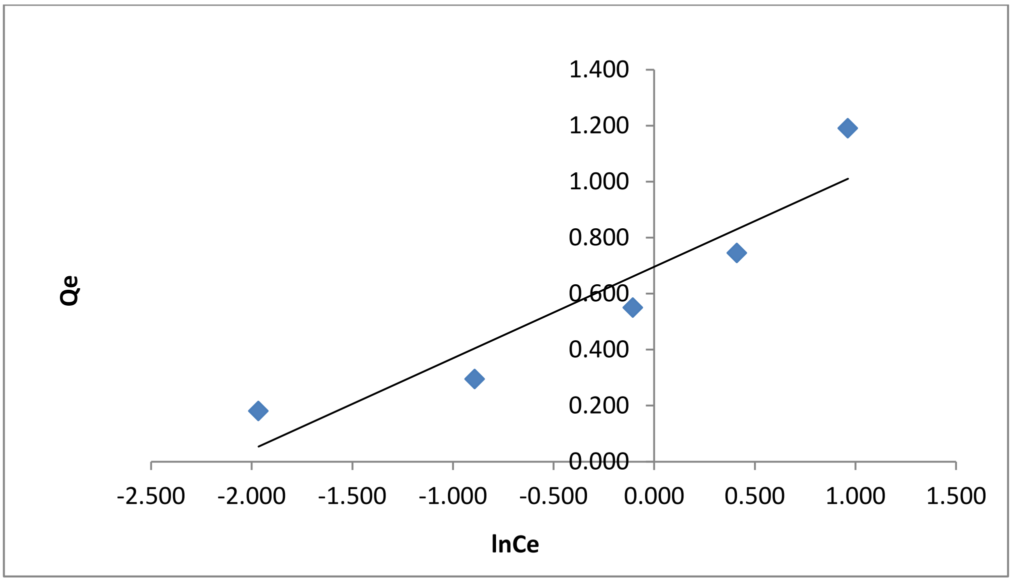

Figure 4.38: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; temp. = 30°C; pH= 8; particle size = 100BSS mesh.

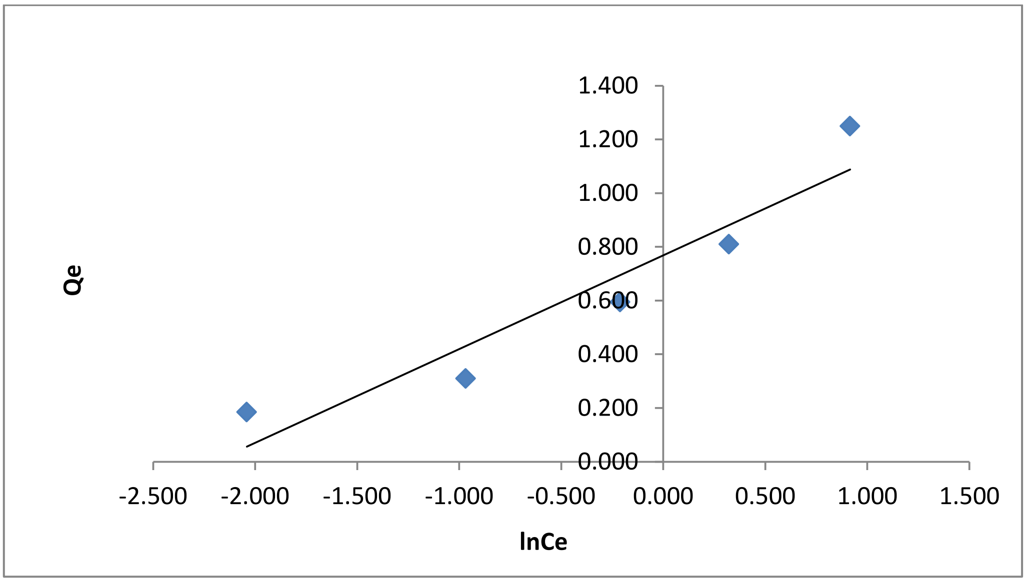

Figure 4.39: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; temp. = 35°C; pH= 8; particle size = 100BSS mesh.

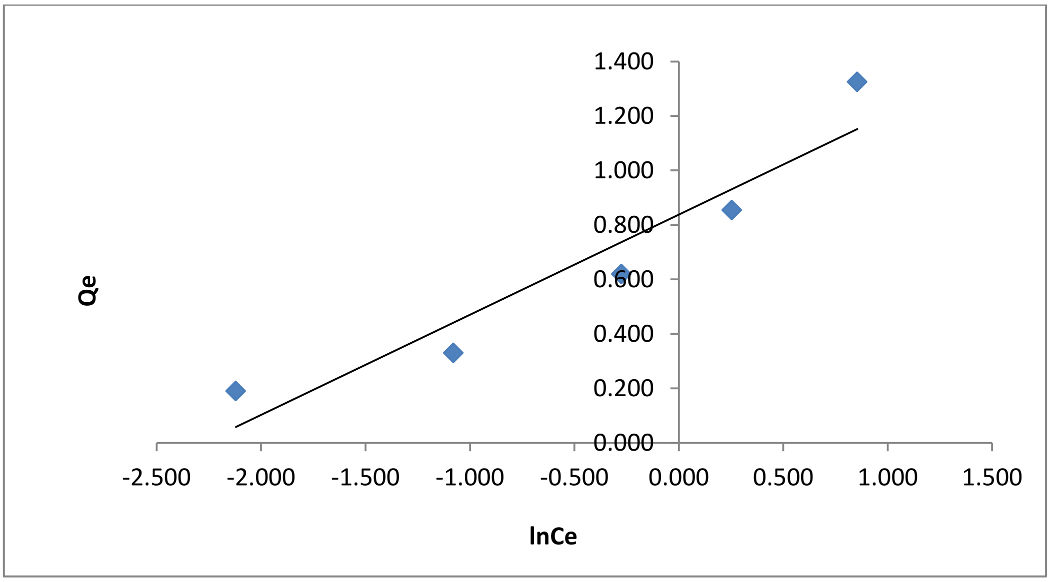

Figure 4.40: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; temp. = 40°C; pH= 8; particle size = 100BSS mesh.

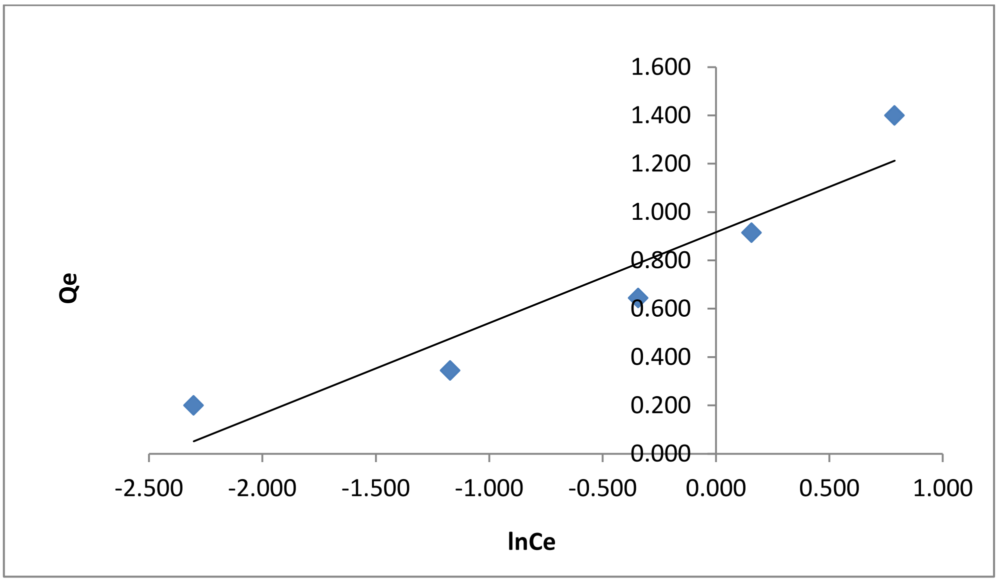

Figure 4.41: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; temp. = 45°C; pH= 8; particle size = 100BSS mesh.

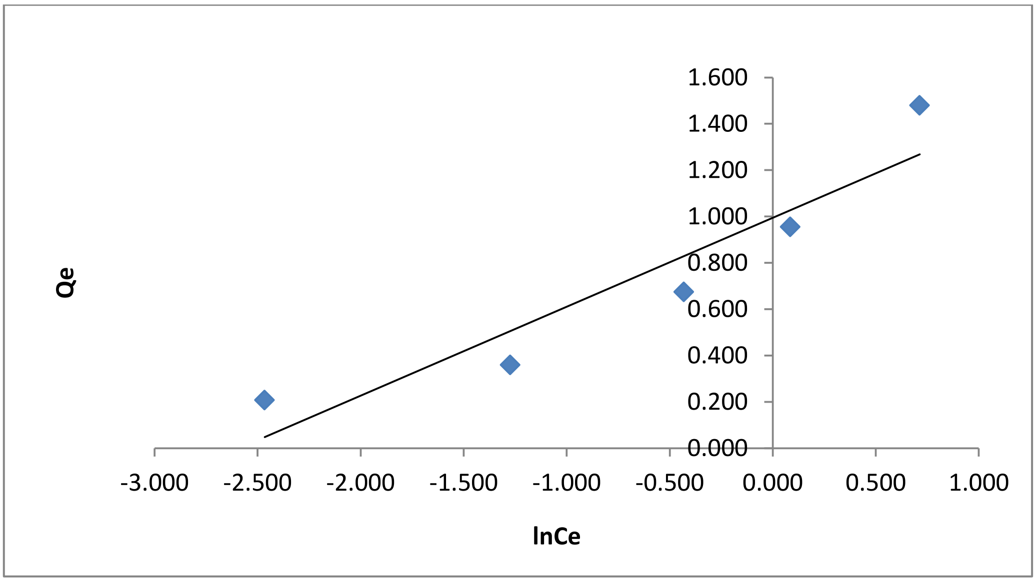

Figure 4.42: The linear Temkin isotherm plot for adsorption of Cr(VI) onto $[S_2]_{15-30}$, [Cr(VI)] = 0.50, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; temp. = 50°C; pH= 8; particle size = 100BSS mesh.

4.6.4 Application to the Kinetic Models

[A] Results for $[S_1]_{0-15}$:

In order to understand the kinetics of adsorption of Chromium(VI), on contaminated soil $[S_1]_{0-15}$, various kinetic models i.e. first order, second order, pseudo first order, pseudo second order, intraparticle diffusion and Elovich were tested with the experimental data at different initial Chromium(VI) concentration. The comparative results and calculated kinetic parameters are given in **Table 4.17** and **4.19** respectively.

The straight line plots of log $(q_e - q_t)$ against time, t for the pseudo first order and t/q_t against time, t for the pseudo second order reaction of the adsorption of Cr(VI) onto $[S_1]_{0-15}$ were shown in the **Figure 4.46** and in **4.47** respectively The plot of q_t versus $t^{1/2}$ for the intraparticle diffusion for the adsorption of Cr(VI) is shown in **Figure 4.48**. The **Figure 4.49** represents the Elovich equation and the **Figure 4.43**, **4.44** and **4.45** represent the zero order, first order and second order kinetic model respectively.

The calculated values of their corresponding regression coefficient (R^2) values, SEE values and the slope values are presented in the **Table 4.17**.

[B] Results for $[S_2]_{15-30}$:

In order to understand the kinetics of adsorption of Chromium(VI), on contaminated soil $[S_2]_{15-30}$, various kinetic models i.e. first order, second order, pseudo first order, pseudo second order, intraparticle diffusion and Elovich equation were tested with the experimental data at different initial Chromium(VI) concentration. The comparative results and calculated kinetic parameters are given in **Table 4.18** and **4.20** respectively.

The straight line plots of log $(q_e - q_t)$ against time, t for the pseudo first order and t/q_t against time, t for the pseudo second order reaction of the adsorption of Chromium(VI) onto $[S_2]_{15-30}$ were shown in the **Figure 4.53** and **4.54** respectively. The plot of q_t versus $t^{1/2}$ for the intraparticle diffusion for the adsorption of Chromium(VI) is shown in **Figure 4.55**. **The Figure 4.56** represents the Elovich equation and the **Figure 4.50**, **4.51** and **4.52** represent the zero order, first order and second order kinetic model respectively.

The calculated values of their corresponding regression coefficient (r^2) value, SEE values and the slope values are presented in the **Table 4.18**.

The correlation coefficients for pseudo second order kinetic model are higher than all other kinetic models for both $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30.}$ This suggests that the present system can be represented better by the pseudo second order model. Similar results were obtained for $[S_2]_{15\text{-}30}$.

The calculated q_e values for $[S_1]_{0\text{-}15}$ and $[S_2]_{15\text{-}30}$ given in **Table 4.19** and **4.20** agreed very well with the experimental data. Thus experimental results supports the assumption behind the model that the rate limiting step in adsorption of Chromium(VI) are chemisorptions involving valence forces through the sharing or exchange of electrons between adsorbent and metal ions.

Some other studies on the kinetics of Chromium(VI) adsorption onto various adsorbents have also reported higher correlations for pseudo-second order model [20, 58, 62].

The coefficient of determination (R^2) for intraparticle diffusion are between 0.8834 to 0.9709 for $[S_1]_{0\text{-}15}$ and 0.9241 to 0.9469 for $[S_2]_{15\text{-}30}$ given in **Table 4.17** and **4.18** respectively and the standard error of estimation (σ) are between 0.0065 to 0.0117 for $[S_1]_{0\text{-}15}$ and 0.0070 to 0.0104 for $[S_2]_{15\text{-}30}$ given in **Table 4.17** and **4.18** respectively. So on the basis of standard error of estimation (σ) intraparticle diffusion model also best suited for the present system. From the parabolic diffusion we can understand the interaction of solid and liquid interface.

The overall rate of adsorption of Chromium(VI) on the soil could be influenced by the following three steps [88]: (a) film or surface diffusion, where the Chromium(VI) is transported from the bulk solution to the external surface of the adsorbent, (b) intraparticle or pore diffusion, where the Chromium(VI) molecules move into the interior of the soil particles, and (c) adsorption of Chromium(VI) ion on the interior sites of the soil.

The rate parameters for intraparticle diffusion (K_{id}) for Chromium(VI) removal were determined by using the **Equation 4.18** Where K_{id} is the rate constant of intraparticle diffusion parameter (mg g^{-1} $min^{-1/2}$) and C is the intercept. The values of K_{id} and C can be determined from the slope and intercept of the plot

Table 4.17 : Coefficient of determination (R^2), standard error of estimation (SEE) and slope for graphical equations of different kinetic models applied on Cr(VI) adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp.= 30°C.

Kinetic model / Cr (VI) mg		Zero Order	First Order	Second Order	Pseudo First Order	Pseudo Second Order	Intraparticle Diffusion	Elovich Equation
0.5	R^2	0.9686	0.9060	0.9498	0.9486	0.9543	0.9709	0.9184
	SEE	0.0134	0.2514	0.0235	0.1063	6.2976	0.0065	0.0108
	Slope	0.0116	0.1215	0.0159	-0.1092	4.4787	0.0351	0.0467
1	R^2	0.8998	0.9010	0.9553	0.9349	0.9959	0.9442	0.9328
	SEE	0.0212	0.2594	0.0086	0.1977	1.3362	0.0079	0.0087
	Slope	0.0099	0.1218	0.0062	-0.1791	3.2597	0.0307	0.0417
2	R^2	0.8998	0.8913	0.9712	0.8470	0.9988	0.8834	0.8736
	SEE	0.0212	0.2662	0.0035	0.5045	0.3931	0.0117	0.0122
	Slope	-0.0099	0.1187	0.0032	-0.2838	1.7937	0.0304	0.0413
3	R^2	0.8998	0.8837	0.9841	0.8372	0.9994	0.9303	0.9001
	SEE	0.0212	0.2617	0.0013	0.3494	0.2137	0.0087	0.0104
	Slope	0.0099	0.1123	0.0016	-0.1894	1.3307	0.0298	0.0401
5	R^2	0.8998	0.9212	0.9479	0.9327	0.9999	0.9125	0.9256
	SEE	0.0212	0.2617	0.0018	0.2812	0.0401	0.0069	0.0064
	Slope	-0.0099	0.1393	0.0012	-0.2502	0.8524	0.0211	0.0291

Table 4.18 : Coefficient of determination (R^2), standard error of estimation (SEE) and slope for graphical equations of different kinetic models applied on Cr(VI) adsorption onto $[S_2]_{15-30}$, [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

Kinetic model Cr (VI) mg		Zero Order	First Order	Second Order	Pseudo First Order	Pseudo Second Order	Intraparticle Diffusion	Elovich Equation
0.5	R^2	0.9238	0.9155	0.9108	0.8611	0.9505	0.9327	0.8817
	SEE	0.0221	0.0873	0.5663	0.2401	6.2194	0.0104	0.0138
	Slope	0.0120	0.0447	0.2817	-0.1429	4.2451	0.0364	0.0484
1	R^2	0.8977	0.8858	0.9177	0.9518	0.9972	0.9435	0.9330
	SEE	0.0204	0.0417	0.0811	0.1648	1.0734	0.0076	0.0082
	Slope	0.0094	0.0181	0.0422	-0.1751	3.1326	0.0291	0.0396
2	R^2	0.8693	0.8638	0.8807	0.9429	0.9996	0.9241	0.9240
	SEE	0.0201	0.0198	0.0209	0.2090	0.2378	0.0077	0.0077
	Slope	0.0081	0.0078	0.0088	-0.2030	1.7629	0.0252	0.0345
3	R^2	0.8982	0.8957	0.9024	0.8884	0.9996	0.9340	0.9113
	SEE	0.0195	0.0139	0.0077	0.2877	0.1697	0.0079	0.0091
	Slope	0.0090	0.0063	0.0037	-0.1941	1.3081	0.0278	0.0376
5	R^2	0.9262	0.9253	0.9276	0.9019	0.9998	0.9469	0.9089
	SEE	0.0164	0.0071	0.0023	0.2038	0.0744	0.0070	0.0091
	Slope	0.0091	0.0039	0.0013	-0.1477	0.8273	0.0277	0.0371

