

JIMMA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY



A THESIS ON:

**KINETIC AND THERMODYNAMIC STUDIES OF THE
ADSORPTION OF Cr (VI) ONTO SOME SELECTED LOCAL
ADSORBENTS**

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**KINETIC AND THERMODYNAMIC STUDIES OF THE
ADSORPTION OF Cr (VI) ONTO SOME SELECTED LOCAL
ADSORBENTS**

**A THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES
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ABBREVIATIONS

CAC	Commercially Activated Carbon
AAS	Atomic Absorption Spectrometer
CNTs	Carbon Nanotubes
SWCNTs	Single Walled Carbon Nanotubes
MWCNTs	Multi Walled Carbon Nanotubes
GAC	Granular Activated Carbon
CSAC	Char of South African Coal
US	Untreated juniperus procera Sawdust
UA	Untreated Avocado kernel seeds
UP	Untreated Papaya peels
ACS	Activated Carbon of juniperus procera Sawdust
ACA	Activated Carbon of Avocado kernel seeds
ACP	Activated Carbon of Papaya peels
MB	Methylene Blue

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ABSTRACT

Adsorption is one of the most widely applied techniques for environmental remediation of Cr (VI). Waste effluent containing Cr (VI) causes a serious environmental problem. Commercially available activated carbon adsorbents are the one that usually applied for the removal of Cr (VI). However; these adsorbents are expensive materials and need to be replaced by cheaper but effective adsorbents. In this study, locally available biomasses obtained from avocado kernel seeds, juniperus procera sawdust and papaya peels were investigated as adsorbents for the removal of Cr (VI). The study employed batch method to investigate the efficiency of the adsorbents. Parameters that influence adsorption such as: effects of pH, adsorbents dose, initial concentration, contact time, and temperature were optimized (pH: 1 for all of untreated and activated carbon of juniperus procera sawdust adsorbents, 2 and 3 for activated carbon of avocado kernel seeds and papaya peels found optimal respectively, adsorbents dose: 0.5 g, [Cr (VI)]: 5 mg/L, contact time: 160 min and temperature: 40 °C). To understand the adsorption isotherm, the Langmuir and Freundlich adsorption isotherm models were investigated and the data was found best fit to Freundlich isotherm model indicating that the heterogeneity of the adsorbents surface. Kinetic studies were made and the pseudo-second order kinetic model was found to be more suitable for describing the experimental data. Thermodynamic parameters (ΔG° , ΔH° and ΔS°) have also been calculated and found that the adsorption process as feasible, spontaneous and exothermic in nature. The positive values of the entropy change suggest that the increased randomness at solid-liquid interfaces during the adsorption. Finally, the efficiencies of the adsorbents towards the removal of chromium from tannery wastewater were also examined and it was found as they have capacity to remove chromium from wastewater solution.

Keywords: Adsorption; adsorbents; chromium (VI); isotherms; Adsorption kinetic; thermodynamic of adsorption.

1. Introduction

1.1. Background of the study

Advances in water and wastewater treatment technology need to be directed to the development of technologies that may be more effective and less costly. Nowadays, the contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem [1]. The term “heavy metal” refers to the metallic elements having density greater than or equal to 6.0 g.cm^{-3} [2]. Numerous heavy metals such as Pb, Cr, Cu, Zn, Hg, Cd etc. have toxic effects on human’s health. Among these toxic metals, chromium has major impact on environment and it has both beneficial and harmful properties. Chromium mostly exists in two oxidation states such as trivalent chromium (i.e., Cr^{3+} as, $\text{Cr}(\text{OH})^{2+}$ or $\text{Cr}(\text{OH})_2^+$, etc.) and hexavalent chromium (i.e., Cr^{6+} as HCrO_4^- , CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$, etc) [3]. Most of the hexavalent compounds are toxic, carcinogenic and mutagenic and even it can also cause lung cancer, [4, 5]. Chromium (VI) ions mostly exists as H_2CrO_4 form at high acidic medium ($\text{pH} = 1.0$). At $\text{pH} 2\text{-}6$ there is equilibrium between $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- species and under alkaline condition ($\text{pH} > 8$) it exists as chromate CrO_4^{2-} anion [6].

