Determination and Removal of Hexavalent Chromium

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Abstract: *This study demonstrated the application of biomaterial for the removal of hexavalent chromium (Cr(VI)).in the primary work of this study; the determination of Cr(VI) in an aqueous solution was conducted by direct UV-visible spectro photometry. The effects of different parameters such as pH, contact time, adsorbent dose and initial concentration of an adsorbate on the adsorption of Cr(VI) were investigated. Equilibrium isotherm data were analyzed and indicated that adsorption process favored on Langmuir isotherm model. The adsorption kinetic data were described very well by the pseudo-second order model. The adsorption efficiency of biosorbent lignin on to Cr(VI) was found to be 99.23%. Therefore, lignin, which is an eco-friendly, low cost and ease of access adsorbent is expected to be feasible adsorbent for the removal of Cr(VI).*

Keywords: *determination, hexavalent chromium, Adsorption, Lignin*

1. Introduction

Chromium (Cr) is a grey, hard metal most commonly found in the trivalent state in nature. Whereas; Hexavalent chromium (Cr(VI)) compounds are also found in small quantities. Chromite ($FeOCr_2O_3$) is the only ore containing a significant amount of chromium. The ore has not been found in the pure form; its highest grade contains about 55% chromic oxide[1]. The metallic chromium is one of the heavy metal; naturally occurring element present in water, sediments, rocks, soils, plants, biota, animals, and volcanic emissions. It can be exists in a number of oxidation states, but only Cr^{6+} (toxic) and Cr^{3+} (less toxic) forms are biologically and environmentally stable[2].

In the Early history of metallic chromium, chromium (III) oxide as (Cr_2O_3)was used in ancient Chinese during the Qin Dynasty (259-210 B.C). They used the chromium oxide as metallic substance for coating of weapons (bronze cross bow, bolts and steel swards at terracotta army also called Terracotta Warriors and Horses)[3]. Later, it was found in a mineral known as

“***Siberian red lead***” which is a lead compound called Crocoite ($PbCrO_4$)[4, 5]. The Reddish yellow (Orangey) colored mineral (Siberian red lead) was first discovered on 26th July 1961; form Ural mountain (Russia) by German mineralogist Johann Gottlob Lehmann (1719-1767) [6]. Later on the French pharmacist and chemist: Louis-Nicolas Vauquelin (1763-1829) convinced that Siberian red was lead contained new metallic element called chromium. He found the trivalent chromium oxide (Cr_2O_3) from Crocoit and the obtained contaminated elemental chromium by reduction of Cr_2O_3 with charcoal[7]. The name of the element is derived from the Greek word "chroma" meaning color, because many of its compounds are intensely colored[7].

Regarding to the physical and chemical characteristics of elemental chromium lustrates that it is a transition metal belonging first upper column element on the group VIB and period 4 in modern periodic table. Chromium (Cr) with atomic number 24 has a molecular weight 51.996 g/mol and density 7.19 g/cm^3[5]. It is a silver (steel-gray) color, crystalline, lustrous, and hard metal; which takes a high polish and a high melting point[7]. Tannery and painting industrial effluents are major sources of chromium. Both are wet operations consuming large amounts of water, chemicals and energy with effluents producing large amounts of chrome polluted water[8].

1.1 Occurrence and Use of Chromium

Metallic chromium is the 21st most abundant element and 7th abundant metal in Earth's crust[6, 9]. It exists primarily in the mineral chromite; which is present in soils, waters, rocks, volcanic dust and gases. Concentration of chromium in soil varies from 1.0 to 3000 mg/kg, while, it existed as 0.005 to 0.8mg/Lin sea water and 2.6 to 5.2 mg/L in rivers and lakes respectively[10]. Chromate or Ferro chrome ($Cr(FeOCr_2O_3$or $FeCr_2O_4))$ is the most crucial mineral ore of metallic chromium. It can also be found as outcome of both marine and terrestrial volcanic eruption. Hence, both the natural processes and anthropogenic emissions contribute to the presence of chromium in aquatic systems. For instance, Weathering of rocks and soil erosion and leaching by rainwater are major natural processes favoring the input of chromium to rivers, lakes, estuaries, and ocean[11].

In acidic soils (pH<4) it is $Cr(H_2O)_6^{3+}$, whereas at pH<5.5 is its hydrolysis products, mainly $CrOH^{2+}_{(aq)}$[12]; both these forms are easily absorbed by macro-molecular soil component (e.g. clay and humic acid) compounds. Moreover, through different processing, chromium occurs in several chemical species as follows[6];

Metallic chromium (Cr(0)):- which is mainly found in alloys, such as stainless steel and in chrome-plated objects.

Trivalent chromium (Cr(III)):- which exists in natural waters in hydrolyzed $Cr(H_2O)_4(OH)_2$ form and like complexes even adsorbed on colloidal matter.

Hexavalent chromium (Cr(VI):- found as chromate ion (CrO_4^{2-}), chromic acid ($HCrO_4^-$) or dichromate ions ($Cr_2O_7^{2-}$) depending on the pH of the medium; It occurs in a range of compounds used in industrial processes. Each ionic forms of chromium in the solution are always pH dependent. Hence, metallic chromium present as insoluble $Cr_2O_3.H_2O$ in soil and only a very small parts it may leached from soil[13].

Chromium has oxidation states ranging from -4 up to +6. But oxidation states−4, −3, −2, −1 and 0 are very rare and un stable; while the most stable forms in a large number of its compounds are chromium (III) and chromium (VI) oxidation states. Hence, Chromium metal can exist both in trivalent and hexavalent states abundantly in the environment. Though, the hexavalent chromium with its complexes has more than 500 times toxic than trivalent form and trivalent complexes. The solubility of Cr (III) compounds is sparingly soluble in water; while, the Cr (VI) compounds are readily soluble in water.