Table 4.19: Kinetic parameters of different kinetic models applied on Cr(VI) adsorption on adsorption onto $[S_1]_{0-15}$, [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

Kinetic model	Cr (VI) mg	0.5	1	2	3	5
Pseudo First Order	**K_{ad} (min^{-1})**	**0.251**	**0.412**	**0.654**	**0.436**	**0.576**
	q_e (mg g^{-1})	**0.009**	**0.011**	**0.029**	**0.012**	**0.008**
Pseudo Second Order	**K_2 (g mg^{-1} min^{-1})**	**0.704**	**1.842**	**2.409**	**2.396**	**4.211**
	$q_{e\ (cal)}$ (mg g^{-1})	**0.223**	**0.307**	**0.557**	**0.751**	**1.173**
	$q_{e\ (exp)}$ (mg g^{-1})	**0.170**	**0.280**	**0.535**	**0.730**	**1.160**
	h (mg g^{-1} min^{-1})	**0.035**	**0.173**	**0.749**	**1.353**	**5.796**
Intraparticle Diffusion	**K_{id} (mg g^{-1}min$^{-1/2}$)**	**0.035**	**0.031**	**0.030**	**0.030**	**0.021**
	C (mg g^{-1})	**0.019**	**0.154**	**0.412**	**0.607**	**1.075**
Elovich Equation	**ln α (mg·g^{-1}·min^{-1})**	**-2.472**	**0.654**	**6.916**	**12.062**	**33.565**
	β (g·mg^{-1})	**21.424**	**23.997**	**24.200**	**24.919**	**34.420**

$q_{e\ (cal)}$ = Calculated adsorbed amount of Cr(VI) (mg/g); $q_{e\ (exp)}$ = Experimental adsorbed amount of Cr(VI) (mg/g)

Table 4.20: Kinetic parameters of different kinetic models applied on Cr(VI) adsorption on adsorption onto $[S_2]_{15\text{-}30}$, [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

Cr (VI) mg **Kinetic model**		**0.5**	**1**	**2**	**3**	**5**
Pseudo First Order	**K_{ad} (min^{-1})**	**0.329**	**0.403**	**0.468**	**0.447**	**0.340**
	q_e ($mg\ g^{-1}$)	**0.013**	**0.009**	**0.008**	**0.010**	**0.007**
Pseudo Second Order	**K_2 ($g\ mg^{-1}\ min^{-1}$)**	**0.734**	**2.054**	**3.058**	**2.676**	**2.671**
	$q_{e\ (cal)}$ ($mg\ g^{-1}$)	**0.236**	**0.319**	**0.567**	**0.764**	**1.209**
	$q_{e\ (exp)}$ ($mg\ g^{-1}$)	**0.180**	**0.295**	**0.550**	**0.745**	**1.190**
	h ($mg\ g^{-1}\ min^{-1}$)	**0.041**	**0.209**	**0.984**	**1.564**	**3.903**
Intraparticle Diffusion	**K_{id} ($mg\ g^{-1} min^{-1/2}$)**	**0.036**	**0.029**	**0.025**	**0.028**	**0.028**
	C ($mg\ g^{-1}$)	**0.027**	**0.176**	**0.447**	**0.631**	**1.075**
Elovich Equation	**ln α ($mg{\cdot}g^{-1}{\cdot}min^{-1}$)**	**-2.278**	**1.342**	**9.739**	**13.653**	**25.859**
	β ($g{\cdot}mg^{-1}$)	**20.652**	**25.281**	**29.025**	**26.618**	**26.974**

$q_{e\ (cal)}$ = Calculated adsorbed amount of Cr(VI) (mg/g); $q_{e\ (exp)}$ = Experimental adsorbed amount of Cr(VI) (mg/g)

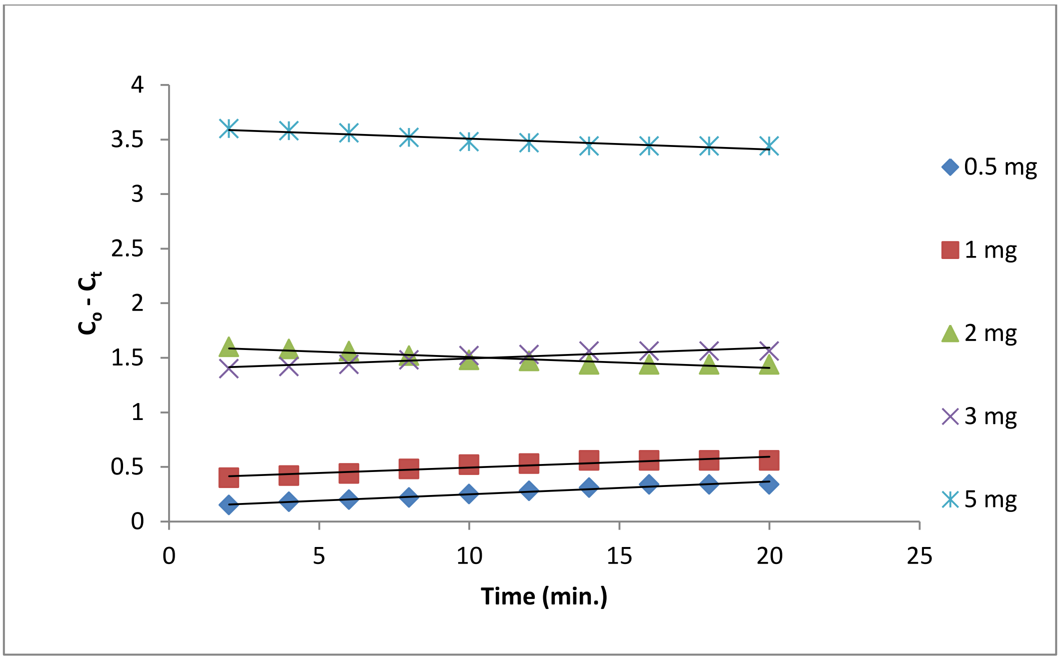

Figure 4.43: Zero order equation plot for Chromium(VI) adsorption onto $[S_1]_{0-15}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

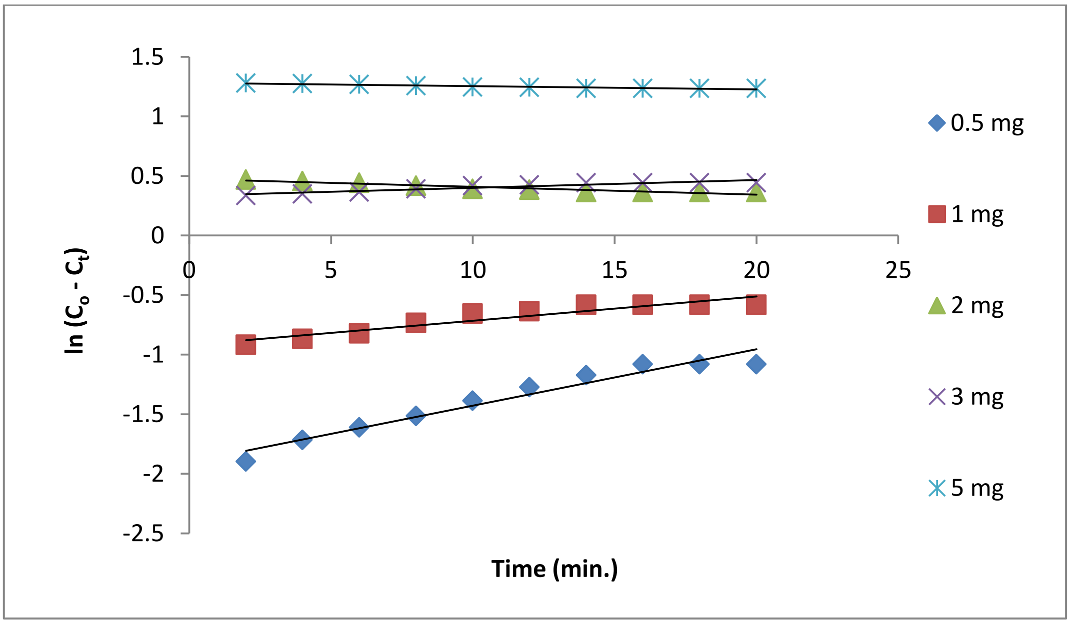

Figure 4.44: First order equation plot for Chromium(VI) adsorption onto $[S_1]_{0-15}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

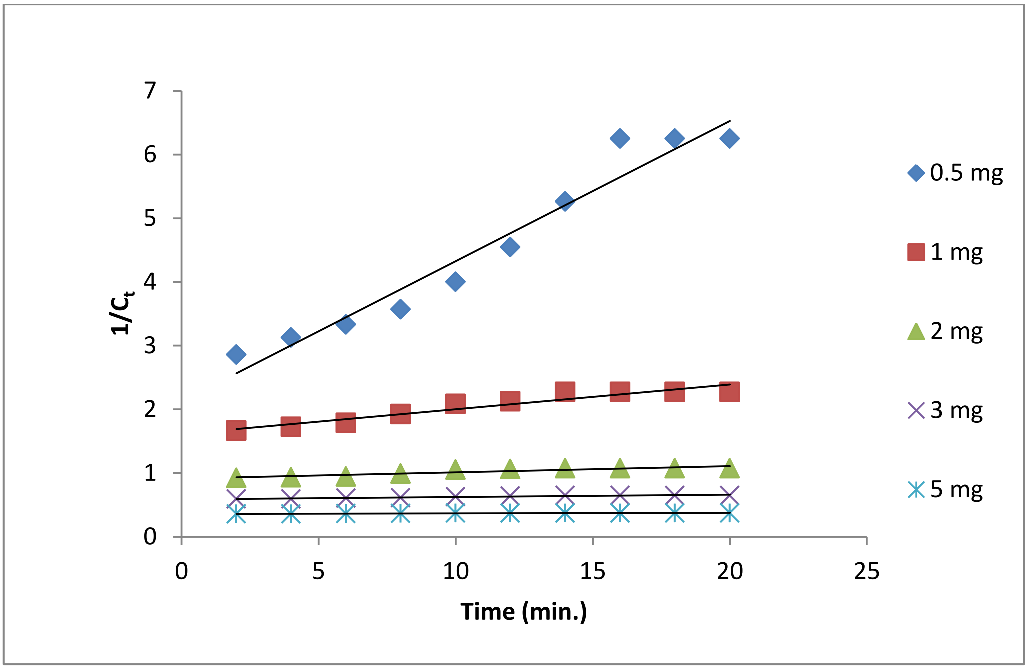

Figure 4.45: Second order equation plot for Chromium(VI) adsorption onto $[S_1]_{0\text{-}15}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

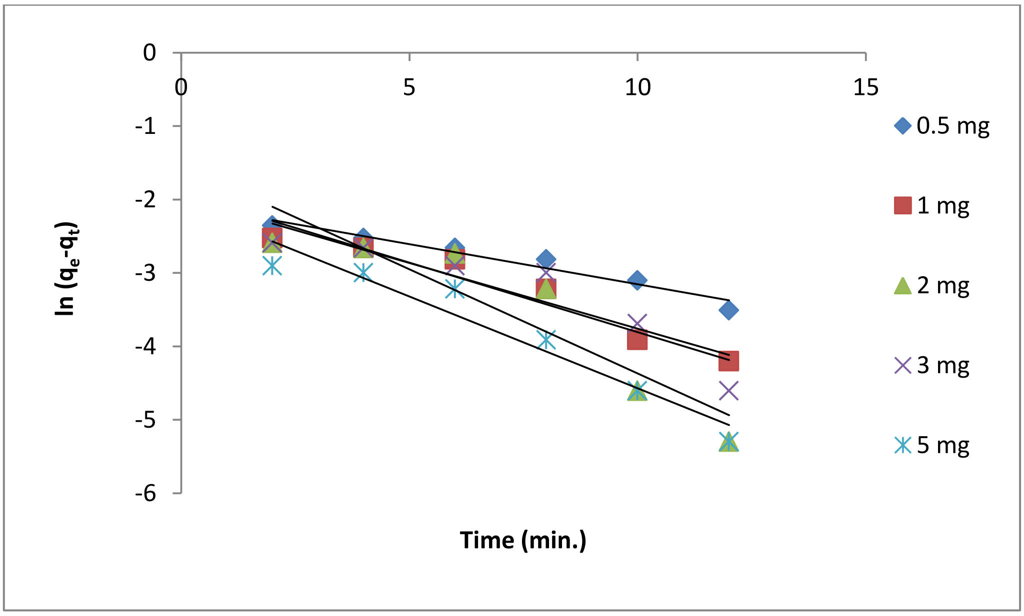

Figure 4.46: Pseudo first order equation plot for Chromium(VI) adsorption onto $[S_1]_{0\text{-}15}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0\text{-}15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

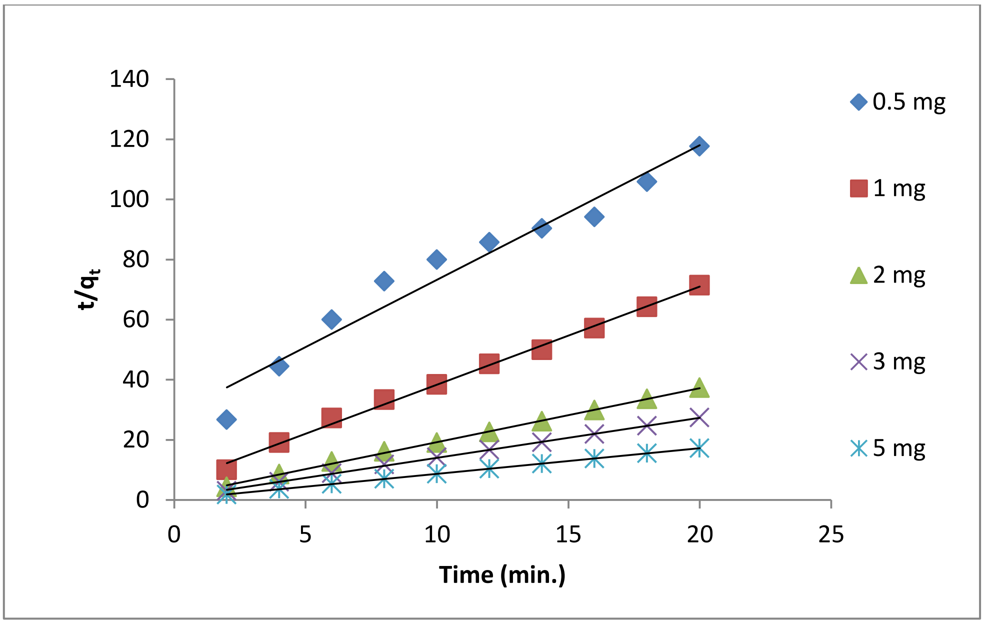

Figure 4.47: Pseudo second order equation plot for Chromium(VI) adsorption onto $[S_1]_{0-15}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

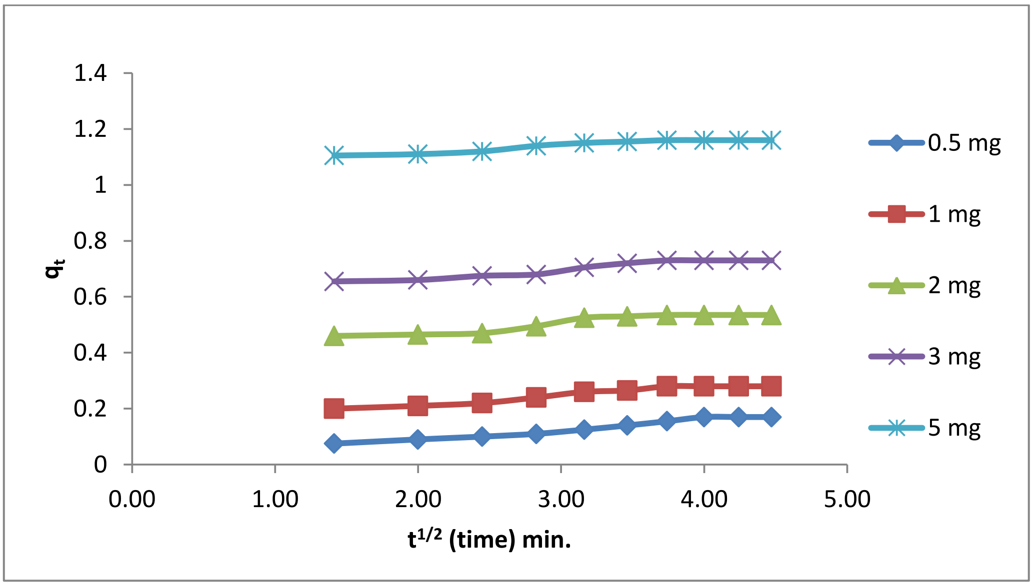

Figure 4.48: Intraparticle diffusion equation plot for Chromium(VI) adsorption onto $[S_1]_{0-15}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