Chromium and its compounds are widely used in electroplating [7], leather tanning [8], cement [7], dyeing [1], metal processing [9], wood preservatives [10], paint and pigments [11], textile and steel fabrication [12] industries. These industries may release large quantities of toxic metal wastewater effluents above the permissible limit. But the maximum exit Cr (VI) concentration based on USEPA (United State Environmental Protection Agency) guidelines for potable water is 0.05 mg/L and the United Nations Food and Agricultural Organization recommended maximum level for irrigation water is 0.1 mg/L [2]. The World Health Organization (WHO) has also set the maximum permissible level of 0.05 mg/L for Cr (VI) in drinking water [13].

In general, a wide range of processes have been reported to eliminate the Cr (VI) from water and wastewater such as chemical precipitation [14], electrochemical reduction [15], sulphide precipitation [16], cementation [17], ion-exchange [18], reverse osmosis [19], electro dialysis [20], solvent extraction [21] and evaporation [22].

The application of such methods is however cost intensive [15] and is unaffordable for large scale treatment of wastewater [23]. Because of this most of the time more economical means such as adsorption for the removal of toxic metals have been applied.

1.1.1. Adsorption

Adsorption is a separation process in which certain components of the liquid phase are transferred to the surface of the solid adsorbents. When a solid surface is exposed to a liquid phase, the molecules from the bulk of the liquid phase have tendency to accumulate or concentrate at the surface of a solid. The phenomenon of the enrichment of chemical substances at the surface of a solid is called adsorption. All adsorption processes are dependent on solid-liquid equilibria and on mass transfer rates [24]. If the mass transfer is in opposite direction then it is called desorption. Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at the specific sites inside the particle. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. The overall rate of adsorption is controlled by the rate of diffusion of solute within the capillary pores of the adsorbent. The adsorption operation can be batch, semi-batch and continuous. Batch operations are generally conducted when small amounts are to be treated. The equilibrium distribution depends on the contact time in batch operation [25].

In semi-batch operations, a reactant may be added with no product removal, or a product may be removed with no reactant addition, or a combination of both. From a process systems point of view, the key feature that differentiates continuous processes from batch and semi-batch processes is that continuous processes have a steady state, whereas batch and semi-batch processes do not [26].

1.1.2. Types of Adsorption

At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed.

a. Physical Adsorption: It is a result of intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. In this case the molecular attractive forces that retain the adsorbate on the surface are purely physical are called Vander Walls forces. This is a readily reversible phenomenon. The energy of interaction between the adsorbate and adsorbent has the same order of magnitudes as, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed.

b. Chemical Adsorption: It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption which is irreversible. It is particularly important in catalysis. Therefore, the energy of chemisorptions considered like chemical reaction. It may be exothermic or endothermic processes ranging from very small to very large magnitudes. The elementary step in chemisorptions often involves large activation energy (Activated adsorption). Adsorption has been found to be superior compared to the other techniques for water reuse in terms initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants and does not result in formation of harmful substances [27].

1.1.3. Adsorption at Activated Carbon Surface

Adsorption by activated carbon is one of the effective techniques for chromium removal from wastewater because of high surface area, highly porous character and relatively low-cost. The use of activated carbon for removing chromium from wastewater has been received a great attention from decades [28]. Activated carbon was especially known for the effectiveness in removing organic chemicals from wastewater and also for removal of inorganic and heavy metal pollutants in laboratory as well as in industries [29]. Activated carbon can be prepared from readily available carbonaceous precursors such as coal [30], wood [31], coconut shells [32] and agricultural wastes [33], etc. They are extensively used in water treatment [34]. These carbonaceous materials possess the potential for the removal of inorganic and organic pollutants from effluent streams. The activated carbon possesses a

significant weak acidic ion exchange character so as to remove trace metal contaminants and to adsorb pollutants from wastewater [35].