The Cr(VI) species has been got unique properties of corrosion resistance, hardening the materials and color formation. Therefore, in the findings a large number of applications in industries like chrome-plating, automobiles, steel and alloys, paints, leather tanning and ammunition factories. Especially from these painting and tannery industries a large amount of chromium effluents discharge.

The reduction of Cr(VI) to Cr(III) as well as Cr(0) can be done as a key process for recovery from chromium contaminated water and wastewater. Moreover, transition metal ions present in soil act as a catalyst in this reduction process. M^{n+} (II) present in soil particles acts as a key factor leading to the fast transformation of Cr(VI) to Cr(III). For instance, Fe ions in presence of light account for reduction of Cr(VI) to Cr(III) and Cr(0).

The role of Fe(II)/ Fe(III), which acts as a catalyst by shuttling electrons from dissolved organic matter (DOM) to Cr(VI), can be demonstrated through a series of reaction as shown in the (Figure 1.3); below. Similarly; in natural aquatic environments, the significant red-ox couples (reducing/oxidizing agents) are: H_2O/O_2, Fe (II)/Fe (III), Mn (II)/ Mn (IV), S^{2-}/ SO_4^{2-}, CH_4/CO_2[14].

Commonly the simultaneous red-ox reaction of chromium is the most noticeable fact of the chromium cycle. For instance, Cr(III) is oxidized into Cr(VI) in soils and sediments spontaneously with manganese oxide (MnO_2), While reduction of Cr(VI) to Cr(III) takes place through various oxidizing agents of the soil carbon compounds: some of the oxidation and reduction reactions are shown below for the flow of chromium cycle[15].

$$Cr^{3+} + 1.5MnO_2 + H_2O \rightarrow HCrO_4^- + 1.5\, Mn^{2+} + H^+ \quad \text{(1)}$$

$$C_6H_6O_2 + CrO_4^{2-} + 2H_2O \rightarrow 0.5Cr_2O_3 + 1.5\, C_6H_4O_2 + 2.5H_2O + 2OH^- \quad \text{(2)}$$

The chromium cycle:- $H_2CrO4 \rightarrow H^+ + HCrO_4^-$ (pH ~ 1.6) .... (3)

$H_2CrO_4^- \rightarrow H^+ + CrO_4^{2-}$ (pH >7) .... (4)

Speciation of Cr: - $2HCrO4^- \rightarrow Cr_2O_7^{2-} + H_2O$ .... (5)

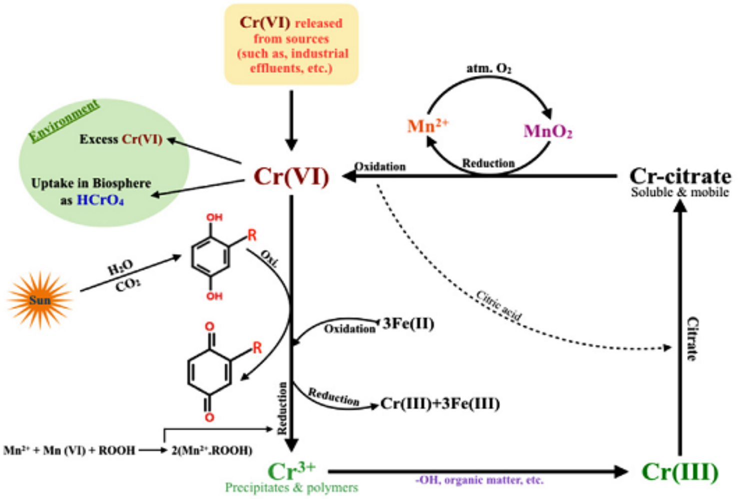

Figure 1 **The chromium cycle [15].**

1.2 Uses of Chromium and its Compounds

Chromium is one of such heavy metal commonly used in many industrial processing as additive of substrate and in finished products; particularly for making steel and other alloys[1]. Compounds of chromium, in either the chromium (III) or chromium (VI) forms, are used for chrome plating, the manufacture of dyes and pigments, leather and wood preservation, and treatment of cooling tower water. Smaller amounts are used in drilling muds, textiles, and toner for copying machines[16].

- **Metallurgy:** Chromium is characterized by its high corrosion resistance and hardness. A major development was the discovery of stainless steel that might be made highly resistant to corrosion and discoloration by adding chromium and the metal. This application, along with chromium electroplating is currently the highest availability on uses of the metal. Chromium and ferro-chromium are produced from the ore chromite (Alumino-thermic reduction). Similarly chromium carbides are materials with great technical importance. In the Cr−C modification, three carbides with the compositions Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$ exist (Carbo-thermic reduction). From these Cr_3C_2 is used as an additive in the manufacturing of tungsten carbide *hard metals* (WC−Co) by directly milling *WC* with *Co* powders or cemented carbides[5].

- **Chromium Electroplating:** Chromium surfaces are produced on the other metals by electroplating and arc chromizing[5].

- **Tanning:** Salts of Cr(III), especially $KCr(SO_4)_2{\cdot}12H_2O$ (Potassium chromium (III) sulfate Dodeca-hydrate the so called chromium alum), and $Cr_2(SO_4)_3{\cdot}12H_2O$ (chromium(III) sulfate Dodeca-hydrate) are used in the tanning of leather. [5].Alum (chromium alum) is a specific chemical compound and a class of compounds.

- **Wood preservatives:** Because of their toxicity, chromic acids of Cr (VI) salts are used for the preservation of wood and wooden materials. For example, 'Chromated Copper Arsenate' (CCA) is used in timber treatment to protect wood decay from fungi, wood attacking insects, termites, and marine borers. The CCA is known by many trade names, including the brands Tanalith®, SupaTimber®, and Clcure®[7] are some commonly known items.

- **Pigments and dyes:** Scientists have found that people are able to see yellow objects in their peripheral field 1.24 times better than red[7]. The Chromate colour (orange-yellowish colour) officially known in the US and Canada as 'the National School Bus 'is also called 'Glossy Yellow'. Before this standard; the school buses in the USA and Canada were a pure yellow, closer to the color of a lemon.