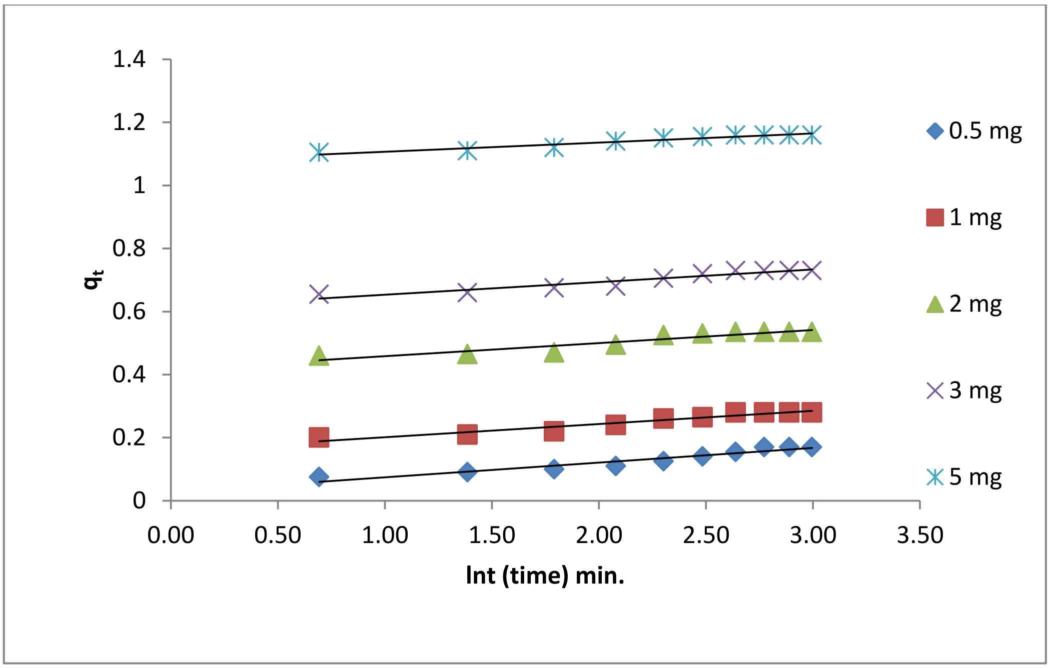

Figure 4.49: Elovich equation plot for Chromium(VI) adsorption onto $[S_1]_{0-15}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_1]_{0-15}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

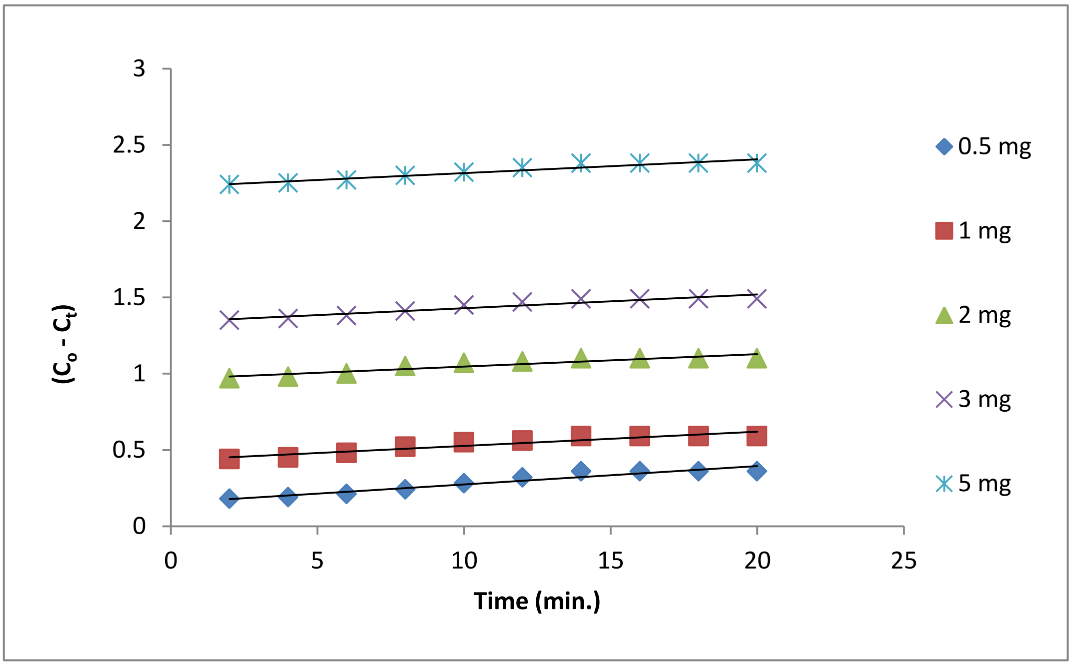

Figure 4.50: Zero order equation plot for Chromium(VI) adsorption onto $[S_2]_{15-30}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

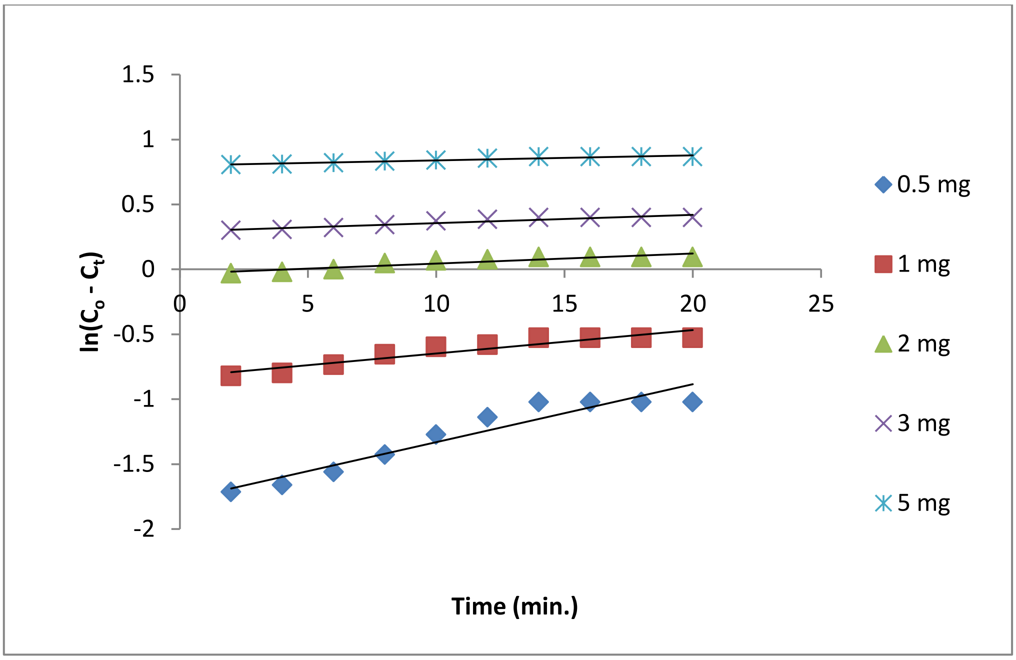

Figure 4.51: First order equation plot for Chromium(VI) adsorption onto $[S_2]_{15\text{-}30}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^{o}C.

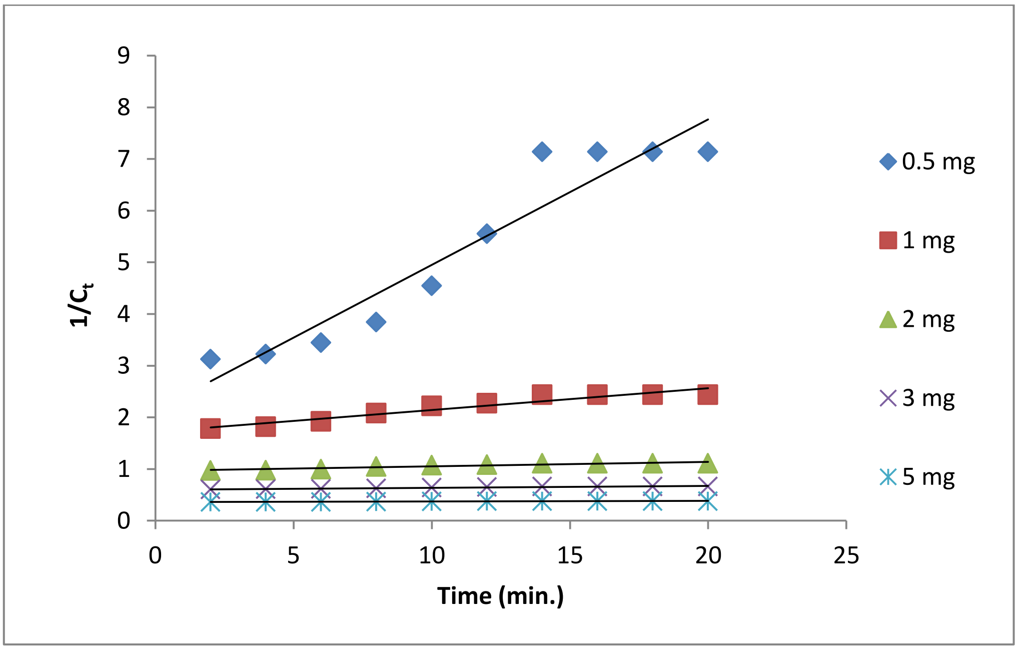

Figure 4.52: Second order equation plot for Chromium(VI) adsorption onto $[S_2]_{15\text{-}30}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^{o}C.

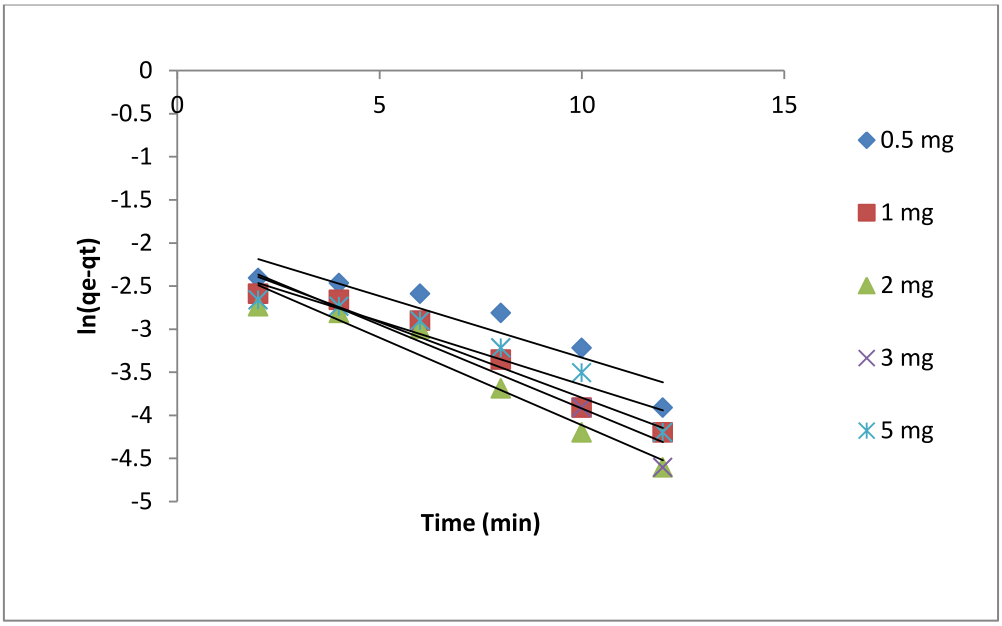

Figure 4.53: Pseudo first order equation plot for Chromium(VI) adsorption onto $[S_2]_{15\text{-}30}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^{o}C.

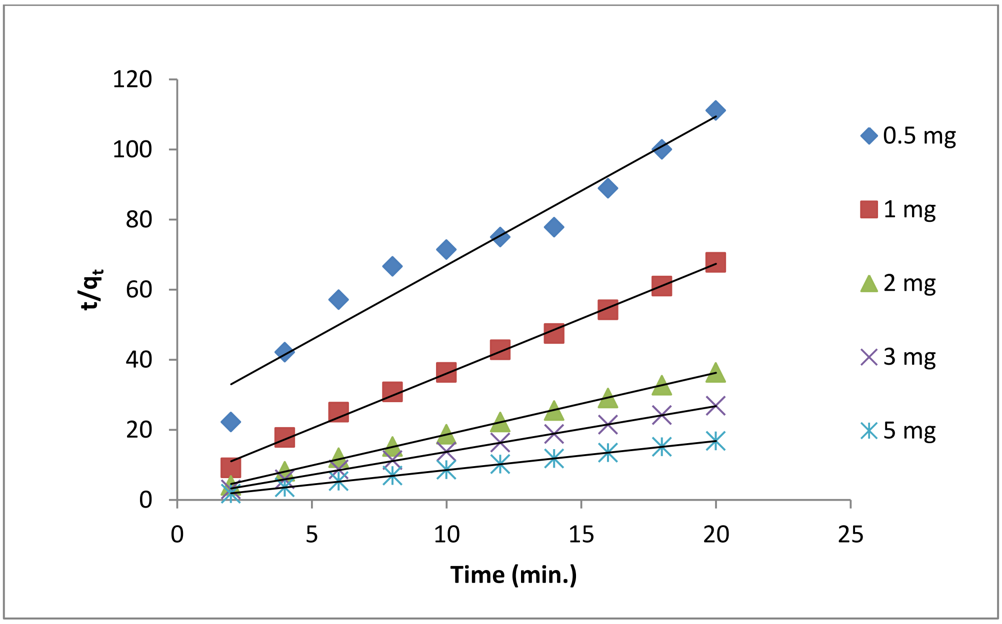

Figure 4.54: Pseudo second order equation plot for Chromium(VI) adsorption onto $[S_2]_{15\text{-}30}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15\text{-}30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30^{o}C.

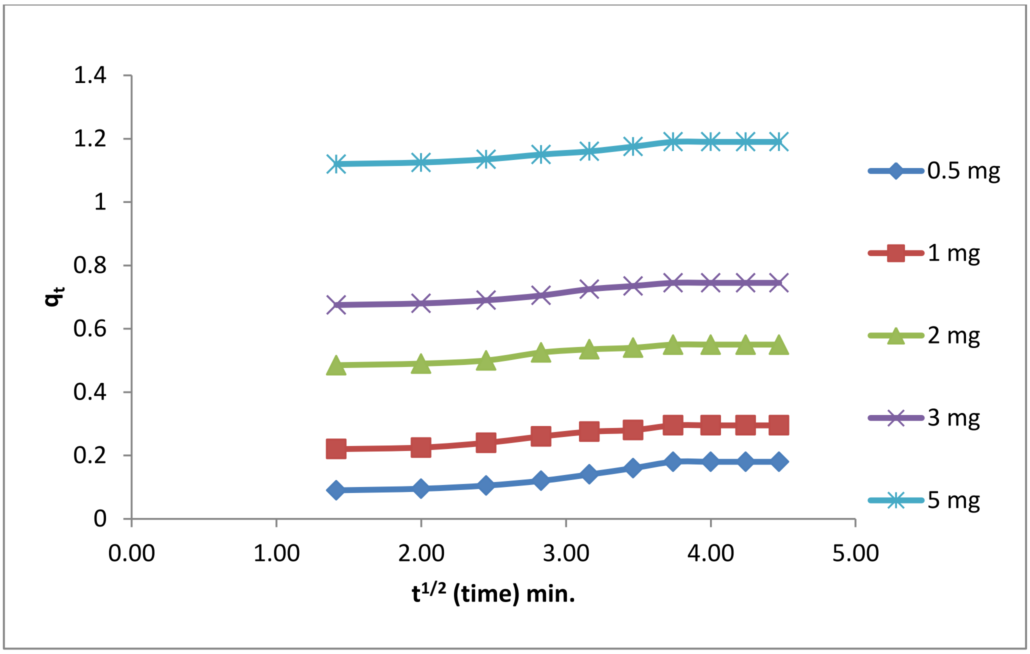

Figure 4.55: Intraparticle diffusion equation plot for Chromium(VI) adsorption onto $[S_2]_{15-30}$ at different initial concentration of Cr(VI), [Cr (VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

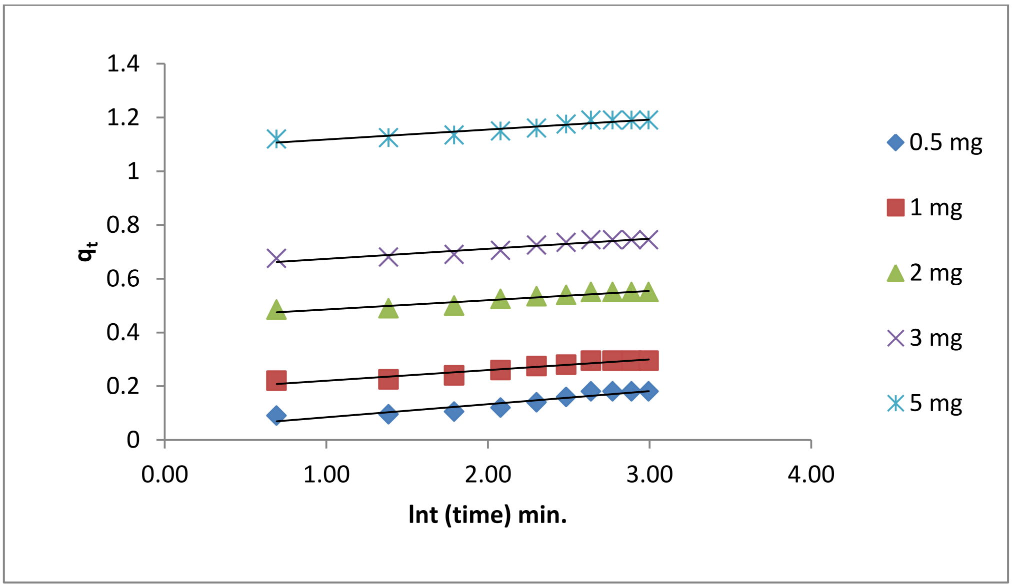

Figure 4.56: Elovich equation plot for Chromium(VI) adsorption onto $[S_2]_{15-30}$ at different initial concentration of Cr(VI), [Cr(VI)] = 0.5, 1, 2, 3 and 5 mg, $[S_2]_{15-30}$ = 2 g; pH= 8; particle size = 100BSS mesh; temp. = 30°C.

q_t versus $t^{1/2}$ (**Figure 4.48** and **4.55**). Values of C give an idea about the thickness of boundary layer i.e. the larger the intercept, the greater the contribution of the surface sorption in the rate controlling step [60]. Based on these plots (**Figures 4.48** and **4.55**) it was concluded that the adsorption of Chromium(VI) is comprised of two phases, suggesting that intraparticle diffusion mechanism is not the rate limiting step for the whole reaction. The initial portion of the plot indicated an external mass transfer whereas the second linear portion is due to intraparticle or pore diffusion. The two phases in the intraparticle diffusion plot suggest that the adsorption of Chromium(VI) ions proceed by surface sorption and intraparticle diffusion.