The adsorption capacity of AC depends not only on its surface area, but also on its internal pore structure and surface characteristic. To reduce the cost of mass production, an inexpensive and local raw material with high carbon and low ash contents is preferred as precursor for preparing AC [36]. Various carbon materials have unique pore distributions, which result from the precursors and processes involved. Pores are formed within the particles of a fine powder, the primary particles, or in the aggregated secondary particles that are formed when primary particles stick together. The total surface area of a fine powder is the sum of the pore wall area of all the pore sizes [37].

Chromium is one of the contaminants which exist in hexavalent and trivalent forms. Trivalent chromium is an essential element in human nutrition and is much less toxic than the hexavalent one, which is recognized as a carcinogenic and mutagenic agent [1]. Chromium compounds are widely used by different industries, so huge quantity of wastewater containing chromium is discharged into the environment. Removal of Cr (VI) from wastewater is essential before disposal.

1.1.4. Removal of Cr (VI) by adsorption

Adsorption is an effective and flexible method for removing chromium. Natural materials that are available in large quantities or certain waste products from industrial or agricultural operations may have potential as inexpensive adsorbents [15]. Attempts have been made by a number of investigators to find cheap adsorbents from locally available biomass and further investigation need to be made to achieve the most suitable adsorbents and describe the chemistry behind the adsorption process.

In this study, adsorbents such as avocado kernel seeds, Papaya peels and juniperus procera sawdust were studied as potential adsorbents for chromium (VI).

2. Literature Review

Adsorption is widely used as effective physical method of separation in order to eliminate or lower the concentration of a wide range of dissolved pollutants (organics or inorganics) in the effluent [38]. The various solutes on a solid remain an active area of research [39]. The importance of adsorption is seen in the need for choosing effective adsorbent for the adsorption or purification needs. The determination of adsorption capacity is a necessary advantage for selecting adsorbent [40].

The removal of toxic metal ions from wastewater is an important and widely studied research area. One of the heavy metal that has been a major focus in wastewater treatment is chromium. The toxicity caused by hexavalent chromium is high and therefore priority is given to regulate this pollutant at the discharged level. In recent years, the researchers have developed many biomass adsorbents to remove the heavy metals from aqueous solution. The adsorption of chromium (VI) from the aqueous phase on dried roots of water hyacinth revealed a very high degree of removal efficiency (almost 100%) [41]. Beech (*Fagus orientalis* L.) sawdust had shown 100% as maximum adsorption efficiency at pH 1 [42]. The maximum Cr (VI) ion percentage removal of walnut (*Juglans regia*), hazelnut (*Corylus avellana*) and almond (*Prunus dulcis*) were 88.46% and 55.00% respectively [43].

The removal rate of Cr (VI) depended on the types of biomaterials; the pine needle completely removes Cr (VI) in 5 h while Ecklonia and rice husk needed 126 h and 1270 h for the complete removal of Cr (VI) respectively [44]. The biosorption by various biosorbents such as coconut shell, wheat bran and rice bran have been reported. Coconut shell had 80% removal [45] and wheat bran had 87.8% removal in 1 h at pH 2 [46]. The rice bran as an adsorbent is used to remove the metal ions from aqueous solutions and the sorption capacity was strongly dependent on the nature and the initial metal ions concentration, initial pH and rice bran concentration showed 0.069 mg/g Freundlich adsorption capacity [47]. Adsorption capacities of some other adsorbents of food waste such as cooked waste tea (30.39 mg/g) [48] and potato peel waste (8.012 mg/g) are also reported [49]. Along with this agro waste such as sunflower stem was investigated for removal of Cr (VI) with adsorption technique. Pre-boiled sunflower stem and formaldehyde treated

sunflower stem have 4.9 and 3.6 mg/g adsorption capacity and 81.7 and 76.5% removal efficiency of Cr (VI) respectively [50]. Oak saw dust soaked by HCl [51], rice straw [52] and almond shells [53] were found to show 93.4%, 95.4% and 98.00% removal of Cr (VI) respectively. The Cr (VI) removal of rosewood sawdust that was treated with H₂SO₄ and formaldehyde was found to be 99.8% and 87.8% respectively [54].