1.3 Toxicity and Health Effect of Chromium

Trivalent chromium (Cr(III)) plays almost irreplaceable role in leather industry; however, the accessible oxidation and natural bio-transformations in the environment to hexavalent chromium (Cr(VI)) made it inevitable to become a widespread pollutant in leather industries producing tannery effluents [17]. Particularly in developing countries like Ethiopia, which under the edge of fast tracking on industrial processes. While, proper treatment of industrial effluents scared; Consequently the carcinogenic and hazardous effects of Cr (VI) induce to the environment and human welfare[18]. The Cr(VI) induced toxicity, contains acute and chronic toxicity, neurotoxicity, dermato-toxicity, geno-toxicity, carcinogenicity and hepato-toxicity, that seriously endangers the physical health of both to humans and experimental animals.

The Cr(VI) and its compounds have a chronic toxic effect upon aquatic life especially, dichromate's are toxic to fish as rapidly penetrate cell walls of aquatic plants. They are mainly absorbed through the gills of fishes and the effect cans easily accumulate. Though, Cr(III) is an essential nutrient, that required for normal energy metabolisms in animals. Ingesting small amounts of chromium will generally not harm, however ingesting above recommended levels over long periods of time can result in adverse health effects including gastro-intestinal irritation, stomach ulcers, heart burning, respiratory tract infection, sever cough, fever and loss of eyesight. Thus, Cr(VI) taken as potent pollutant with much more harmful effect to the health though extensive concern. Many strategies for removal of hexavalent chromium including physical adsorption, chemical reduction and biological remediation have been reported[17].

For example, inhaling Cr(VI) as Cr(VI) oxide ((CrO_3)) causes nasal damage; though; there is no irritation effect from inhalation of Cr(III)[19]. Further, the inhalation effects of Cr(VI) oxide leads to lung cancer, kidney and causes of many health failure even to sever problems to death. Skin contact to CrO_3 also cause to suffer in systemic poisoning, damage or even severe burns, interference with the healing of cut or scrapes unless treated properly, leads to ulceration and severe chronic allergies. In addition, Eye exposure to Cr(VI) oxide may cause permanent damage. Generally, Cr (VI) and its oxide is more toxic, more soluble, more mobile and hence absorbed into cells more readily than Cr(III) and Cr(0). Because, Cr(VI) is 500 times more toxic than Cr(III) and human toxicity of Cr (VI) exposure leads to sever health problems like skin irritation, lung cancer, kidney, liver and gastric damage. Considering the toxic and carcinogenic nature of heavy metal Chromium and its compounds, the maximum levels permitted for Cr(VI) in waste water is 5 mg/L and for Cr(VI) is 0.05 mg/L[20].

In aqueous environments under low Eh conditions, the main Cr(III) species are the cations of Cr(III) (i.e. Cr^{3+} and $Cr(OH)^{2+}$). Furthermore, in a standard condition of Cr-O-H_2O system, the governing reactions are explained as follow in the reaction below[22]:

$$Cr + H_2O \leftrightarrow Cr(OH)^{2+} + H^+ \quad \ldots\ldots (6)$$

$$Cr(OH)^{2+} + H_2O \leftrightarrow Cr(OH)_2^{+} + H^+ \quad \ldots\ldots (7)$$

$$Cr(OH)_2^{+} + H_2O \leftrightarrow Cr(OH)_3 + H^+ \quad \ldots\ldots (8)$$

$$Cr(OH)_3 + H_2O \leftrightarrow Cr(OH)_4^{-} + H^+ \ldots\ldots (9)$$

On other hand, Cr(VI) species primarily occur under oxidizing (Eh > 0) and alkaline (pH > 6.0) conditions. At these ranges, the Cr(VI) forms soluble chromate $(CrO_4)^{2-}$, hydrogen chromate ($HCrO_4^{-}$), or dichromate ($Cr_2O_7^{2-}$) anions depending on the concentration and acidity. For instance, at pH > 6.5 chromate ion is the dominant species whereas at pH < 6.5, $HCrO_4^{-}$ dominates with low concentrations (<0.03 mol/L), but at concentrations > 0.001 mol/L, $HCrO_4^{-}$ ions begin to change in to $Cr_2O_7^{2-}$ and becomes the dominant entity at concentrations > 0.03 mol/L[23].

Now days, there are above 24 tanneries in Ethiopia under operation and those produce daily more than 11,312 m^3 wastewater; which disposed to the surrounding without proper treatments[15, 24]. From these tanneries annually generates beyond 70,104 tons of solid waste and 3,393,600 m^3 wastewater in the pre-tanning leather processing stage and dispose into the surrounding environment without proper treatment (according to ELIDI, 2010 reports)[25]. From these only 10% of the existing tanning industries treat their wastewater to any degree, while the majority (90%) discharges their wastewater into nearby bodies, streams and open land without any kind of treatment[18, 26].

2. Methodology for Determination and Removal of Cr(VI)

The common analytical methods for determination and removal of chromium have been reported in the literature. The most widely used optical methods are: atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and spectro photometric techniques are well known. Though, these methods are reliable and selective, but expensive and time consuming, which needs derivatization[27]. The Spectro photometric methods of Cr(VI) determination and its removal from chrome contaminated effluents was based on conventional methods of coloured Cr^{+6} with 1,5–Diphenyl carbazaide complex measured around 540 nm in acid solution. The optimization procedure that employed for both in the determination and removal on to adsorption techniques; with appropriated instrumental system, chemical species, operating conditions and ease of equipment management were investigated in the experimental section[22].