Obtained plots for $[S_1]_{0-15}$ and $[S_2]_{15-30}$ did not pass through the origin. This deviation from the origin was attributed to the difference in the rate of mass transfer in initial and final stages of adsorption. This is indicative of some degree of boundary layer control and this further showed that the intraparticle diffusion was not the only rate limiting step, but also be controlling the rate of adsorption or all may be operating simultaneously [89]. Similar results were obtained in previous studies [90-92].

So among the all kinetic models pseudo second order and intraparticle diffusion model both are best fitted for $[S_1]_{0-15}$ as well as for $[S_2]_{15-30.}$

4.7 Conclusion

It is concluded on the basis of the experimental results that adsorption of Chromium(VI) onto $[S_1]_{0-15}$ and $[S_2]_{15-30}$ increases on increasing temperature due to formation of new binding sites. The ΔG^o was observed to be more negative with increase in temperature for $[S_1]_{0-15}$ and $[S_2]_{15-30}$, indicates that adsorption process is spontaneous and spontaneity is increasesing on increasing temperature with depth of Chromium(VI) contaminated site. The Value of ΔH^o was found positive indicates the adsorption process is endothermic and takes place via surface complex formation for both soil samples. The values of ΔS^o are found to be positive for both $[S_1]_{0-15}$ and $[S_2]_{15-30}$. Thus the thermodynamic parameters confirmed the spontaneous and endothermic nature of the adsorption process. On the basis of coefficient of determination (R^2) and standard error of estimation (σ), equilibrium isotherm data fitted well to the Freundlich isotherm model for both $[S_1]_{0-15}$ and $[S_2]_{15-30}$, indicates that adsorption was on heterogeneous surface. From the values of R_L and n_f it is concluded that adsorption of Chromium(VI) onto soil is a favorable process. On the basis of Temkin isotherms parameters the adsorption process in the present study involves chemisorptions and physisorption. The experimental data of adsorption of Chromium(VI) onto $[S_1]_{0-15}$ and $[S_2]_{15-30}$ were applied on the seven different Kinetic models and on the basis of Coefficient of determination (R^2) pseudo second order model was found best fitted for both $[S_1]_{0-15}$ and $[S_2]_{15-30}$. The calculated values of adsorbed amount of Chromium(VI) for pseudo second order kinetic model agreed very well with the experimental data for both soil samples, suggests that the rate limiting step in adsorption of heavy metals are chemisorptions involving valence forces through the sharing or exchange of electrons between adsorbent and metal ions. Intraparticle diffusion kinetic model also considered the best to explain the behavior of the adsorption process on the basis of the values of standard error of estimation (σ).

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Chapter – 5

Kinetics of Desorption of Chromium(VI) from Chromium Contaminated Soil

ABSTRACT

The present study describes the desorption of Chromium(VI) from contaminated soil of RIICO industrial area Bhilwara. The desorption test were carried out on the prepared Chromium(VI) enriched soil samples with double distilled water. The effect of initially adsorbed amount of Chromium(VI) concentration, pH of solution and temperature on desorption were investigated and it was observed that desorption increases on increasing, initially adsorbed amount of Chromium(VI) concentration, pH and temperature. Effect of NaOH concentration was also studied. Effect of chelating agent EDTA was investigated by varying different concentration of EDTA, incubation period and pH. The maximum percentage desorption was observed for 0.1 M EDTA, for 96 and 120 hour incubation period and at pH 10. The desorption experimental data were applied on seven different kinetic models and second order kinetic model and parabolic diffusion model are best fitted for the present desorption study.

5.1 Introduction

Soil is a heterogeneous mixture of several components, many of which are organic and inorganic compounds of varying composition and surface activity [1]. They can bind heavy metal like Chromium and reduce their availability. Thus, knowledge of the adsorption-desorption characteristics of soil is necessary for predicting their mobility and fate in soil environment and also to understand whether remediation is a feasible option for the cleanup of contaminated soil or not. Heavy metals introduced on the soil surface, undergo downward transportation, which does not occur to any greater extent unless the metal retention capacity of the soil is overloaded or metal interaction with associated waste matrix enhances mobility [2]. Adsorption and desorption are most important chemical processes in soils and soil constituents.

Desorption is a phenomenon or process where some of adsorbed substance is released. Adsorption of solute on any adsorbent can either be by physical bonding, ion exchange or combination of both. If the adsorption is by physical bonding then the loosely bound solute can be easily desorbed with distilled water in most of the cases. However, if the mode of adsorption is by chemical bonding or ion exchange or combination of both, then the adsorption can be affected by stronger desorbents like acid or alkali solutions [3, 4].

Often wastes from textile, paint, pigment and Chromium chemicals production industries (e.g., sludge, fly ash, slag, etc.) are used as a fill material at numerous locations to reclaim marshlands, for tank dikes, and for backfill at sites following demolition [5]. At many such sites, leaching and seepage of Chromium(VI) from the soil into the groundwater poses a considerable health hazard. The tanning industry is an especially large contributor of Chromium pollution to water resources. There appears to be little correlation between Chromium concentrations in plant tissues and that in soil. Generally, only a very small fraction of the total Chromium content in soil is plant available. This fraction, often determined as ‘extractable Chromium’, is highly variable, ranging from 0.01 to 4 mg kg^{-1} [6, 7]. Investigation of adsorption desorption phenomena of heavy metals in soils is of great importance from environmental point of view as heavy metal adsorption affects processes like transport, degradation, volatilization, bioaccumulation, etc. which influence the final fate of the compounds in the soil environment [8]. All these processes influence the extent of surface water and ground water contaminations too. Since, soil is a heterogeneous mixture of several components, many of which are organic and inorganic compounds of varying composition and surface activity; they can bind heavy metals and reduce their bioavailability [9].

Disposal of Chromium(VI) loaded adsorbents in the environment is hazardous in nature. Desorption of metals from adsorbent helps in recovery of metals and reduces the disposal problem of metal loaded adsorbents [10].

Adsorption reaction is fast and probably diffusion controlled, whereas the diffusion reaction step has a rate constant that may be as much as three orders of magnitude slower. Adsorption reaction is energetically favorable, desorption always requires an activation energy to overcome the adsorption energy [11]. Consequently, many chemisorption reactions have much higher activation energy in the reverse than in the forward direction. The commonly observed no reversibility in metal adsorption may be the result of the long time period that could be required for desorption to be completed [12, 13]. Generally, adsorption of metals seems to be more nearly reversible at low pH than at high pH [14].

Soil remediation is a challenge for scientist and regulatory authorities. This can be done by using physical, chemical and biological techniques but they do not offer satisfactory solution for many sites especially for agricultural lands. The addition of chelating agents to the soil can also bring metals into solution through desorption of adsorbed species, dissolution of Fe and Mn oxides, and dissolution of precipitated compounds. These complexes can greatly alter the reactivity of the metal ion. They can alter the oxidation-reduction properties of transition-metal ions, such as iron (Fe) and manganese (Mn), and therefore increase or decrease the reactivity of these systems [15]. Among the most important classic reagents, containing many industrial applications, which can be used to remove toxic metal ions from contaminated water and soil, stand out ethylenediaminetetraacetic acid (EDTA) [16-18]. These ligands, in the form of alkali metal salt, contain the respective polyacetate anion forming very stable complexes with most metallic ions. The evidenced importance of these ligands as chelating agents supports the need for an exploration of their properties. Given these concepts, theoretical studies concomitant with the experimental, addressing the understanding of the phenomenon involving a metal complexation by organic ligands, are always needed [19, 20].

Thousands of sites contaminated with heavy metals need to be remediated in many countries, which requires new development of effective soil treatment technologies [21-23]. Several remedial options could be considered for cleaning the Chromium contaminated sites. The first option is excavation and disposal of soil. This option is expensive. This technique is costly and not sufficient to handle such large amounts of waste. Also, the transportation of large quantities of waste from one place to another is a hazard.

The second option is on-site fixation. It would stabilize the contaminated soil through a chemical or physical fixation. The chemically fixated soil would be replaced on-site and then covered with a clean soils cap. So far, no satisfactory analysis has been obtained on the fixation of Chromium contaminated soils. It is also uncertain as to whether the site would be usable following the chemical fixation process or not. Questions such as long term stability and integrity of the cap have also been considered. Fitzpatrick et al (1986) [24] used in situ vitrification to stabilize the contaminated soil. In situ vitrification is a thermal treatment process that converts contaminated soil into a chemically inert, stable glass and crystalline product.

The last option is soil washing. Soil washing process can be carried out in the contaminated site. In this case, the soil can be put back where it came from and without transportation and other relative problems. Ellis et al (1986) [25] performed a series of tests of soil washing. The tests demonstrated that sequential treatment of soil with ethylenediaminetetraacetic acid (EDTA), hydroxylamine hydrochloride, and citrate buffer was effective in removing metals from soil, and all were necessary for good cleanup. The EDTA chelated and solubilized all of the metals to some degree; the hydroxylamine hydrochloride reduced the soil iron oxide, manganese oxide matrix, releasing bound metals, and also reduced

Chromium and additional acid-labile metals. The best removals observed were: cadium, 98 percent; lead, 96 percent; copper, 73 percent; Chromium, 52 percent; and nickel, 23 percent [26]. Dugan et al (1984) [27] investigated that hexavalent Chromium in the soil sample could be readily leached to the concentration less than 5 mg/L by using water.

Since the behavior of the elements in soil and water systems depends largely on their existing forms therefore the determination of heavy metals in soils is succeeded by the application of single or sequential extraction and or derivatization techniques. Extraction involves subjecting a solid matrix to successive attacks by reagents of different chemical properties (acidity, redox potential, complexing properties) with each extract representing a fraction of element associated with the sample [28]. In general, there are currently many extractants in application but the choice largely depends on the nature of metal (e.g., hard metals are better extracted with solvents containing oxygen while soft metals are better extracted with solvents containing sulphur or phosphorus) [29].

A large number of different reagents, can extract almost all or part of the metals commonly found in soils, namely water, sodium nitrate, ammonium nitrate, ethylenediaminetetraacetic acid, potassium nitrate, calcium chloride, ammonium acetate, and acetic acid have been reported [29-35]. Therefore, the use of sequential extraction in connection with physical speciation can be used to define bioavailable metal soluble metal fractions both of these metal fractions in soils can provide a good indication to the possible extent of groundwater contamination by metal leaching [36].

Heavy metals are toxic to human as well as to other organisms [37]. Contaminated sites are also pose a threat to groundwater supplies, if the metals are not properly contained and treated. Heavy metals interact with soil matrix and may persist for a long period of time creating long term hazards to the environment. A promising method for removing heavy metals from soil is chelating extraction [38]. Chromium remediation in soil may involve extraction from the soil matrix by washing with an aqueous solution containing a chelating agent [39]. A chemical agent may be a chelate which composed of a metal ion and a chelating agent. It can form several bonds to a single metal ion and also form strong, water soluble metal complexes with di and trivalent cations [40].

Soil washing is considered as one of the most suitable on site techniques for removing heavy metals. Recently increased attention has been focused on the use of acidic or chelating agents to dislodge and dissolve heavy metals from solids into solution. Citric acid, nitrilo tri acetic acid and EDTA are the common alternatives suggested for chelating polluted soils [41, 42]. EDTA is one of the most successful and admired chemical reagent because it is a powerful, recoverable and comparatively biostable chelator which has ability to remediate soil [43].

The process of EDTA addition is considered as an important aspect controlling the leaching of metals [44]. Chelating agents like EDTA has ability to form water soluble complexes by increasing uptake of metals desorbing from the solid phase of soil [45]. Metal is basically portioned in two phases: Reversible and irreversible. Chelats try to absorb metals from reversible and then from irreversible phase [46]. This basic principle is used to test the chelating agent, that how well chelate can free the metals from the bounded phase. If they can unlock from irreversible phase their efficiency is more [47].

The effectiveness of the extraction is strongly dependent upon the presence of easy exchangeable ions in the soil matrix which are able to form stable complexes with low selective chelating agent [48]. Using EDTA to remove heavy metals has been proven to be an effective method due to strong complexing ability of EDTA [49].

Shaking time is an important factor in governing the heavy metals solubilization in soil matrix. The ability of chelating agent to sustain heavy metals in a soluble form is affected by the stability of the complex. So by studying the time factor we can determine the availability and persistence of the chelant in the soil matrix. Incubation time should also be taken in to account when evaluating the metals solubilization efficiency of the chelants. C. Kim et al (2003) [50] reported that oxidation of metal ion and formation of metal-chelate complex may take different period of time for different metals. So, incubation time should not be ignored while evaluating other environmental impacts. Even though EDTA has shown to be a suitable chelating agent for remediation of heavy metal, not much information is available with high heavy metal removal efficiency [51].

Numerous studies have reported about the heavy metal extraction from different adsorbents by using various extractants. However, only a few studies are being conducted on desorption characteristics of Chromium(VI) from soil though they are of fundamental importance to quantify the transport of Chromium(VI) and selection of proper remediation technique. The desorption kinetics of Chromium(VI) removal from soil by batch method have not been studied in detail, although Chromium(VI) is carcinogenic and causes severe health problems. Therefore, investigation of desorption study will provide a better understanding of transport of Chromium(VI) in environment. The goal of this study was to further investigate the feasibility of Extractant (i.e. NaOH and EDTA) to achieve high removal efficiency of Chromium(VI) from polluted soil and evaluate the best fitted kinetic model.

5.2 Experimental

In order to carry out the desorption test, soil sample were prepared first. Initially, adsorption study was performed using 2 g of the soil and 100 ml of different concentration Chromium(VI) solutions (0.5 mg, 1 mg, 2 mg, 3 mg and 5 mg). After batch adsorption experiment, supernatant were removed from the flask, the residual Chromium contaminated soil was dried and treated as the initial contamination condition for desorption test. For the study of effect of initially adsorbed Chromium(VI) concentration on desorption of Chromium(VI) distill water was used. Desorption of Chromium(VI) ions were performed at different pH values ranging between 2 to 10. The pH of extractant was adjusted by adding 0.1 N and 0.1 N H_2SO_4. The effect of temperature (30^o, 35^o, 40^o, 45^o and 50^oC) and different extractant like NaOH and EDTA was investigated. The effect of extractant concentration and incubation period with EDTA was also studied. The contaminated soil samples for all experiments were prepared by adding 100 ml of 5 mg Chromium(VI) into 2 g of soil. Before carry out desorption test, contaminated soil sample was kept in contact of extractant (i.e. NaOH and EDTA) for 24 hr in every experiment, except effect of incubation period in which contact time was varied from 1 hr to 120 hr. After each 2 min shacking, 5 ml of supernatant removed and concentration of supernatant were measured by the spectrophotometric diphenylcarbazide method, this method is stated earlier in **Section 2.6** of **Chapter 2** [52]. Similarly, all the experiments were carried out in triplicate and the mean values were reported.

The desorption ratio was calculated from the amount of metal ions adsorbed and the final Chromium(VI) ion concentration in the adsorption medium.

$$Desorption \quad ratio \ \% \ = \frac{Amount \quad of \quad metal \quad ion \quad desorbed}{Amount \quad of \quad metal \quad ion \quad adsorbed} \times 100 \tag{5.1}$$

5.3 Results and Discussion

5.3.1 Effect of Variation of initial Chromium(VI) Concentration on Desorption

It is apparent from the **Table 5.1** and **Figure 5.1** that as initial Chromium(VI) concentration increases, percent desorption also increases. On increasing initially adsorbed Chromium(VI) concentration from 0.34 mg to 2.32 mg, desorption of Chromium(VI) increases from 12.94% to 26.29%. **Figure 5.1** indicates that 12.94%, 15.36%, 20.56%, 23.97% and 26.29% Chromium(VI) were removed from the surface of the soil containing 0.34 mg, 0.56 mg, 1.07 mg, 1.46 mg, and 2.32 mg respectively.

The possibility of increasing desorption is associated with physisorption. In physical bonding metal is bound with weak Vander waal forces to the surface of soil. Since in the present study adsorption occur by physisorption to some extent, described in **Chapter 4** in **Section 4.6.2**, so desorption increased with the initially adsorbed Chromium(VI) concentration with distill water.