Many reports have appeared on the development of low-cost activated carbon from renewable resources and also how to purify water in an environmentally friendly manner [55-57]. Agricultural and industrial waste materials such as Hazelnut-AC [58], Neem leaves [59], Black tea leaves [60], Nitric-oxidized CAC [61], Waste tyre [62], Leaf mould [63], Alligator weed [64], Alfa grass [65], etc. have been utilized as activated carbon precursors by a large number of researchers for the removal of heavy metals.

Carbon nanotubes (CNTs) have attracted great attention because of their small size, large surface area, unique hollow structure, high mechanical strength and remarkable electrical conductivity. According to the carbon atom layers on the sidewalls of the nanotubes, CNTs can be visualized as a sheet of graphite that has been rolled into a tube and divided into single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs). The oxidized MWCNT may be promising materials in environmental pollution management [66]. MWCNT developed by chemical vapor deposition of acetylene in hydrogen flow at 1033 K using Ni-Fe nanoparticles as catalysts (Fe (NO₃)₂ and Ni (NO₃)₂ were treated by sol-gel process and calcinations to get FeO and NiO and then deoxidized by H₂ to get Fe and Ni as catalysts. The developed MWCNTs were used to remove Cr (VI), which shows the maximum adsorption capacity to be 4.434 and 4.2615 mg/g in two cases [67]. Researchers found no functionalized multi-walled carbon nanotubes which showed the highest adsorption capability up to 98% of a 100 ppb Cr (VI) solution being adsorbed [68].

In another case imidazole functionalized sol-gel adsorbent had 152 mg/g adsorption capacity [69] while montmorillonite-supported magnetite nanoparticles prepared by coprecipitation and hydrosol method show the 20.16 mg/g and 13.88 mg/g adsorption capacity respectively while unsupported magnetite had 10.6 mg/g adsorption capacity [70].

CNTs showed exceptionally high sorption capacity and efficiency for Pb (II), Cd (II) and Cr (VI) from water. They were found as good adsorbents for multi-component sorption of

metal ions [35]. The factors affecting the sorption of transition metal ions on oxidized CNTs and found that the sorption mechanisms were governed by the surface features, ion exchange process and electrochemical potential [71].

The removal of divalent metal ions (Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) from aqueous solution using various kinds of CNTs and suggested that CNTs are promising adsorbents for environmental protection application because of the superior sorption capacity and effective desorption of divalent metal ions [72].

Activated carbon adsorption seems to be an attractive choice for chromium removal both for its removal efficiency and for the rapid adaptation to pollutant loading alteration. For these reasons, activated carbon adsorption has been widely used for the treatment of wastewater containing chromium. Adsorption isotherms of chromium ions in aqueous solution on a granular activated carbon (GAC) and on a Char of South African coal (CSAC) have been studied. The adsorption capacity for the GAC strongly depends on pH of solution and salinity with maximum values around 7 mg/g at neutral pH and low salinity levels. The CSAC shows a smaller adsorption capacity near 0.3 mg/g which slightly decreases by increasing pH and salinity levels [73]. Fresh activated carbon and waste activated carbon that were pretreated by heating with mineral acids H_2SO_4 and HNO_3 at high temperature to prepare several grades of adsorbents and their Langmuir isotherm maximum adsorption capacities were reported to be 7.485 and 10.929 mg/g respectively [74]. A composite adsorbent was prepared by coating poly (4-vinylpyridine) on a granular activated carbon followed by cross-linking and quaternization processes which estimated maximum equilibrium uptake of Cr (VI) 53.7 mg/g at pH 2.25 [75].