The Standard method for the determination of hexavalent chromium and its removal techniques was used by UV-VIS spectrometry. This study was important for regular monitoring of toxic chromium concentrations in the real samples of wastewater. The instrumentation technique consists of three principal components. Light source which holds, (tungsten-iodine lump near UV–VIS to IR region in the range of 380-1000 nm and deuterium discharge lump, also for UV region is in the range of 200 –380 nm), beam splitter, sample holder (reference cell and sample cell), detector, display ratio. The solution with analyte is directly exposed to the light and corresponding absorption of the characteristics wavelength of peak generates. During this step a maximize amount of metal deposited can be produced from the peak absorbance of characteristics wave length at about 540nm for Cr (VI)[28].

Thus, UV-VIS spectroscopy method is a promising way and a high sensitive, easy and accurate technique for the determination of trace amounts of metals in solution [27]. In this regard the UV-VIS spectrometers can be used to measure the absorbance of ultra violet or visible light on a sample, either at a single wavelength or scan over in the range of the spectrum. [Note; the UV region ranges from 190 to 400 nm and the visible region from 400 to 800 nm][28].

The technique can be used in both quantitative and qualitative determination for further analysis of research and development works[29]. Also in modern applications of UV-visible spectroscopy is a technique that readily allows determining the concentrations of substances. Therefore, it enables scientists to study the rates of reactions and determine rate equations for reactions, from which a mechanism can be proposed. As such UV –VIS spectroscopy is used extensively in academics, research and health care analytical laboratories for the quantitative analysis of all molecules through which ultraviolet and visible electromagnetic radiation absorbs. In dyestuff, and paint industries UV-visible spectroscopy is used for quality control in the development and production of dyeing reagents, inks and paints and the analysis of intermediate dyeing reagents. In environmental and agricultural fields the quantification of organic materials and heavy metals in fresh water can be carried out using UV-visible spectroscopy.

2.1 Surface Adsorption for Removal of Hexavalent Chromium

Adsorption is the process in which molecules are concentrated on the surface of the sorbent: where molecules go from the bulk phase being adsorbed in the pores of a semi-liquid state[30].

Adsorption is widely employs in the process to remove chromium metals from surface waters (industrial wastewaters)as a means of treatment technique[31]. For adsorption the driving force is the ratio of the adsorbent concentration to the solubility of the adsorbate molecule. Also, several methods such as adsorption, bio sorption, reduction, filtration reverse osmosis, ion-exchange, foam flotation, electrolysis, and surface adsorption have been reported for chromium removal [10, 30, 32]. Though, some physical and chemical treatment procedures are simple, fast and possibly helpful chromium recuperation, many still have meet the demand of high operational cost, high energy consumption and production of secondary pollutants, subjected to high detection limit and high interference.

An adsorbent Lignin is covalently linked with xylans in the case of hardwoods and galacto-glucomannans in softwoods[33]. Even though mechanically cleavable and powdered to a relatively low molecular weight, lignin is insoluble in water. Also lignin has strong resistance to chemical reactions, with the high surface area (about180 m^2/g). Molecular weight of the polymeric lignin changes from 2,000 to 15,000 g/mol[33]. These properties of lignin reveal that it has a potential to be used as low cost and easily access adsorbent with an efficient adsorption capacity to remove heavy metals from waste waters. At present time the lager chrome contamination of the industrial effluents becomes to the environment that endanger to humans and ecosystem credibly. Hence, scientifically sustainable work of treatment required using such eco-friendly material with biosorption techniques.

2.2 Sorption Studies

The promising sorption experiment, has been designed with the effect of adsorbent dose, optimum pH, contact time and initial concentration of Adsorbate[34]. Kinetic and isotherm sorption studies also conduct at optimum parameters for the equilibrium models[30]. The calculation of the removal efficiency and adsorption capacity of heavy metal onto a sorbent are important test for the promising adsorbent and the method through[29].

3. Experimental

3.1 Instruments

For this study the most essentials and frequently used materials were; volumetric flasks within (5 - 1000 mL), measuring cylinders and pipettes and micro pipette, beakers, analytical balance, pH meter, filter paper, funnel and Buchner funnel, flask shaker, sonycator, hot plate, thermometer, quartz cubits and UV-VIS spectrometry (Aligilant technology-carry 600).

3.2 Chemicals

The analytical standard solution of the following chemicals and reagents has been required with appropriate buffer solutions, 0.2 M H_2SO_4, Potassium dichromate ($K_2Cr_2O_7$), de ionized water, distilled water, conc.H_2SO_4, conc.HNO_3, 1:1 ratio of conc.H_2SO_4 and conc.HNO_3, 0.5%(v/v),10 % (w/w) MgO, 3 molar KCl (potassium chloride as pH salt), Acetone, 1,5-di phenyl carbazaide (1,5-DPC) complexing agent[39], and paraffin oil for digestion in oil bath were used. Lignin from bio-sorbent (water hyacinth) was used for Cr(VI) remover on to its surface adsorption.

3.3 Procedure

The adsorbent biomass materials (Emboch); the so called water hyacinth (Eichornia Crassipes) was collected. The freshly dry weight of the water hyacinth was chopped and powdered in to smallest particulates. The fine powder of lignin; as bio adsorbent was prepared for Cr(VI) removal. Lignin of lingo-cellulose component, other than Carbon, Nitrogen, Cellulose, Hemicelluloses, Protein, Lipid, Ash and Calorific value was separated [41]. The adsorbate concentration of Cr(VI) at pH 2 were adjusted in the acidic media[35, 38, 40]. The concentration for standard solution was prepared to the corresponding level of real sample hexavalent chromium concentration (i.e. 3 mg/L) and the 100µml complexing agents 1, 5-DPC also added to each 10 ml standard solution after shacked and filtered. Note; the shaking time was varied with the different interest of contact time and filtration accomplished by using 0.22 – 0.45 µm pore size micro filter paper.

Finally the prepared samples ware measured in UV-VIS spectrometry of its absorbance vs wavelength. From this the quantitative amount of hexavalent chromium was determined. Similarly the amount of removed chromium and its percentage recovery was easily calculated.