In accordance to previous study [53], the preloaded amount of heavy metal on soil increased with the increase of organic matter contents in soil, while the removal efficiency decreased, indicating soil properties affects binding of heavy metal like Chromium(VI) on soil and interaction between metal ion and the removal efficiency of soil.

Table 5.1: Influence of variation of initial Cr(VI) conc. on desorption of Cr(VI) $[S_1]_{0-15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30^oC.

$[Cr]_{Ad}$ mg	0.34		0.56		1.07		1.46		2.32	
Time, min.	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$
0	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00
2	0.015	4.41	0.032	5.71	0.065	6.07	0.103	7.05	0.200	8.62
4	0.019	5.59	0.038	6.79	0.075	7.01	0.110	7.53	0.240	10.34
6	0.023	6.76	0.042	7.50	0.092	8.60	0.140	9.59	0.290	12.50
8	0.025	7.35	0.048	8.57	0.103	9.63	0.170	11.64	0.340	14.66
10	0.029	8.53	0.057	10.18	0.130	12.15	0.210	14.38	0.390	16.81
12	0.035	10.29	0.068	12.14	0.170	15.89	0.260	17.81	0.450	19.40
14	0.040	11.76	0.078	13.93	0.200	18.69	0.300	20.55	0.520	22.41
16	0.044	12.94	0.083	14.82	0.220	20.56	0.350	23.97	0.580	25.00
18	0.044	12.94	0.086	15.36	0.220	20.56	0.350	23.97	0.610	26.29
20	0.044	12.94	0.086	15.36	0.220	20.56	0.350	23.97	0.610	26.29
∞	0.044	12.94	0.086	15.36	0.220	20.56	0.350	23.97	0.610	26.29

$[Cr]_{de}$ - Desorption of Cr(VI); % $[Cr]_{de}$ - Percentage Desorption of Cr(VI); $[Cr]_{Ad}$ =Adsorbed amount of Cr(VI);

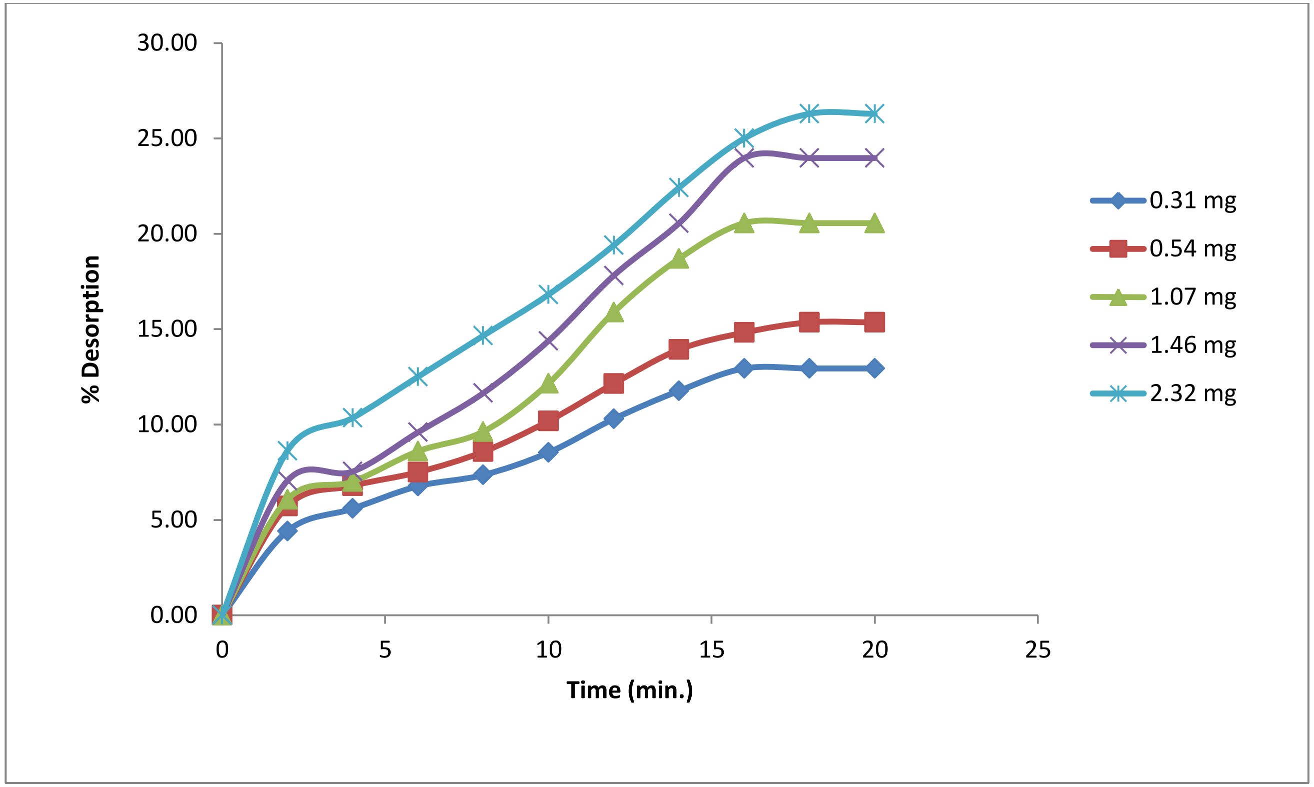

Figure 5.1: Influence of variation of initially adsorbed Cr(VI) conc. on desorption of Cr(VI) $[S_1]_{0\text{-}15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C.

Organic carbon content in soil in the present study is very low (0.18%) given in **Table 2.1** of **Chapter 2**. Due to low amount of Organic carbon Chromium(VI) bound loosely on the surface of soil, so on increasing adsorbed amount of Chromium(VI) desorption also increases. The overall percentage desorption is less than 30% and it was attributed to the fact that after adsorption of Chromium(VI) it binds with calcium and form $CaCrO_{4,}$ which is also in good agreement with results of XRD in **Section 2.9** of **Chapter 2**. Desorption studies help to elucidate the nature of adsorption. The percentage desorption less than 75% indicates that in present study the process of adsorption was not reversible.

5.3.2 Effect of Variation of pH on Desorption

Desorption was tried at different pH values ranging between 2 to 10. The desorption results in **Table 5.2** and **Figure 5.2** indicates that 23.71%, 26.29%, 29.31%, of Chromium(VI) were removed from the surface of the soil containing 2.32 mg of Chromium(VI) at pH 2, 7, and 10 respectively. Increasing the pH of the desorbing medium increased the desorption of Chromium(VI) and maximum desorption of 29.310% was found at pH 10.

Increasing the pH would deprotonate the surface and hence the adsorbent surface would suspend the negatively charged $HCrO^{-}_{4}$ species [54]. The incomplete desorption is due to the presence of impurities and Chromium binding substances in heterogeneous soil system, which may also act as an adsorbent for Chromium(VI). The rate of desorption was thus highly pH dependend. The weakly bonded negatively charged Chromium(VI) species were removed at acidic or neutral pH, while they were completely desorbs in alkaline solution owing to the formation of soluble sodium chromate [55]. So it can be inferred that risk of ground water contamination by leaching of Chromium(VI) from soil, increases in alkaline condition.

5.3.3 Effect of Variation of Temperature on Desorption

The effect of temperature on desorption of Chromium(VI) is shown in **Table 5.3** and **Figure 5.3**. It’s obvious from this Figure that, increasing in temperature from 30^{o} to $50^{o}C$, desorption of Chromium(VI) increases from 26.29% to 33.62%.

Table 5.2: Influence of variation of pH on desorption of Cr(VI), $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; particle size = 100BSS mesh; temp. = 30°C.

pH	pH = 2		pH = 7		pH = 10	
Time, min.	**$[Cr]_{de}$**	**% $[Cr]_{de}$**	**$[Cr]_{de}$**	**% $[Cr]_{de}$**	**$[Cr]_{de}$**	**% $[Cr]_{de}$**
0	0.000	0.00	0.000	0.00	0.000	0.00
2	0.170	7.33	0.200	8.62	0.220	9.48
4	0.210	9.05	0.240	10.34	0.270	11.64
6	0.250	10.78	0.290	12.50	0.330	14.22
8	0.290	12.50	0.340	14.66	0.380	16.38
10	0.340	14.66	0.390	16.81	0.420	18.10
12	0.410	17.67	0.450	19.40	0.500	21.55
14	0.480	20.69	0.520	22.41	0.590	25.43
16	0.550	23.71	0.590	25.43	0.630	27.16
18	0.550	23.71	0.610	26.29	0.680	29.31
20	0.550	23.71	0.610	26.29	0.680	29.31
∞	0.550	23.71	0.610	26.29	0.680	29.31

$[Cr]_{de}$ - Desorption of Cr(VI); % $[Cr]_{de}$ - Percentage Desorption of Cr(VI); $[Cr]_{Ad}$ =Adsorbed amount of Cr(VI);

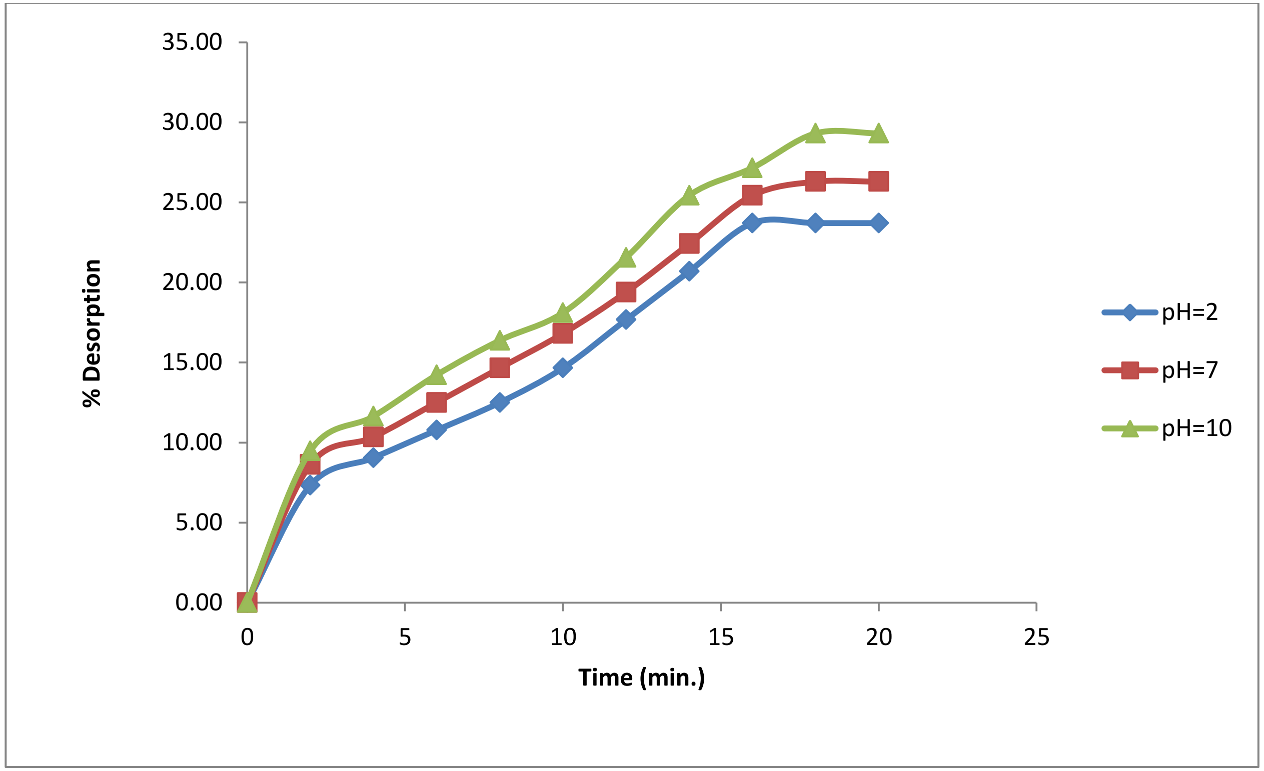

Figure 5.2: Influence of variation of pH on desorption of Cr(VI) $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; particle size = 100BSS mesh; temp. = 30°C.

Figure 5.3 indicates that 26.29%, 27.59%, 29.31%, 31.03%, 33.62%, Chromium(VI) were removed from the surface of the soil containing 2.32 mg of Chromium(VI) at temperature 30^o, 35^o, 40^o, 45^o and 50^oC respectively

Desorption always requires an activation energy to overcome the adsorption energy. Particle movements increases on increasing temperature and this phenomenon was facilitated the detachment of Chromium(VI) from the treated soil. So desorption was increased on increasing temperature and that increase in percentage desorption with temperature also shows that the desorption process is exothermic. Results were in good agreement with the results reported by earlier researchers [56, 57].

5.3.4 Effect of Variation of NaOH Concentration

Desorption of Chromium(VI) from enriched soil was conducted with different concentration of NaOH. Results are given in **Table 5.4** and **Figure 5.4**. It was found that Chromium(VI) desorption was 29.31%, 30.60% and 32.33% with 0.05 M, 0.1 M and 0.5 M NaOH respectively.

Adsorption of solute on any adsorbent can either be by physical bonding, ion-exchange or combination of both. If the adsorption is by physical bonding then the loosely bound solute can be easily desorbed with distilled water in most of the cases. However, if the mode of adsorption is by chemical bonding or ion-exchange or combination of the both, then the desorption can be effected by stronger desorbents like acid or alkali solutions. On the basis of these facts the results of desorption of Chromium(VI) by NaOH suggest either chemisorption or ion-exchange as the possible mechanism of Chromium(VI) adsorption onto soil. From the results of desorption studies, the following inference was made:

The highest percent desorption of Chromium(VI) with NaOH indicates that the phenomenon are consistent with the results observed for the effect of pH of solution for adsorption. At high strength of NaOH solution, the abundance of hydroxide ions (-OH) increased competition between Chromium(VI) anions and hydroxide ions for the adsorption at surface of soil, So detachment of the Chromium(VI) anions was increased from the surface of soil.

Table 5.3: Influence of variation of Temperature on desorption of Cr(VI) $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; pH = 7; particle size = 100BSS mesh.

Temperature (^{o}C)	30		35		40		45		50	
Time, min.	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$
0	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00
2	0.200	8.62	0.220	9.48	0.230	9.91	0.240	10.34	0.260	11.21
4	0.240	10.34	0.270	11.64	0.290	12.50	0.300	12.93	0.330	14.22
6	0.290	12.50	0.320	13.79	0.350	15.09	0.380	16.38	0.420	18.10
8	0.340	14.66	0.370	15.95	0.400	17.24	0.440	18.97	0.480	20.69
10	0.390	16.81	0.420	18.10	0.450	19.40	0.500	21.55	0.570	24.57
12	0.450	19.40	0.480	20.69	0.520	22.41	0.560	24.14	0.630	27.16
14	0.520	22.41	0.540	23.28	0.580	25.00	0.620	26.72	0.700	30.17
16	0.580	25.00	0.600	25.86	0.640	27.59	0.680	29.31	0.740	31.90
18	0.610	26.29	0.640	27.59	0.680	29.31	0.720	31.03	0.780	33.62
20	0.610	26.29	0.640	27.59	0.680	29.31	0.720	31.03	0.780	33.62
∞	0.610	26.29	0.640	27.59	0.680	29.31	0.720	31.03	0.780	33.62

$[Cr]_{de}$ - Desorption of Cr(VI); % $[Cr]_{de}$ - Percentage Desorption of Cr(VI); $[Cr]_{Ad}$ =Adsorbed amount of Cr(VI);

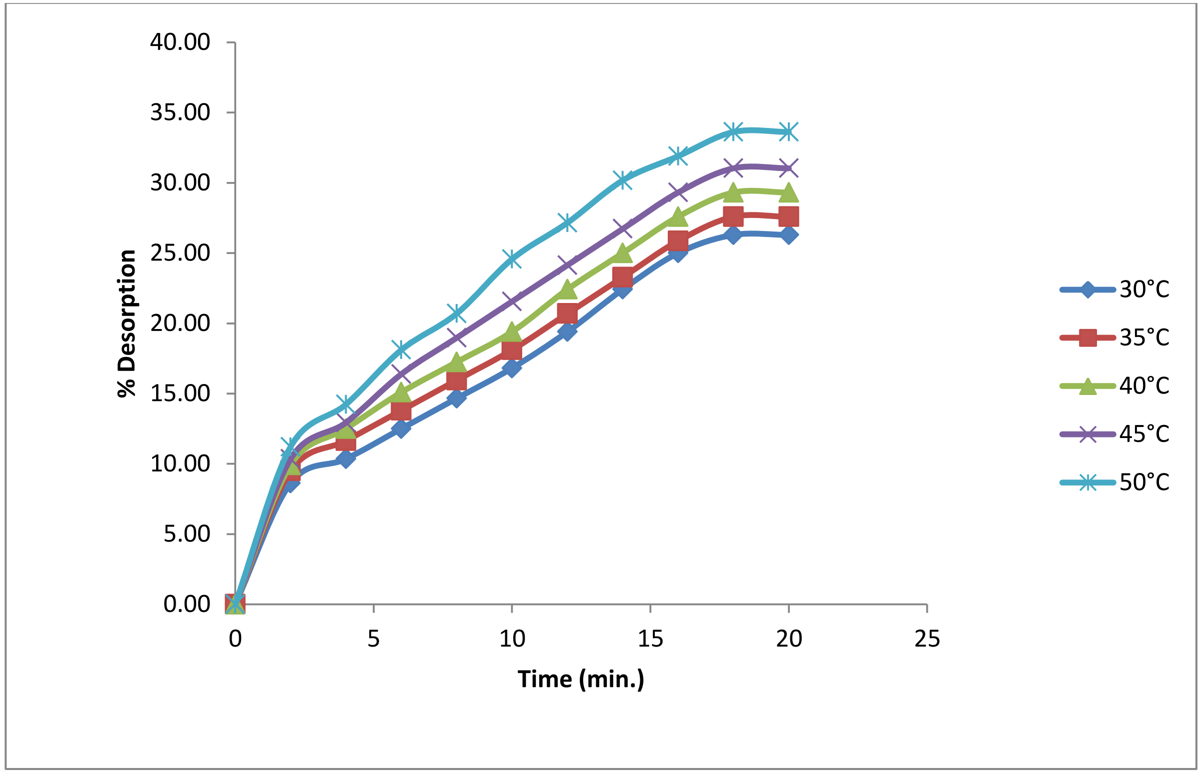

Figure 5.3: Influence of variation of Temperature on desorption of Cr (VI) $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; pH = 7; particle size = 100BSS mesh.