However, commercially available activated carbons may be expensive and for this reason the knowledge of the optimal working conditions to maximize the adsorbent capture capacity is required. Similarly, the production of low cost, not reusable adsorbents for chromium removal is also worth considering. In recent years, development of surface modified activated carbons using plant biomass is generating a diversity of activated carbon with superior adsorption capacity. These are available in large quantities and can be disposed of without regeneration due to their lower cost. A variety of natural plant biomass

like bael fruit (*Aegle marmelos correa*) shell had shown 17.27 mg/g adsorption capacity [76].

The low cost agricultural waste by-products such as sugarcane bagasse [77, 78], rice husk [79] and neem bark [80] for the elimination of heavy metals from wastewater have been investigated by various researchers. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing is abundant in nature or is a by-product or waste material. Of course improved sorption capacity may compensate the cost of additional processing [81]. Therefore, there is an urgent need that all possible sources of agro-based low-priced adsorbents should be explored and their feasibility for the removal of Cr (VI) should be studied.

In this study, untreated and activated carbon adsorbents were developed from locally available adsorbents and applied for removal of Cr (VI) from aqueous solution and wastewater. The adsorption isotherms, kinetic and thermodynamic models were discussed successively. The activated carbons developed from juniperus procera sawdust, avocado kernel seed and papaya peel were economical and environmentally friendly and so they were used for further application.

3. Statement of the problem

Clean drinking water is one of the understood basics for the health of humans. However, the growing industrialization and extensive use of chemicals for various concerns has increased the burden of unwanted pollutants of drinking water in developing and developed countries all over the world. Heavy metal like Cr (VI) which is especially a tannery waste has a great concern because of its extreme toxicity even at trace concentration. Since it is impossible to prevent completely these chemicals from draining into the drinking water sources, the researchers' devised different conventional and advanced methods such as chemical precipitation, electrochemical reduction, sulphide precipitation and so on. However, the application of such methods is cost intensive and is unaffordable for large scale treatment of wastewater. Thus, the way to maintain safer water bodies are using of efficient purifying technologies. One such beneficial and successful procedure that has been in use is that of purification of water using natural and modified adsorbents. Several natural adsorbents are being used for treatment of contaminated drinking water and its sources [82].

Adsorption has been described as an effective separation process for treating industrial and domestic effluents [83]. Therefore, in this study, this method was applied in the removal of highly toxic chromium (VI) from both aqueous solution and wastewater using various locally available low-cost adsorbents such as avocado kernel seed, papaya peel and juniperus procera sawdust because they are friendly to the environment.

4. Objectives of the study

4.1. General objective

- ❖ To investigate kinetic and thermodynamic of Cr (VI) adsorption onto locally available adsorbents.

4.2. Specific objectives

- Determine the adsorption efficiencies of some selected local adsorbents.
- Determine the effects of parameters such as pH, mass of adsorbents, initial concentration, contact time and temperature on the adsorption efficiencies of adsorbents.
- Describe the responsible adsorption isotherm models.
- Assess the kinetic and thermodynamic of the adsorption of chromium (VI) onto the adsorbents.
- Apply the adsorbents to the removal of chromium from tannery wastewater.

5. Significance of the study

In order to meet the growing require of drinking water and water of good quality for industrial use, it has become necessary to treat wastewater for renewal, reuse, and pollutant removal before mixing with natural water bodies containing good quality water. Various methods have been adopted to treat wastewater for pollution control. Adsorption was found to be as one of the most widely used means. Natural biomasses have long been known as adsorbents for metal ions and offer alternative means for costly adsorbents known by their high adsorption capacity.

In this study, locally available adsorbents were investigated to evaluate their efficiency and suitability as part of the effort to find less costly and environmentally friendly adsorbents.