4. Result and Discussion

4.1 Determination of Cr(VI) using UV-VIS spectrometer

The UV-VIS spectrometer is used to determine the concentration of Cr(VI). For the simplicity, lower and higher concentration ranges were employed for the determination of hexavalent chromium. The lower concentration calibration curve was within a linear range of 0.025 to 4.0 mg/L, at $A = 0.614C + 0.046$ with a correlation coefficient of ($R^2 = 0.996$) as shown in Figure 3.

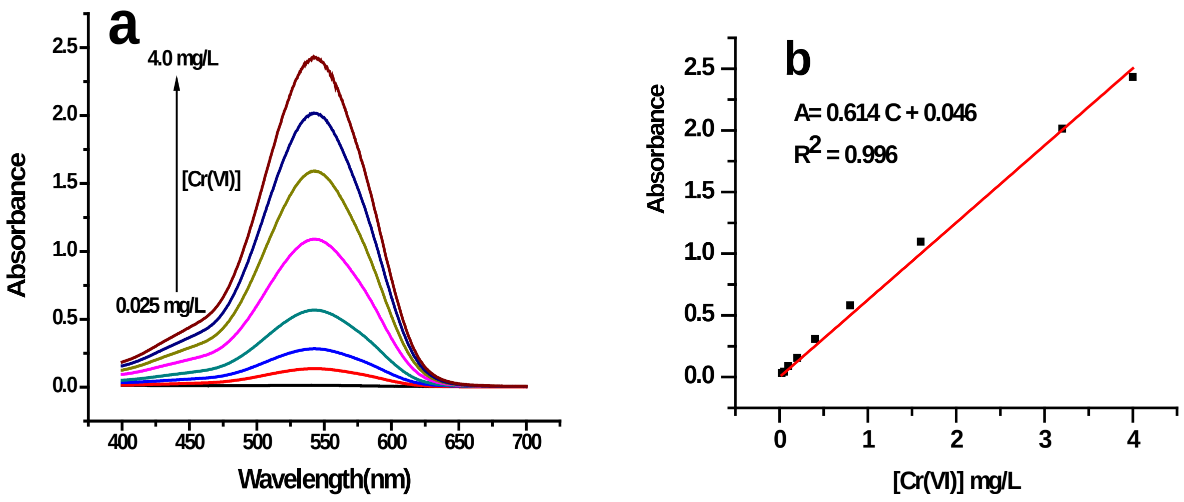

Figure 2: (a) UV-VIS spectroscopy; and (b) calibration curve analysis: for the concentration range was 0.025 to 3.2 mg/L (low concentration) of $K_2Cr_2O_7$ standard solution diluted from 1000 mg/L.

Similarly, the high concentration calibration curve of Cr(VI)was in the range of 5to 100mg/L, at A = 0.028c – 0.0098 with a correlation coefficient of (R^2=0.9999) was investigated as shown in Figure 4.

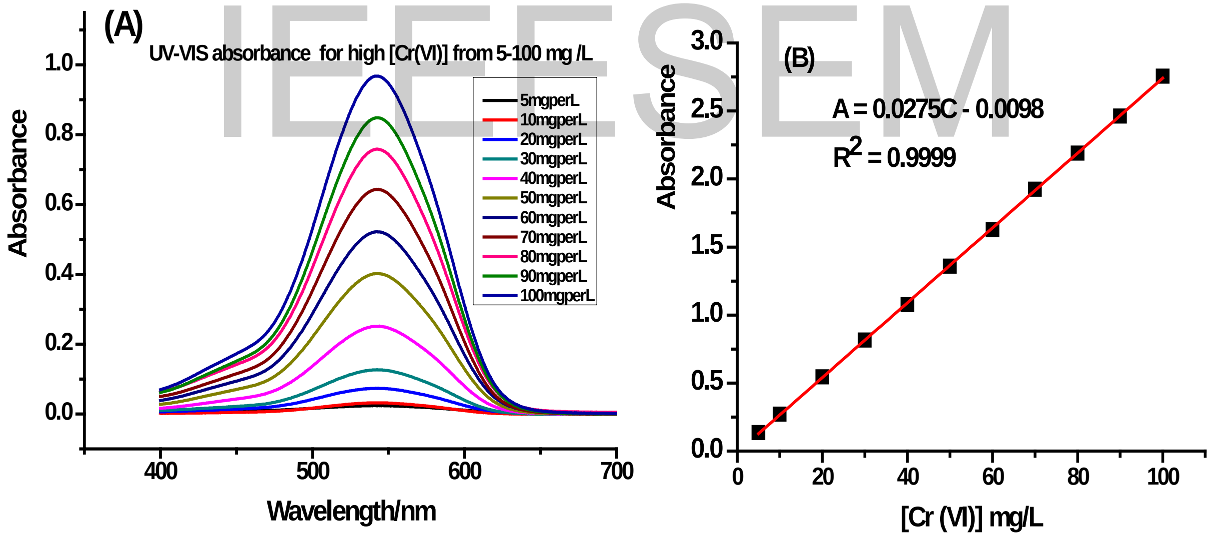

Figure 3: (A) UV-VIS absorbance spectra at 540 nm for the standard solution; (B) Calibration curve of high concentration [Cr (VI)] 5-100 mg/L.

4.2 Real Sample Analysis for Cr(VI) Determination

The samples of a paint industry wastewater were collected from different areas. The concentration of Cr(VI) in the paint industry was found to be 2.8 mg/L. Due to this high concentration of Cr(VI) in the paint industry it was used as a model sample for the removal analysis using adsorbent lignin extracted from water hyacinth.

4.3 Removal of Cr(VI) on Adsorption Process

4.3.1 Effect of pH

When the adsorption of hexavalent chromium was studied at various pHs, maximum adsorption capacity (92.36 %) of Cr(VI) was found around pH 2-3 from previous study [42]. Hence, removal study on Cr(VI) on adsorbent lignin extracted from water hyacinth at pH 2 was taken as optimum value.