Table 5.4: Influence of variation of NaOH conc. on desorption of Cr(VI) $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; particle size = 100BSS mesh; temp. = 30°C.

NaOH conc.	0.05 M		0.1 M		0.5 M	
Time, min.	**$[Cr]_{de}$**	**%$[Cr]_{de}$**	**$[Cr]_{de}$**	**%$[Cr]_{de}$**	**$[Cr]_{de}$**	**% $[Cr]_{de}$**
0	**0.000**	**0.00**	**0.000**	**0.00**	**0.000**	**0.00**
2	**0.220**	**9.48**	**0.230**	**9.91**	**0.250**	**10.78**
4	**0.270**	**11.64**	**0.290**	**12.50**	**0.310**	**13.36**
6	**0.330**	**14.22**	**0.360**	**15.52**	**0.380**	**16.38**
8	**0.380**	**16.38**	**0.400**	**17.24**	**0.430**	**18.53**
10	**0.420**	**18.10**	**0.440**	**18.97**	**0.480**	**20.69**
12	**0.500**	**21.55**	**0.550**	**23.71**	**0.580**	**25.00**
14	**0.590**	**25.43**	**0.620**	**26.72**	**0.640**	**27.59**
16	**0.630**	**27.16**	**0.650**	**28.02**	**0.690**	**29.74**
18	**0.680**	**29.31**	**0.710**	**30.60**	**0.750**	**32.33**
20	**0.680**	**29.31**	**0.710**	**30.60**	**0.750**	**32.33**
∞	**0.680**	**29.31**	**0.710**	**30.60**	**0.750**	**32.33**

$[Cr]_{de}$ - Desorption of Cr(VI); % $[Cr]_{de}$ - Percentage Desorption of Cr(VI); $[Cr]_{Ad}$ =Adsorbed amount of Cr(VI);

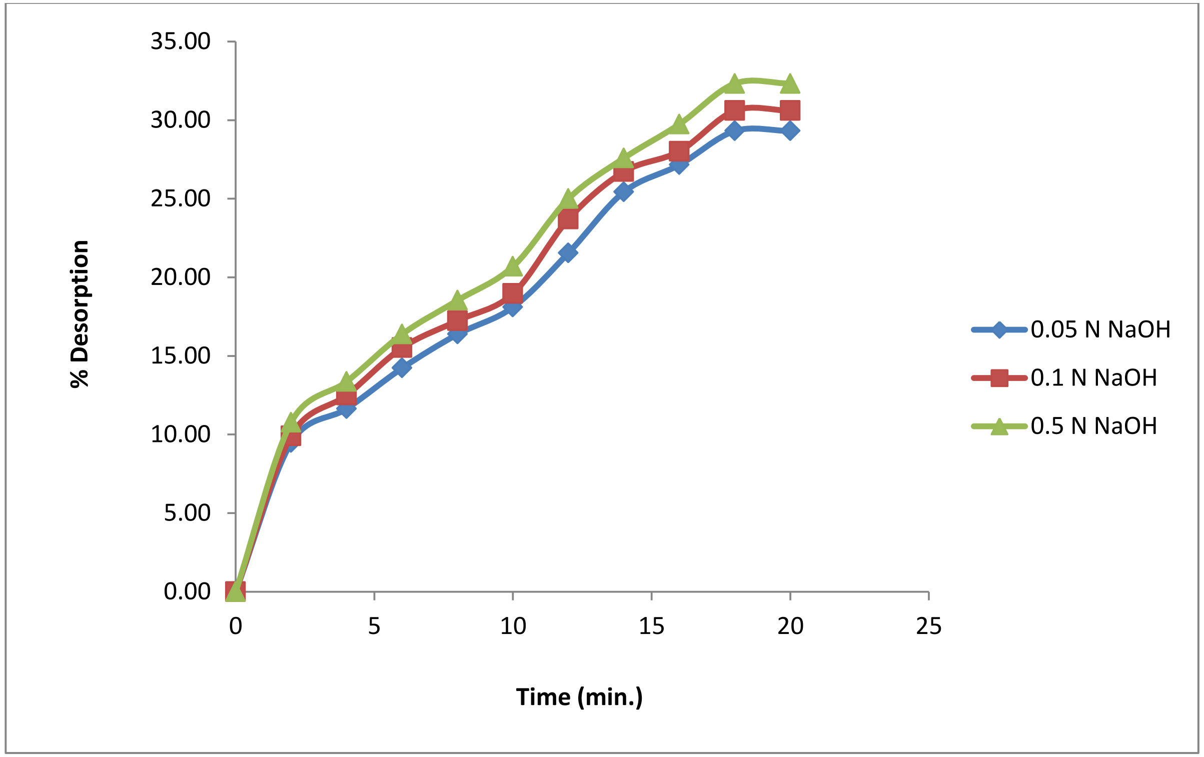

Figure 5.4: Influence of variation of NaOH conc. on desorption of Cr(VI) $[S_1]_{0\text{-}15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; particle size = 100BSS mesh; temp. = 30°C.

It was observed that complete desorption of Chromium(VI) from the surface of soil was not possible even at high alkali or acid concentration. The incomplete desorption was also attributed to the non homogeneity of the soil and the presence of impurities which may also act as an adsorbent for Chromium(VI). Similar results were observed in previous studies [58, 59].

5.3.5 Effect of Variation of EDTA Concentration

It is apparent from **Table 5.5** and **Figure 5.5**, that EDTA application for Chromium(VI) extraction showed good results and maximum percentage desorption was observed by 0.1 M concentration of EDTA among all the applied four different concentrations of EDTA. On increasing concentration of EDTA from 0.005 M to 0.1 M percentage desorption also increases from 32.76% to 40.52%.

In chelant-assisted metal extraction the ratio of chelant to metal is factor of primary importance. This ratio is calculated from the concentration and volume of chelating agent and the mass of soil [61, 62], The higher the ratio, the more uncomplexed ligand is present in the extraction solution and the faster and more complete is the extraction. The major cations in the soil such as mangnese, magnesium, iron, and calcium present in smaller amounts competes with Chromium(VI) being studied for the chelating agent and are extracted too. So it was the reason of an excess of chelating agent was needed for extraction of Chromium(VI). Hence it is concluded that the application of EDTA to the contaminated soil increased the levels of desorbed Chromium(VI) as has been reported in previous studies [63-67] and the addition of EDTA to contaminated soil increases the soluble or exchangeable fraction of Chromium(VI) in the soil solution.

5.3.6 Effect of Variation of Incubation Time

It is observed from **Table 5.6** and **Figure 5.6**, that maximum Chromium(VI) percentage desorption (50.09%) was obtained at 120 hr or day 5 at 0.1 M EDTA concentration. At 120 and 96 hr better results were observed for the applied concentration of EDTA. But at 72 hr a slight declined was noticed. It was

Table 5.5: Influence of variation of EDTA conc. on desorption of Cr(VI) $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; particle size = 100BSS mesh; temp. = 30°C.

EDTA conc.	0.005 M		0.01 M		0.05 M		0.1 M	
Time, min.	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$
0	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00
2	0.250	10.78	0.280	12.07	0.300	12.93	0.330	14.22
4	0.320	13.79	0.350	15.09	0.380	16.38	0.420	18.10
6	0.380	16.38	0.420	18.10	0.460	19.83	0.500	21.55
8	0.460	19.83	0.480	20.69	0.540	23.28	0.580	25.00
10	0.530	22.84	0.550	23.71	0.640	27.59	0.670	28.88
12	0.600	25.86	0.630	27.16	0.720	31.03	0.760	32.76
14	0.670	28.88	0.690	29.74	0.790	34.05	0.830	35.78
16	0.720	31.03	0.750	32.33	0.880	37.93	0.900	38.79
18	0.760	32.76	0.820	35.34	0.880	37.93	0.940	40.52
20	0.760	32.76	0.820	35.34	0.880	37.93	0.940	40.52
∞	0.760	32.76	0.820	35.34	0.880	37.93	0.940	40.52

$[Cr]_{de}$ - Desorption of Cr(VI); % $[Cr]_{de}$ - Percentage Desorption of Cr(VI); $[Cr]_{Ad}$ =Adsorbed amount of Cr(VI);

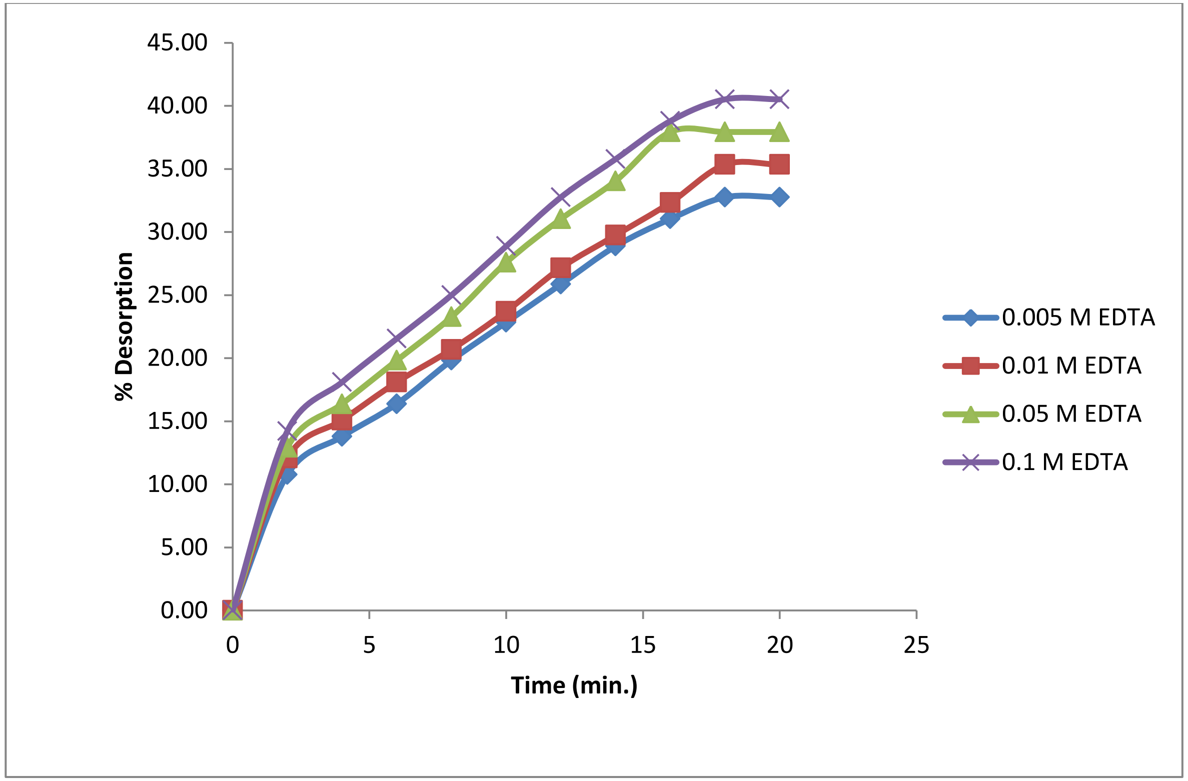

Figure 5.5: Influence of variation of EDTA conc. on desorption of Cr(VI) $[S_1]_{0\text{-}15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; particle size = 100BSS mesh; temp = 30^{o}C.

Table 5.6: Influence of variation of incubation period on desorption of Cr(VI) $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; EDTA conc. = 0.1 M; particle size = 100BSS mesh; temp. = 30°C.

Incubation period of EDTA (hr.)	1		24		48		72		96		120	
Time, min.	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$	$[Cr]_{de}$	% $[Cr]_{de}$
0	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00
2	0.330	14.22	0.350	15.09	0.380	16.38	0.410	17.67	0.420	18.10	0.425	18.32
4	0.420	18.10	0.450	19.40	0.490	21.12	0.510	21.98	0.520	22.41	0.526	22.67
6	0.500	21.55	0.540	23.28	0.560	24.14	0.590	25.43	0.610	26.29	0.618	26.64
8	0.580	25.00	0.620	26.72	0.650	28.02	0.680	29.31	0.690	29.74	0.700	30.17
10	0.670	28.88	0.690	29.74	0.730	31.47	0.750	32.33	0.760	32.76	0.770	33.19
12	0.760	32.76	0.790	34.05	0.810	34.91	0.830	35.78	0.840	36.21	0.850	36.64
14	0.830	35.78	0.860	37.07	0.880	37.93	0.910	39.22	0.950	40.95	0.965	41.59
16	0.900	38.79	0.930	40.09	0.960	41.38	0.980	42.24	1.050	45.26	1.065	45.91
18	0.940	40.52	1.000	43.10	1.070	46.12	1.130	48.71	1.150	49.57	1.162	50.09
20	0.940	40.52	1.000	43.10	1.070	46.12	1.130	48.71	1.150	49.57	1.162	50.09
∞	0.940	40.52	1.000	43.10	1.070	46.12	1.130	48.71	1.150	49.57	1.162	50.09

$[Cr]_{de}$ - Desorption of Cr(VI); % $[Cr]_{de}$ - Percentage Desorption of Cr(VI); $[Cr]_{Ad}$ =Adsorbed amount of Cr(VI);

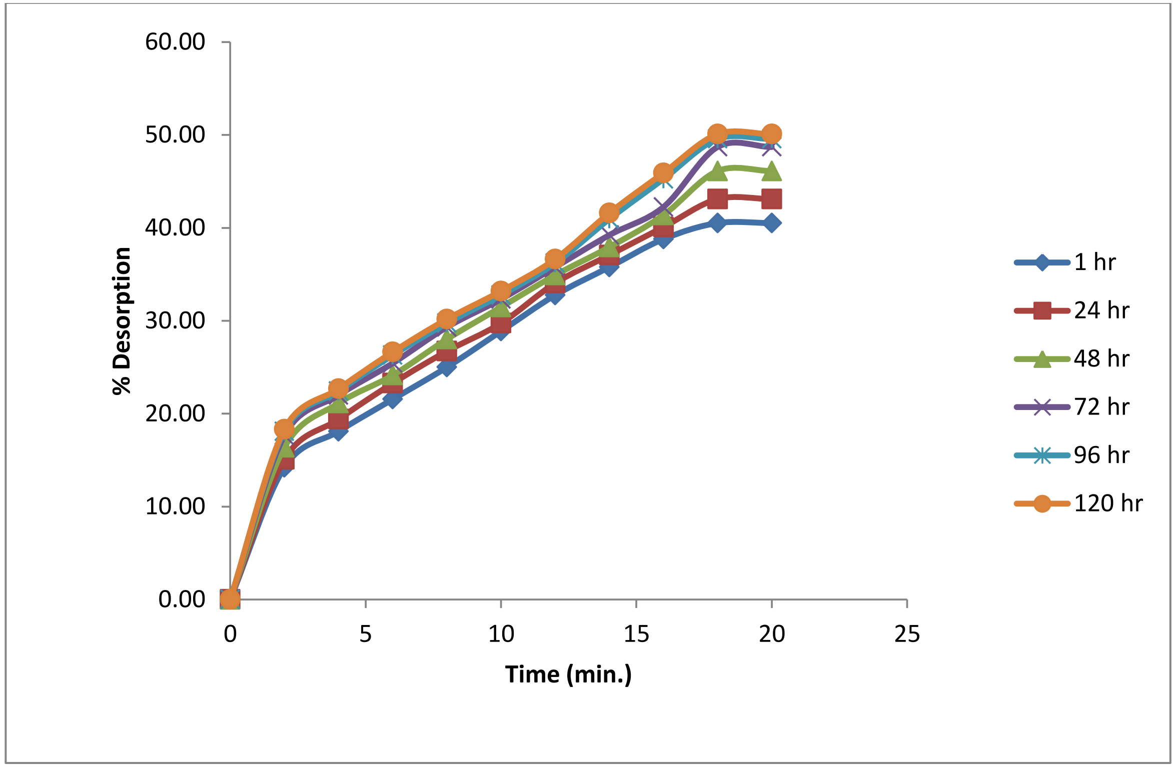

Figure 5.6: Influence of variation of incubation period on desorption of Cr(VI) $[S_1]_{0\text{-}15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; EDTA conc. = 0.1 M; particle size = 100BSS mesh; temp. = 30^oC.

observed that Chromium(VI) percentage desorption continuously increased from 40.52% to 50.09% for 1 hr to 120 hr respectively.