6. Materials and Methods

6.1. Chemicals and Materials

6.1.1. Chemicals

The chemicals used for this study were: sulfuric acid, H_2SO_4 (98%, UNI-CHEM, Germany), hydrochloric acid, HCl (37%, Riedel-deHaën, Germany), potassium hydroxide, KOH (90%, BDH, England), potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ (99.5%, FINKEM, England), glacial acetic acid, CH_3COOH ($\geq 99.99\%$, Riedel-deHaën, Germany), sodium acetate, CH_3COONa ($\geq 98\%$, Riedel-deHaën, Germany), ammonia, NH_3 (23-25%, Mumbai, India), ammonium chloride, NH_4Cl ($\geq 99.5\%$, Riedel-deHaën, Germany) and methylene blue, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS}\cdot 3\text{H}_2\text{O}$ ($\geq 96\%$, Cyanamid, America). All chemicals used in this study were analytical reagent grade and were used without further purification.

6.1.2. Materials

The materials used for this study were: standard sieves (Model DSCO 1674 JPG, 150 μm , UK), 'A' shape size clay type crucibles, volumetric flasks, conical flasks, beakers, droppers, mortar and pestle.

6.1.3. Instruments

The instruments used for this study were: Oven (Model GENLAB WIDNES, England), Electrical furnace (Model Nebertherm, Germany), Thermostatic water bath shaker (Model Grant GLS 400, England), pH meter (HANNA instruments, pH 211), Electronic balance that can measure up to 110 g (Model AFP-110L, ADAM, China), Atomic Absorption spectroscopy (AAS) (Model analytik Jena Nov AA 300, Germany) and UV-visible spectrophotometer (Model DR 5000, Hach USA).

6.1.4. Adsorbents

Avocado and papaya fresh rips were bought from local market in Jimma town. The avocado kernel seeds were taken from the interior part of avocado fruits. The papaya peels were obtained from the outer part of papaya fruits which is normally taken as waste and juniperus procera sawdust was collected from woodwork enterprises that produce furniture in the Jimma town, Oromia.

6.2. Methods

6.2.1. Preparation of stock solution

A stock solution of chromium (VI) with a concentration of 1000 mg/L was prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) in 1000 mL distilled water. The working solution was prepared by diluting the stock solution with distilled water to give the appropriate concentration (10 mg/L) of the solution.

6.2.2. Preparation of untreated adsorbents

The adsorbents that were collected from local area are avocado kernel seeds, papaya peels and sawdust. After avocado kernel seeds were cut into small sizes all of the adsorbents were allowed to be air dried for twenty days in the laboratory. The dried adsorbents, avocado kernel seeds and papaya peels were washed by distilled water and again allowed to be dried for three days. After three days the avocado kernel seeds and papaya peels were dried in the oven at 105 °C for 26 h and 7 h respectively which is the time at which their masses become constant. Then the two adsorbents (i.e., avocado kernel seeds and papaya peels) were grinded and three of them were sieved by the standard test sieve of 150 μ m mesh size before used for adsorption study [84].

6.2.3. Preparation of activated carbon adsorbents

The dried, grinded and sieved biomasses were soaked in sulfuric acid solution at 1:1 (weight/volume). The mixtures were dried in an oven for 24 h at 105 °C. The dried biomasses/ H_2SO_4 mixtures then were put in crucibles and placed in an electrical furnace (Model Nebertherm, Germany) for carbonization.

The heating rate of carbonization was 10 °C/min and continues until the final temperature of 450 °C was reached and it was kept at this temperature for an optimum time of 30 min, 60 min and 90 min for juniperus procera sawdust, papaya peels and avocado kernel seeds respectively [85]. The produced new materials were then cooled down to room temperature. Then they are referred to as “activated carbons” of the precursor.

To remove the impurities, the activated carbons were washed several times with distilled water until the washed water pHs becomes that of the distilled water (nearly 7) [86]. The washed activated carbons were dried at 105 °C for 6 h (i.e., the time at which their constant masses were obtained) in the oven and grinded into fine particles of 150 µm (sieve size).