4.3.2 Effect of Adsorption Dosage

The percentage removal of Cr(VI) from aqueous solution was investigated at different lignin dosages in the range of 5 to 35 mg. As the mass of adsorbent lignin increases, the percent removal of Cr(VI) increases sharply up to 30 mg and then after the removal gets constant as shown in Figure 5. Hence, the optimum adsorbent dose of lignin for the removal of Cr(VI) is 30 mg for further experiment.

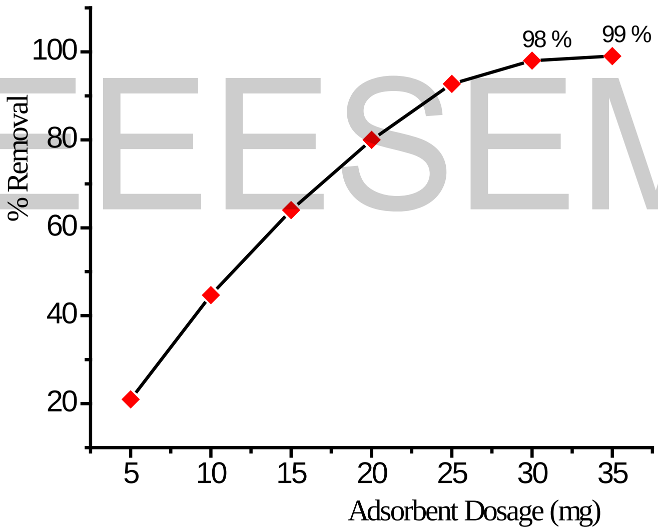

Figure 4: Percentage Removal of [Cr(VI)] in mg/L against adsorbent dosage (mg).

4.3.3 Effect of Initial Concentration

The removal efficiency of the adsorbent was determined by varying the initial concentration of Cr(VI) under the optimized condition. The highest removal percentage was obtained at 3 mg/L as shown Figure 6. Hence, the optimum initial concentration of 3 mg/L Cr(VI) was taken for further experiment.

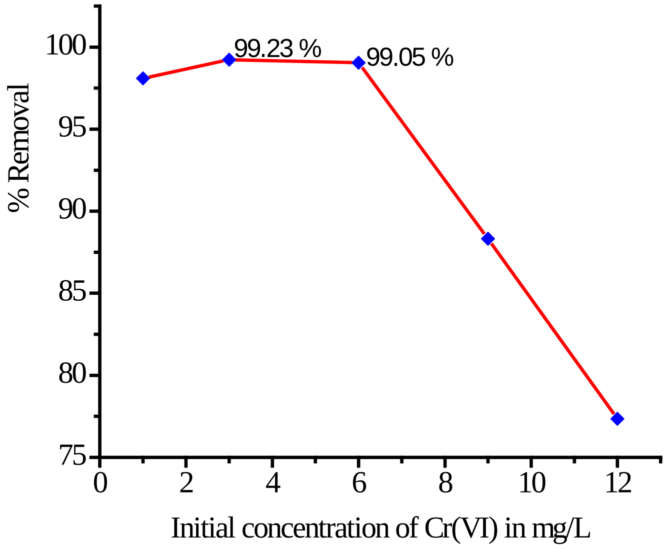

Figure 6: Percentage removal of Cr(VI) *vs* initial concentration of Cr(VI) for the range 1-15 mg/L at pH 2 and 20 minute.

4.3.4 Adsorption Isotherm

The adsorption isotherm for a solid surface adsorbent in the aqueous solution was studied using two different models, namely Freundlich and Langmuir Isotherm models. In Freundlich model, hexavalent chromium on the surface of lignin was adsorbed at a varying initial concentration Cr(VI). The varying initial concentrations were fitted in non-linear model in the following equation 10 [41].

$$q_e = K_F\,(C_e)^{1/n} \qquad (10)$$

where, q_e is the adsorption capacity (mg/g), C_e is the equilibrium concentration of the Cr(VI) solution (mg/L), k_f and n are Freundlich constants, which represents adsorption capacity and adsorption intensity, respectively[29, 42, 43].

The Freundlich parameters K_F and n were determined from the plot of “q_e” *vs* “C_e” (Figure 6) and their values was tabulated in Table-1**.** The n value was found to be 4.02 which suggest that the adsorption phenomena be governed by physical process [40, 44].

The model of Langmuir Isotherm was also studied for adsorption of Cr(VI) ion from a liquid solution as monolayer adsorption. The Langmuir isotherm model was fitted for estimation of the maximum adsorption capacity, indicating monolayer coverage on the adsorbent surface. The Langmuir isotherm can be determined in non-linear fit model in equation (11)

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (11)$$

Where, K_L is the Langmuir constant, C_e is the equilibrium metal ion concentration and q_{max} (mg/g) is the monolayer adsorption capacity constant. Here, the q_e value at the equilibrium concentration was found to be 3.77 mg/g which was closer to the Langmuir model (3.31 mg/g) with R^2 0.869 (Figure 6). Hence, the adsorption isotherm of lignin in the removal of hexavalent chromium was best fitted with Langmuir model.