A consistency was observed in the data shows that effective chelation was observed at 96 hr and 120 hr. It was investigated in past study that there are two steps involved in the mobilization of metals: a fast step and a slow step [68]. In the present study Chromium(VI) with 0.1 M EDTA concentration was more solubilized in the fast step, which was the fraction of Chromium(VI) in exchangeable and slightly adsorbed form. The Chromium(VI), which was somewhat less available or mobile and in bounded form with other metals, the chelation of this fraction of Chromium(VI) was occurred in slow step. This would serve as a valid explanation as to why at 96 hr (4 day) and 120 hr (5 day) of treatment, rather than at other time period most active chelation took place, because metals were being extracted from the storage of accessible metals for the limited period, after which the metals could no longer be available.

Maximum concentration of Chromium(VI) was extracted by 0.1 M EDTA at 20 min shacking time and for incubation experiment day 5 (120 hrs). After the application of EDTA the significant amount of soluble fraction of Chromium(VI) was observed in the soil solution from 1 hr to 120 hr, indicates that solubilizing effect of EDTA did not decrease with time and it was due to its high environmental persistence. Similar results were reported in literature by earlier researchers [69, 70].

5.3.7 Effect of Variation of pH of EDTA Solution

It is apparent from the results given in **Table 5.7** and **Figure 5.7** that in the extraction tests performed with EDTA, the maximum Chromium extraction (46.98%) at the end of the experiment was observed at pH = 10, while at pH = 5 and 7 the performances were found to be quite similar.

It was observed that the extraction efficiency of EDTA was strongly affected by pH. At low pH the high concentration of hydrogen ions competes with Chromium(VI) for solubilization by EDTA, thus amount of free EDTA was decreased in the solution, So at pH 5 percentage desorption of Chromium(VI) is less in comparison of pH 10.

Table 5.7: Influence of variation of pH with EDTA on desorption of Cr(VI) $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; EDTA conc. = 0.1 M; particle size = 100BSS mesh; temp. = 30^{o}C.

EDTA solution pH	**pH = 5**		**pH = 7**		**pH = 10**	
Time, min.	**$[Cr]_{de}$**	**% $[Cr]_{de}$**	**$[Cr]_{de}$**	**% $[Cr]_{de}$**	**$[Cr]_{de}$**	**% $[Cr]_{de}$**
0	**s**	**0.00**	**0.000**	**0.00**	**0.000**	**0.00**
2	**0.310**	**13.36**	**0.330**	**14.22**	**0.350**	**15.09**
4	**0.390**	**16.81**	**0.420**	**18.10**	**0.480**	**20.69**
6	**0.460**	**19.83**	**0.500**	**21.55**	**0.600**	**25.86**
8	**0.540**	**23.28**	**0.580**	**25.00**	**0.680**	**29.31**
10	**0.620**	**26.72**	**0.670**	**28.88**	**0.770**	**33.19**
12	**0.710**	**30.60**	**0.760**	**32.76**	**0.880**	**37.93**
14	**0.780**	**33.62**	**0.830**	**35.78**	**0.950**	**40.95**
16	**0.850**	**36.64**	**0.900**	**38.79**	**1.020**	**43.97**
18	**0.870**	**37.50**	**0.940**	**40.52**	**1.090**	**46.98**
20	**0.870**	**37.50**	**0.940**	**40.52**	**1.090**	**46.98**
∞	**0.870**	**37.50**	**0.940**	**40.52**	**1.090**	**46.98**

$[Cr]_{de}$ - Desorption of Cr(VI); % $[Cr]_{de}$ - Percentage Desorption of Cr(VI); $[Cr]_{Ad}$ =Adsorbed amount of Cr(VI);

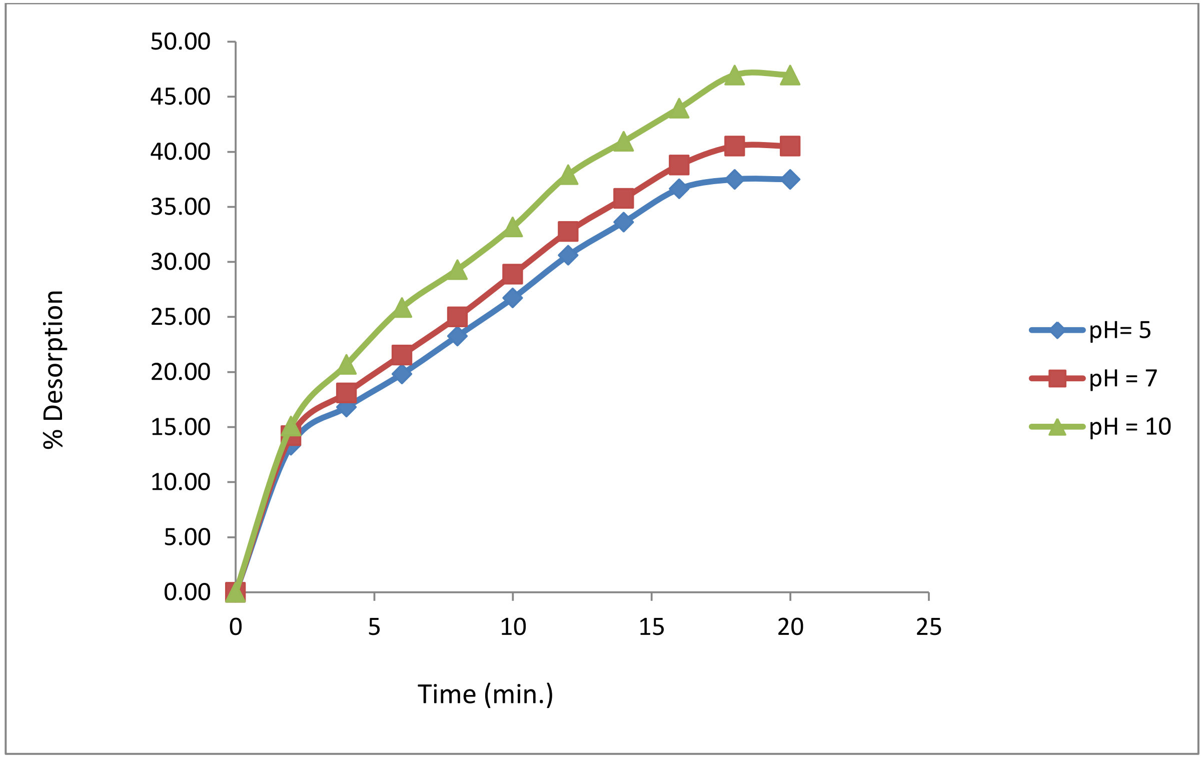

Figure 5.7: Influence of variation of pH with EDTA on desorption of Cr(VI) $[S_1]_{0-15}$ = 2 g; $[Cr]_{Ad}$ = 2.32 mg; EDTA conc. = 0.1 M; particle size = 100BSS mesh; temp. = 30°C.

The soluble Chromium(VI) was reduced to less soluble Chromium(III) under acidic condition, so mobility and availability of Chromium(VI) usually decreased under acidic conditions [71]. This fact favors the highest percentage desorption at alkaline conditions. Results were in accordance to previous study [72].

5.4 Kinetic Study of Desorption

The mobility of a compound in soil can be assessed from desorption studies. The selection of treatment technique is based on its availability in the liquid phase. Desorption kinetic study was conducted to determine the Chromium(VI) availability in the liquid phase with respect to time.

5.4.1 Application to the Kinetic Models

The experimental data of desorption of Chromium(VI) from different Chromium(VI) enriched soil samples were applied on the seven different Kinetic models. All the kinetic models were described in **Chapter 4** in **Section 4.5** in detailed and the linearized equations are given below:

Zero order kinetic model	$C_o - C_t = a - bt$	(5.2)
First order kinetic model	$\ln(C_o - C_t) = a - bt$	(5.3)
Second order kinetic model	$\frac{1}{C_t} = \frac{1}{C_o} + kt$	(5.4)
Pseudo first order kinetic model	$\log(q_e - q_t) = \log(q_e) - \frac{k_{ad}t}{2.303}$	(5.5)
Pseudo second order kinetic model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	(5.6)
Parabolic diffusion model	$q_t = K_{id} t^{1/2} + C$	(5.7)
Elovich Equation	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	(5.8)

The concentration terms used in different equations are as follows-

C_o = initial Chromium(VI) concentration in the reaction suspension

C_t = desorbed Chromium(VI) concentration at time t

C_e = desorbed Chromium(VI) concentration at equilibrium

Q_t = The amount of Chromium(VI) desorbed at time t, which is equal to C_t in the study

Q_e = The amount of Chromium(VI) desorbed at equilibrium, which is equal to C_e in the study

All the models were tested with least squares regression analysis.

Table 5.8 shows coefficient of determination (R^2), standard error of estimate (SEE), and slope for graphical equations of different kinetic models applied on desorption of Chromium(VI) from different prepared Chromium(VI) enriched soil samples at 30°C. On the basis of high value of R^2 and low SEE the most favorable model selected for the present study is second order kinetic model. The average value of R^2 and SEE of all seven kinetic model is shown in **Table 5.9**. Equation of second order model is plotted in **Figure 5.10** while model with deviation are plotted in **Figure 5.8, 5.9** and **5.11** to **5.14**.

On the basis of average value of R^2 and SEE, desorption data was correlated to the kinetic models in the order; second order > zero order > intraparticle diffusion > first order > pseudo first order > Elovich equation > pseudo second order. The rate constant also calculated for Pseudo first order, Pseudo second order, Intraparticle diffusion model and Elovich Equation (**Table 5.10**). It was observed that for intraparticle diffusion model rate of desorption increases as the concentration of prepared Chromium(VI) enriched soil sample increases. So the intraparticle diffusion model is also in good agreement with experimental data.

Conformity to intraparticle diffusion suggested that the process of Chromium(VI) desorption by the soil was diffusion controlled and either intraparticle diffusion or surface diffusion is the rate limiting. Transport of the desorbing ion was through the liquid associated with exchange sites of the desorbing ion along the less accessible space of the adsorbent, then it follows the intraparticle diffusion process, otherwise in determination of the desorption velocity by particle resistance, surface diffusion is generally the rate controlling mechanism [73-75].

The discontinuity in the slope of second order plot for 0.34 mg (**Figure 5.10**), suggests that Chromium(VI) desorbed from a heterogeneous surface with more than one kind of adsorptive sites which have different adsorptive properties [76].

Table 5.8: Coefficient of determination (R^2), standard error of estimation (SEE) and slope for graphical equations of different kinetic models applied on desorption of Cr(VI) by varying initial Cr (VI) conc., $[S_1]_{0-15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C; [Cr(VI)] = 0.34 mg, 0.56 mg, 1.07 mg, 1.46 mg and 2.32 mg.

Kinetic model $[Cr]_{Ad}$ mg		Zero Order	First Order	Second Order	Pseudo First Order	Pseudo Second Order	Intraparticle Diffusion	Elovich Equation
0.34	R^2	0.9648	0.9060	0.9498	0.9167	0.8997	0.9626	0.9063
	SEE	0.0040	0.2514	0.0235	0.1348	31.7252	0.0023	0.0036
	Slope	-0.0034	0.1215	0.0159	-0.1069	14.7961	0.0108	0.0144
0.56	R^2	0.9684	0.9010	0.9553	0.8939	0.8817	0.9548	0.8846
	SEE	0.0040	0.2594	0.0086	0.1472	18.1670	0.0047	0.0076
	Slope	-0.0034	9.5300	0.0062	-0.1022	7.7208	0.0205	0.0270
1.07	R^2	0.9511	0.8913	0.9712	0.8377	0.6741	0.9321	0.8555
	SEE	0.0149	0.2662	0.0035	0.1888	10.1345	0.0176	0.0256
	Slope	-0.0102	0.1187	0.0032	-0.1025	2.2693	0.0613	0.0803
1.46	R^2	0.9638	0.8837	0.9841	0.8923	0.6802	0.9415	0.8612
	SEE	0.0203	0.2617	0.0013	0.1416	6.0943	0.0259	0.0398
	Slope	-0.0163	0.1123	0.0016	-0.0974	1.3837	0.976	0.1276
2.32	R^2	0.9844	0.9212	0.9479	0.9644	0.8798	0.9694	0.8995
	SEE	0.0204	0.2617	0.0018	0.0739	2.4507	0.0286	0.0518
	Slope	-0.0252	0.1393	0.0012	-0.0919	1.0323	0.1514	0.1993

Table 5.9: The average value of Coefficient of determination (R^2) and standard error of estimation (SEE) for graphical equations of different kinetic models applied on desorption of Cr(VI) by varying initial Cr(VI) conc., $[S_1]_{0\text{-}15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C [Cr(VI)] = 0.34 mg, 0.56 mg, 1.07 mg, 1.46 mg and 2.32 mg.

Kinetic model	Average Value of R^2	Standard error of estimation (SEE)
Zero Order	**0.9672**	**0.0127**
First Order	**0.9006**	**0.2601**
Second Order	**0.9617**	**0.0077**
Pseudo First Order	**0.9010**	**0.1373**
Pseudo second Order	**0.8031**	**13.7143**
Intraparticle diffusion model	**0.9521**	**0.0158**
Elovich Equation	**0.8814**	**0.0257**

Table 5.10: Kinetic parameters of different kinetic models applied on desorption of Cr(VI) by varying initial Cr(VI) conc., $[S_1]_{0\text{-}15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30^{o}C; [Cr(VI)] = 0.34 mg, 0.56 mg, 1.07 mg, 1.46 mg and 2.32 mg.

Kinetic model	Cr(VI) mg	0.34	0.56	1.07	1.42	2.32
Pseudo First Order	K_{ad} (min^{-1})	0.246	0.235	0.236	0.224	0.212
	q_e (mg g^{-1})	0.001	0.002	0.031	0.086	0.231
Pseudo Second Order	K_2 (g mg^{-1} min^{-1})	1.401	0.751	0.117	0.066	0.084
	$q_{e\ (cal)}$ (mg g^{-1})	0.068	0.130	0.441	0.723	0.969
	h (mg g^{-1} min^{-1})	0.006	0.013	0.023	0.035	0.079
Intraparticle Diffusion	K_{id} (mg g^{-1}min$^{-1/2}$)	0.011	0.021	0.061	0.098	0.151
	C (mg g^{-1})	-0.003	-0.003	-0.045	-0.076	-0.058
Elovich Equation	ln α (mg·g^{-1}·min^{-1})	-4.233	-3.526	-2.863	-2.426	-1.694
	β (g·mg^{-1})	69.598	37.055	12.458	7.836	5.017

$q_{e\ (cal)}$ = Calculated desorbed amount of Cr(VI) (mg/g);

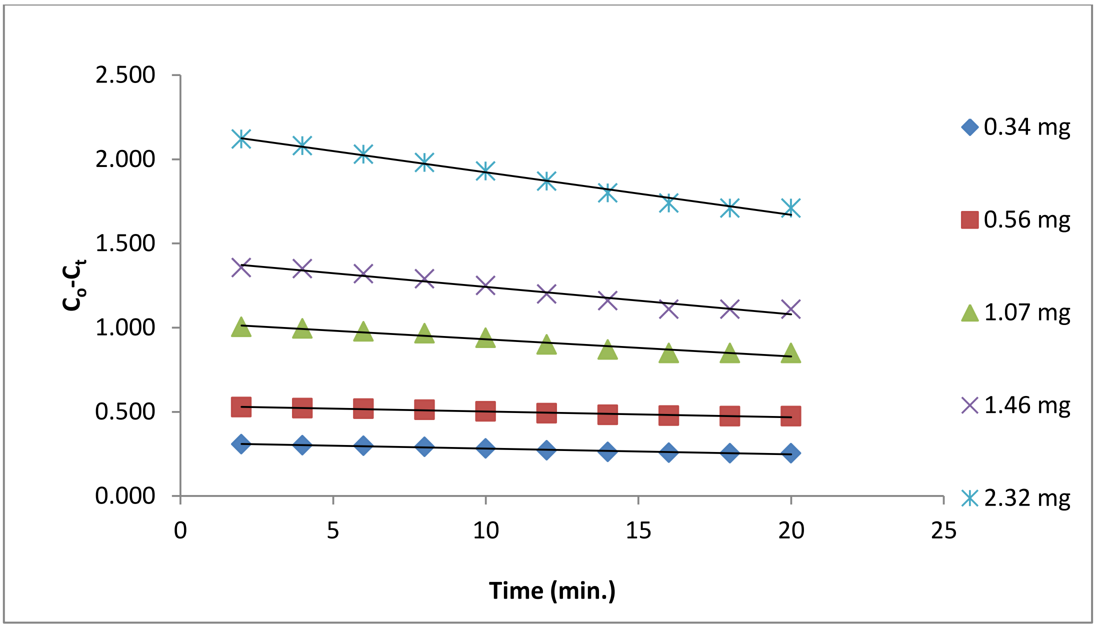

Figure 5.8: Zero order kinetic plots for desorption of Cr(VI). $[S_1]_{0-15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C.