6.2.4. Determination of concentration of chromium by atomic absorption spectroscopy

Flame atomic absorption spectroscopy was used for the analysis of chromium at the optimized parameters (Table 1) that gave maximum response for the metal ion.

Table 1: Parameters for AAS at which the chromium ion was analyzed

Element	λ / nm	DL/mg.L ⁻¹	SW/ nm	Current/mA	Burner height /mm
Cr	357.9	0.001	0.2	5	8

Where: λ : wave length, DL: detection limit and SW: slit width

6.2.5. Determination of adsorption efficiency

The adsorption efficiency studies were carried out after adjusting the pH values before and after adding a measured mass of the adsorbent of interest into 30 mL of the metal ion solution and shaken in thermostatic water bath shaker (Model Grant GLS 400) at the speed of 200 rpm. Depending on the parameters under study, the pH, adsorbents dose, initial metal ion concentration, contact time or temperature were varied to study the adsorption efficiencies. The residue was filtered after the time of adsorption was completed. The final concentration of chromium left in the filtrates was analyzed using atomic absorption spectrophotometer. Then the adsorption efficiency (%), the amount of Cr (VI) adsorbed at

equilibrium, q_e (mg/g) and at time t (min), q_t (mg/ g), were calculated according to the expressions [87, 88]:

$$\%Cr(VI) \text{ removal} = \frac{(C_o - C_e) \times 100}{C_o} \quad (1)$$

$$q_e = \frac{(C_o - C_e) \times V}{M} \quad (2)$$

$$q_t = \frac{(C_o - C_f) \times V}{M} \quad (3)$$

Where:

C_o = initial concentration (mg/L) (i.e., concentration of Cr (VI) ion before adsorption)

C_e = equilibrium concentration (mg/L) (i.e., concentration of Cr (VI) ion after adsorption)

C_f = final concentration (mg/L) of Cr (VI) ion in solution at time, t (min).

V = volume of solution (L)

M = mass of the adsorbents (g)

6.2.6. Specific surface area determination

The surface areas (S_A) of the adsorbents (m^2/g) were determined by the methylene blue adsorption method. Accordingly, a stock solution of 1000 mg/L was prepared by dissolving 1.127 g Methylene blue (MB) in 1000 mL distilled water [89]. The experimental solution was prepared by diluting the stock solution with distilled water in the range of 10, 15, 20, 25 and 30 mg/L. An adsorption study was carried out by adding 0.4 g of each of the adsorbents in 50 mL of working solutions (10, 15, 20, 25 and 30 mg/L) and agitated for 1 h in a thermostatic water bath shaker at 150 rpm. After adsorption time was completed the adsorbents were removed from the solutions and the final concentration of MB in each solution was determined at 630 nm wave length of UV-visible spectrophotometer that was used to calculate Q_m from the intercepts of the plots of C_e / q_e versus C_e using Langmuir isotherm equation (4) for all of the adsorbents [90]:

$$C_e / q_e = 1/ K_L Q_m + (1/ Q_m) C_e \quad (4)$$

Where q_e is the amount of methylene blue adsorbed (mg/g) at equilibrium, C_e is the equilibrium concentration of methylene blue (mg/L) (i.e., the concentration of methylene blue left after adsorption), Q_m and K_L is Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg) respectively.

The surface areas of the adsorbents were estimated using equation (5) [91]:

$$S_A = (6.023 \times 10^{23} \times A_o \times Q_m) / (100 \times M) \quad (5)$$

Where A_o is the area occupied by one molecule of methylene blue which is $197.2 (A^\circ)^2$ and Q_m is related maximum adsorption capacity of adsorbents. M is the molecular weight of methylene blue [90].