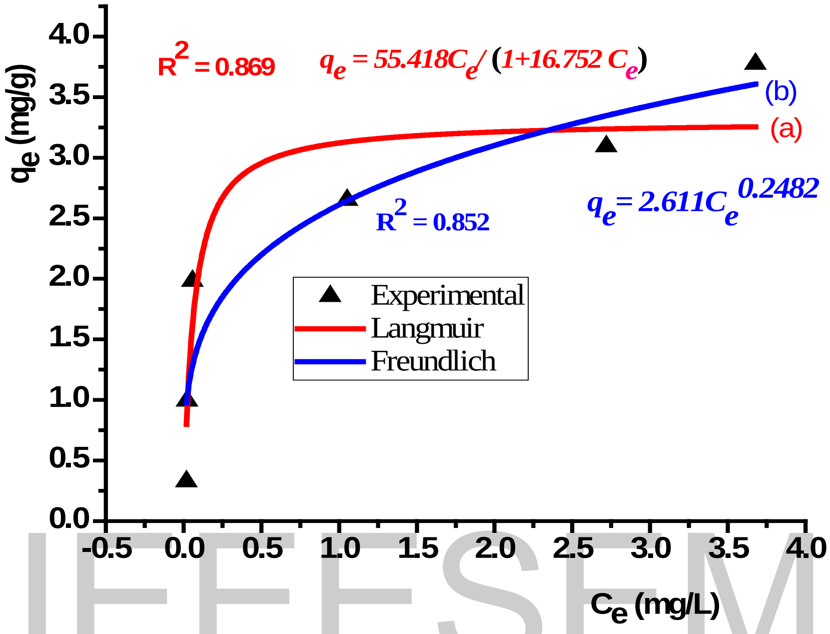

Figure 7: the adsorption models of Langmuir *(a)* and Freundlich *(b)* isotherm fitting.

Table 1: Isotherms studies for adsorption of Cr(VI) on to Lignin from water hyacinth at 25.

Experimental value	Langmuir isotherm $q_e = q_{max} K_L C_e/(1+K_LC_e)$			Freundlich isotherm $q_e = K_fC_e^{1/n}$		
q_{exp}(mg/g)	R^2	K_L	q_{max}(mg/g)	R^2	K_f	n
3.77	0.869	16.752	3.308	0.852	2.611	4.02

4.3.5 Effect of Contact Time for Adsorption kinetics

Adsorption kinetics was also investigated to obtain valuable information about the reaction pathways and the reaction rate mechanism. Within 20 minute maximum adsorption capacity was reached and become constant after 20 minute as shown in Figure 8a. The remaining concentration of Cr(VI) decreases abruptly in two minutes (Figure 8b)

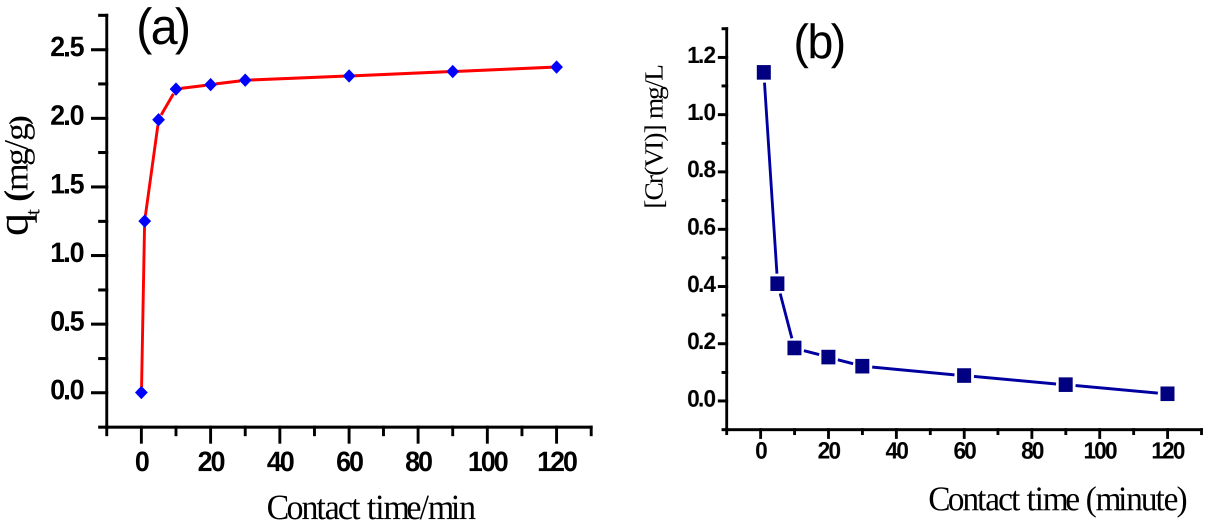

Figure 8: (a) Adsorption capacity of Lignin extracted from water hyacinth and (b) remaining concentration of Cr(VI) in mg/L as a function of contact time at pH 2.

The pseudo first order and pseudo second order models were employed to analyze adsorption kinetics of Cr(VI) ion in aqueous solution. The kinetic expression for pseudo first order adsorption was determined by equation 13.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (13)$$

Where q_t (mg/g) is the amount of adsorbed Cr(VI) onto the lignin at time t, k_1 is the rate constant of first order adsorption and q_e is the equilibrium adsorption capacity. The plot of log ($q_e - q_t$) versus time (t) show very poor linearity with a correlation coefficient ($R^2 = 0.7803$) as illustrated in Figure 9a. The values of q_e and k_1 were determined from their intercept and slope, respectively as depicted in Table 2. There is a significant difference between the experimental and theoretical values adsorption capacity at equilibrium, which doesn't obey pseudo first order reaction.