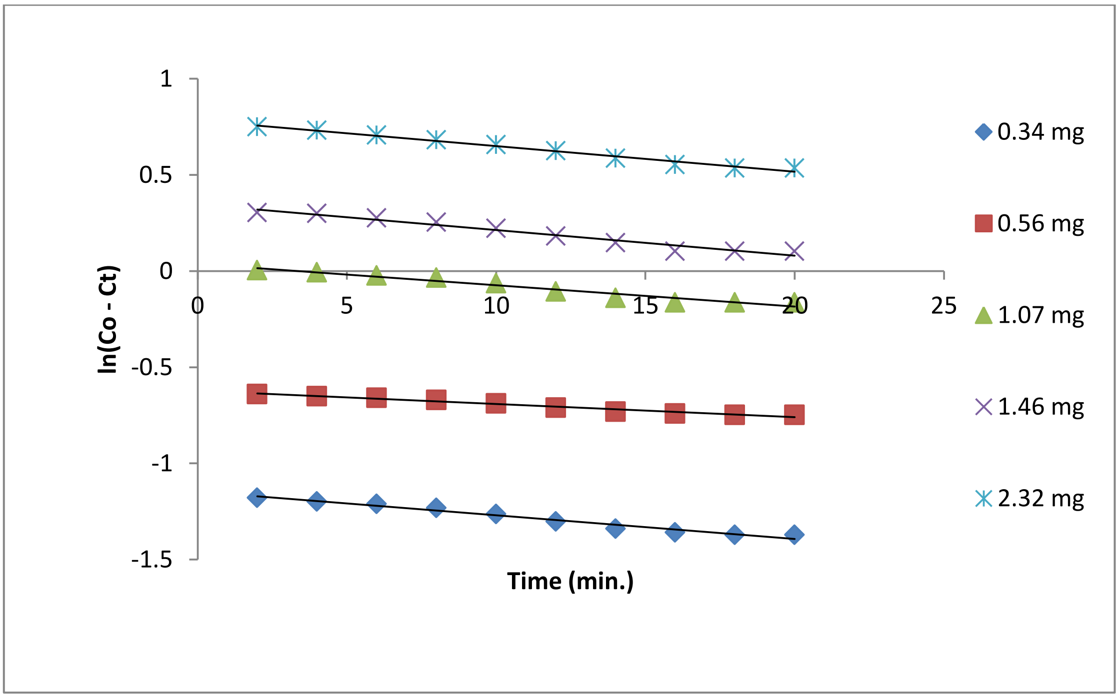

Figure 5.9: First order kinetic plots for desorption of Cr(VI). $[S_1]_{0-15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C.

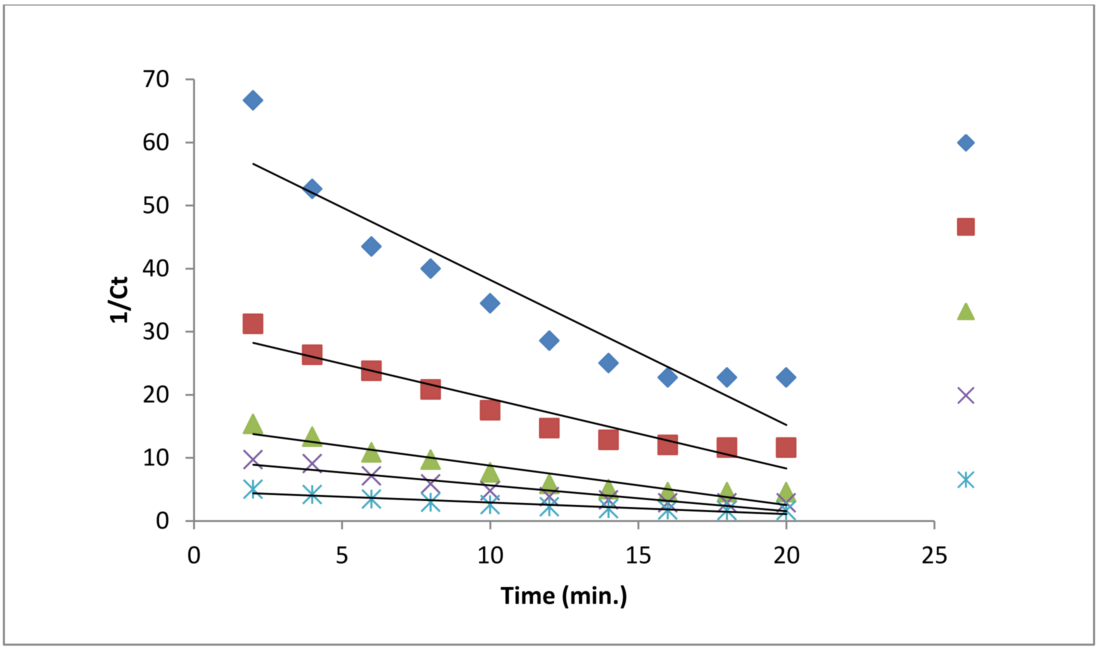

Figure 5.10: Second order kinetic plots for desorption of Cr(VI). $[S_1]_{0\text{-}15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C.

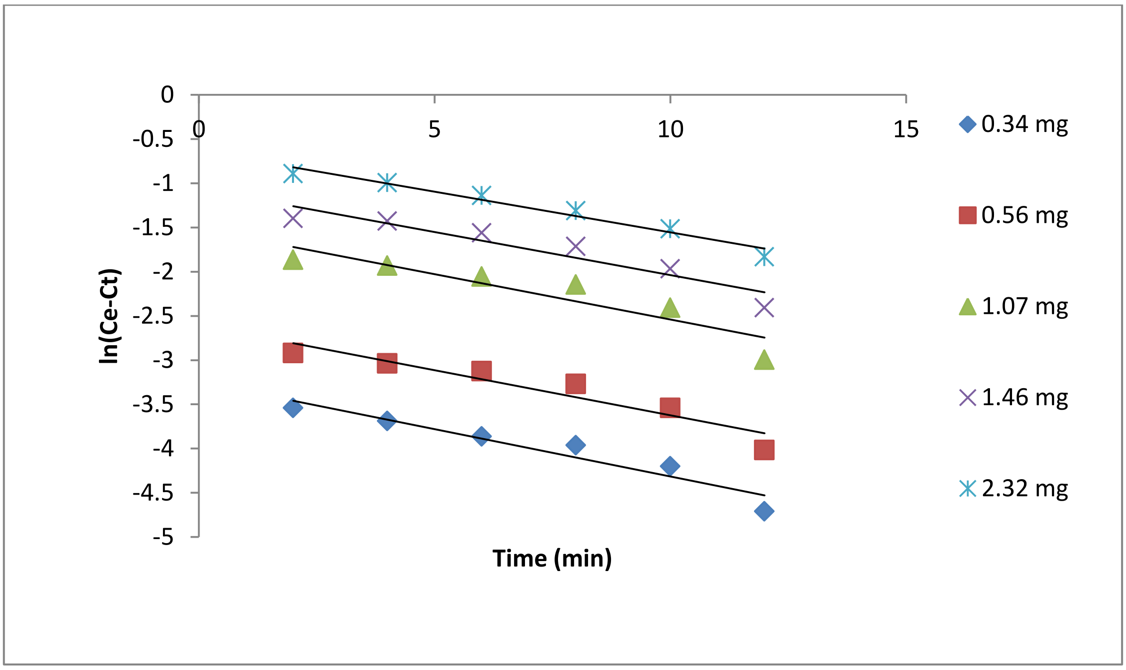

Figure 5.11: Pseudo first order kinetic plots for desorption of Cr(VI). $[S_1]_{0\text{-}15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C.

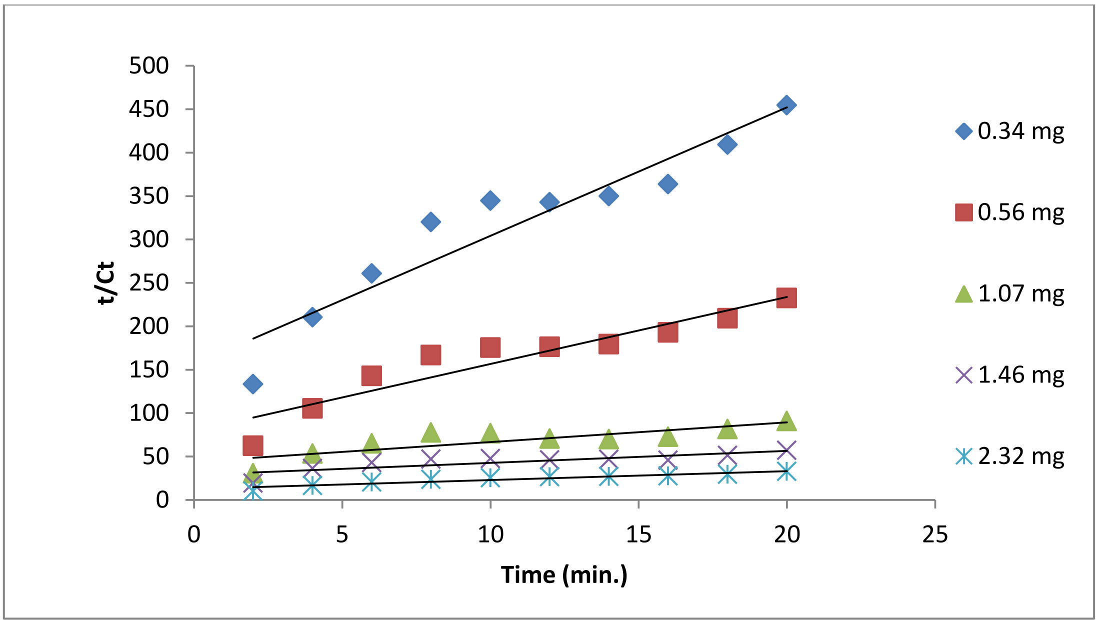

Figure 5.12: Pseudo second order kinetic plots for desorption of Cr(VI). $[S_1]_{0-15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C.

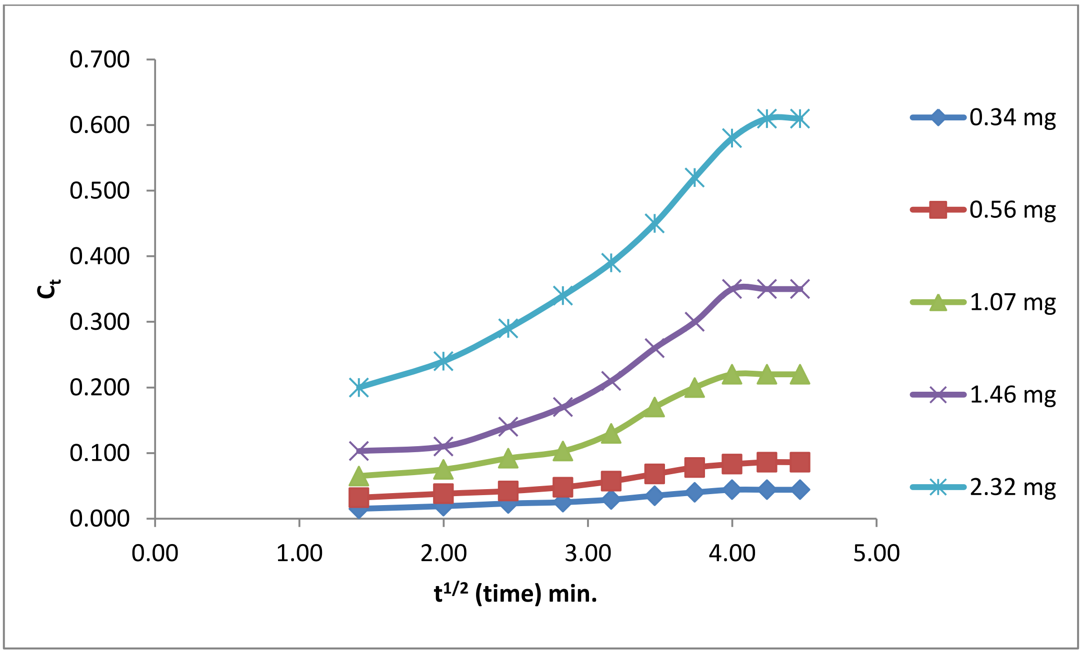

Figure 5.13: Intraparticle diffusion kinetic plots for desorption of Cr(VI). $[S_1]_{0-15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30°C.

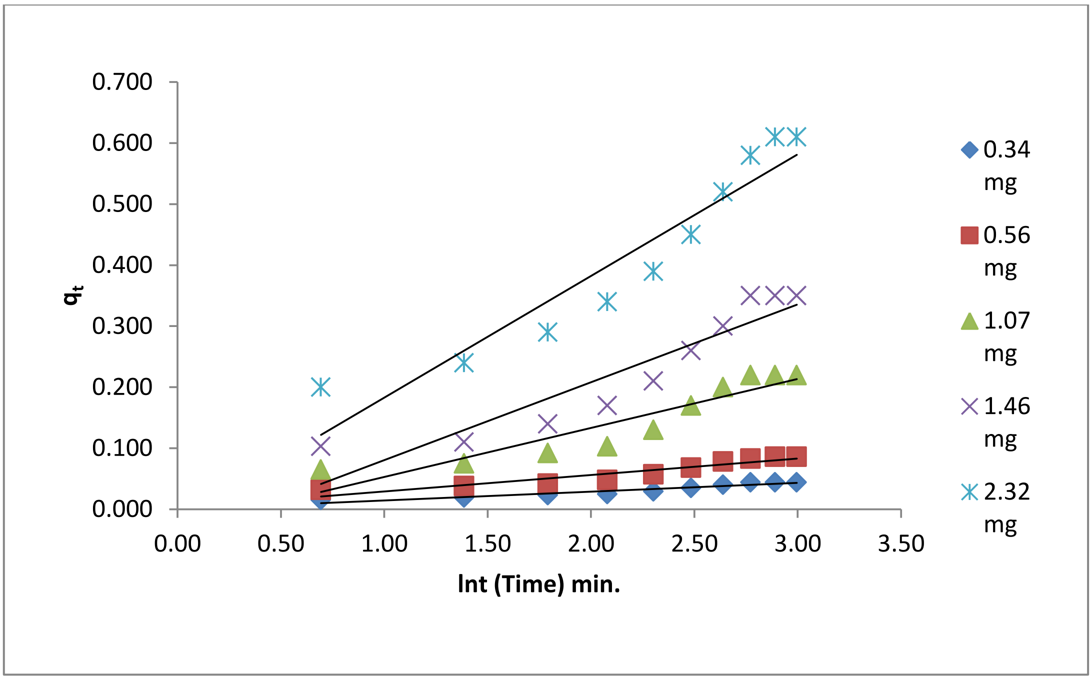

Figure 5.14: Elovich equation kinetic plots for desorption of Cr(VI). [S_1] $_{0\text{-}15}$ = 2 g; solution pH = 7; particle size = 100BSS mesh; temp. = 30^{o}C.

5.5 Conclusion

It is concluded from the desorption studies that desorption increases on increasing initial Chromium(VI) concentration due to physical bonding of Chromium(VI) onto the soil. Like adsorption desorption is also pH dependent. On decreasing pH desorption decreases because of attraction of positively charged soil surface and negatively charged Chromium(VI) species. With increasing temperature desorption also increases due to increasing of particle movements. On increasing strength of extractant NaOH, desorption increases, so it may be concluded that desorption occur via ion exchange. Among the NaOH and EDTA, EDTA is best extractant, because it has ability to form water soluble complexes. By increasing concentration of EDTA and incubation time desorption increases. The extraction efficiency also strongly affected by the pH of solution and maximum desorption with EDTA was observed at pH 10. The experimental data of desorption of Chromium(VI) were applied on the seven different Kinetic models and on the basis of Coefficient of determination (R^2) and standard error of estimation (σ) , second order kinetic model was found best fitted in present study. Rate of desorption increases on increasing concentration of Chromium(VI) on enriched soil sample for intraparticle diffusion model, so intraparticle diffusion model also fits in the present system. The results of study can be used for remediation of Chromium(VI) contaminated soil, preferably in Bhilwara industrial area in Rajasthan and elsewhere in the world.

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ANNEXURE – I

LIST OF PAPERS PUBLISHED: 3

1. "Batch Sorption Study of Chromium (VI) on Dye Contaminated Soil", **Priya Vijayvergiya**, Shweta Saxena, International Journal of Innovative Research in Science, Engineering and Technology, 3(8), 15425-15430, 2014.
2. "Leaching Kinetics of Flouride from Flouride Contaminated Soil of Sambhar Region by Loading Magnesium Flouride Salt", Shweta Saxena, **Priya Vijayvergiya**, International Journal of Basic and Applied Chemical Sciences, 4(2), 58-64, 2014.
3. "Study of sorption of Cr (VI) on the soil of industrial area of Bhilwara region", **Priya Vijayvergiya** and shweta Saxena, Proceeding of 3rd International Conference on "Advance Trends in Engineering, Technology and Research" ICATETR-2014; 22-24th, Dec 2014.

ANNEXURE – II

PARTICIPATION IN CONFERENCES, SEMINARS/SYMPOSIUM

1. Actively participated in a three day first Rajasthan Science Congress on New Frontiers of Science and Technology and Innovation for Development in Rajasthan, on May 11th – 13th, 2013, held at Tagore International School Campus Jaipur, Rajasthan.
2. Actively participated in the 5th National Academic Workshop on “Organic Reaction Mechanism and Analytical Techniques used in Chemical Sciences” held during October 21-25, 2013 in the Department and sponsored by the University Grants Comission, New Delhi.
3. Prsented research paper and poster in “National Conference on Global Environmental changes and Disaster Management for Sustainable life on Earth- A burning issue” held at Mahirshi Arvind College of Engineering & Technology, Ranpur, Kota on 21st October, 2013.
4. Actively participated in National Seminar on Pure & Applied Chemical Sciences (Current Trends & Future Prospects) in association with Indian Chemical Society, Kolkata, 2014, January 10-11, 2014 Organised by Department of Chemistry, Faculty of Science, Jai Narain Vyas University, Jodhpur (Rasjasthan) India.
5. Participated in National Seminar & Science Model Exhibition on “Innovations in Science & Technology for Inclusive Development” on 16th & 17th January, 2014.
6. Presented research paper in “3rd International Conference on Advanced Trends in Engineering, Technology and Research” Organized during December 22th – 24th, 2014 at Bal Krishna Institute of Technology, Kota, Rajasthan, India.