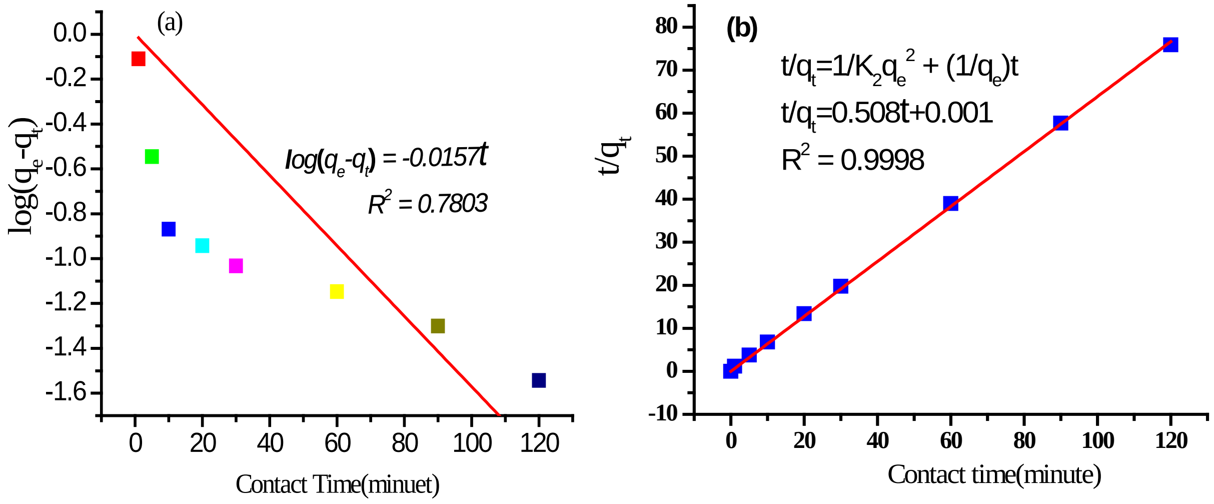

Figure 9. (a) Pseudo first order and (b) Pseudo second order rate models for adsorption kinetics for [Cr(VI)] in Lignin.

On the other hand, the pseudo second order kinetics was tried by applying equation (14)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (14)$$

Where, k_2 (mg/g min) is rate constant of second order equation at a time t. The plot t/q verses t exhibits an excellent linearity with a correlation coefficient (R^2=0.9998), indicating that Cr(VI) adsorption on lignin favors pseudo second order kinetic. Furthermore, the values of q_e and K_2 were calculated from the slope and intercept as tabulated in Table 2.

Table 2**:** Interpretations of pseudo first order and pseudo second order adsorption kinetics.

Experimental and calculated Values of Kinetic Sorption at Equilibrium.						
Psedo First Order model				**Psedo Second Order model**		
$Q_{e,Exp}$.(mg/g)	$Q_{e,cal}$.(mg/g)	K_1(1/min)	R^2	$Q_{e,cal}$.(mg/g)	K_2(1/min)	R^2
2.012	0.651	-0.0362	0.7803	1.969	-0.001	0.9998

5. Application of the Lignin for Adsorption of Cr(VI) in Real Sample

The application of lignin for Cr(VI) removal were studied using synthetic(standard) solution and real sample. The result shown in figure 10 confirmed that lignin extracted from water hyacinth have similar Cr(VI) removal efficiency both in standard solution and real samples.

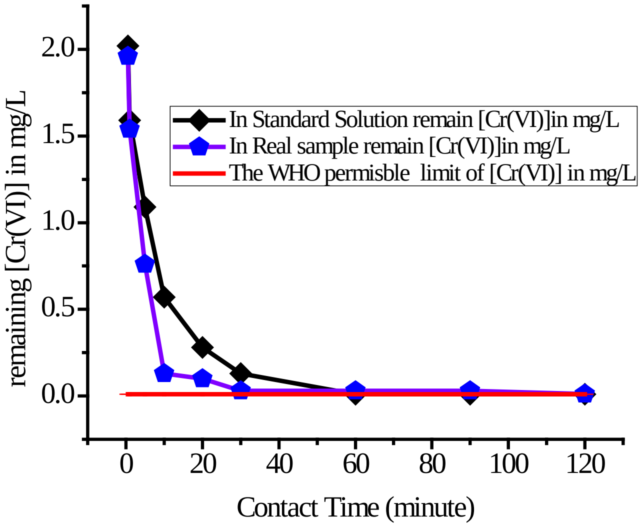

Figure 10: The removal of Cr (VI) as the function of time in standard solution and real samples to convene the WHO permissible limits using lignin adsorbent for 3 mg/L initial concentration of Cr(VI).

5.1 Comparison of Different Bio Sorbent on to Cr (VI) Removal

The removal capacity and efficiency of the material was compared with other adsorbents. It is important to analyze the previous work and their adsorbent percentage removal with their adsorption capacity. Aiming to provide a comprehensive property of lignin extracted from water hyacinth (Eichornia Crassipes) to the comparative study of other bio sorbent related adsorption techniques were compared from the literature as shown in the Table 3.

Table 3: Adsorption capacity f different adsorbents and with the specified parameters as comparisons to this work.

Adsorbents’	q_e (mg/g)	% Removal	References
Agricultural wastes (pea pod, tea & ginger and banana peels)	7.29	80%	[41]
Fe(III)impregnated sugarcane bagasse *via* activation in a muffle furnace	13.37	95 %	[40]
Activated Carbon (Locally Available Bamboo Waste)	59.23	98.28%	[36]
Activated Lignin (lignin sulfate treated by 30% H_2O_2 and carbonized at 300°C)	75.75	92.36%	[45]
Sewage sludge compost biomass	2.2	99%	[46]
Modified Lignin	9.3	39.5%	[33]
Magnetic bio char composite (Fe_3O_4 free radical)	8.35	84.3%	[47]
Lignin from water hyacinth	3.774	99.23%	This work

6. Conclusion

The percent removal of Cr(VI) on adsorbent lignin extracted from water hyacinth was demonstrated in this work. Under the optimized condition (30 mg dose, pH 2 and 20 min contact time), the adsorption capacity of lignin was found to be 3.77 mg/g and its percent removal Cr(VI) was 99.23 %. The physical adsorption of Cr(VI) on lignin obeys pseudo-second order kinetic with correlation coefficient (R^2=0.869) and the equilibrium process has been well fitted the Langmuir isotherm. The cost-effective, relatively high adsorption capacity and successful application in removing Cr (VI) from industrial effluents demonstrate that lignin extracted from water hyacinth is an effective adsorbent for the removal of Cr(VI).

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