6.2.7. Study of the effect of pH

The study of effect of pH on the adsorption of the metal ion was done by contacting 0.5 g of both the untreated and activated carbon adsorbents with 30 mL of 10 mg/L concentration of Cr (VI) ion solution within buffer solution ranging from pH 1 to 9. The pH of each solution was adjusted to the desire values by drop wise addition of 0.1 M HCl and/or 0.1 M KOH both before and after adsorbents of 0.5 g were added to 30 mL of working solution. The flasks containing the mixture were left in a thermostatic water bath shaker and shaken at 200 rpm and 25 °C for 180 min. The biomasses were removed from the solution by filtration. The residual metal ion concentration left in the solutions was analyzed. Then the optimum pH was determined as the pH with the highest adsorption efficiency of metal ion.

6.2.8. Study of the effect of adsorbents dose

The adsorption of Cr (VI) ion by untreated and activated carbons of avocado kernel seeds, papaya peels and saw dust at different adsorbent doses in the range of 0.1-0.7 g was investigated. This was carried out by adding a weighed mass of adsorbents (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g) in 30 mL of 10 mg/L Cr (VI) by keeping other variables constant (at optimal pH of US, UA, UP and ACS 1, but for ACA 2 and for ACP 3, shaking speed = 200 rpm, contact time = 180 min and temperature = 25 °C). After adsorption time was completed

the adsorbents were removed from the solution and the concentration of residual metal ion in each solution was determined using AAS.

6.2.9. Study of the effect of initial chromium (VI) concentration

In order to determine the effect of initial chromium (VI) concentration on the adsorption efficiency, the batch adsorption study onto all of the adsorbents was done by introducing various chromium concentration (5, 10, 20, 30, 40, and 50 mg/L) of 30 mL in conical flasks keeping constant the pH of US, UA, UP and ACS 1, but for ACA 2 and for ACP 3, adsorbents dose (0.5 g), shaking speed (200 rpm), contact time (180 min) and temperature (25 °C). Then conical flasks were left in a thermostatic water bath shaker and shaken. After adsorption time was completed the adsorbents were removed from the solution and the concentration of residual metal ion in each solution was determined using AAS.

6.2.10. Study of the effect of contact time

The adsorption of Cr (VI) ions by untreated and activated carbon adsorbents were studied at various adsorption times (10, 40, 70, 100, 130, 160 and 180 min). This was done by weighing 0.5 g of each of the adsorbents into the conical flasks containing 30 mL of 5 mg/L of Cr (VI) ion solutions at the optimized pH and the flasks were shaken in thermostatic water bath shaker at 200 rpm (25 °C) for various period of time. The solutions in the conical flasks were filtered at different time intervals from the first to the last flask. The filtrates were then taken for analysis using an atomic absorption spectrophotometer.

6.2.11. Study of the effect of temperature

The batch adsorption process was studied at different temperatures (20-45°C) in order to investigate the effect of temperature on the adsorption process by keeping other parameters constant (pH of US, UA, UP and ACS at 1, pH of ACA at 2, pH of ACP at 3, adsorbents dose: 0.5 g and 5 mg/L of Cr (VI) ion) at 200 rpm for 160 min.

6.2.12. Preparation of real sample

Effluent at discharge point from Mojo tannery (which is a private leather tanning industry in Mojo, Oromia) was collected. To study the efficiencies of the adsorbents for the removal of chromium from the effluent which had pH 4.95 and 4085 mg/L initial chromium concentration, 30 mL of effluent was measured and added into equal (50 mL) conical flasks and the pH was adjusted to their corresponding optimum values (US, UA, UP and ACS of pH 1, ACA of pH 2 and ACP of pH 3) by drop wise addition of 0.1 M HCl and/or 0.1 M KOH before and after addition of 0.5 g of both kinds of adsorbents (i.e., untreated and activated carbon adsorbents) within buffer solution. Then they were shaken in thermostatic water bath shaker at the speed of 200 rpm and temperature of 40 °C for 160 min. After completion of the shaking time the solutions were filtered and made ready for analysis but since the chromium concentration (4085 mg/L) initially in the effluent was high in order to study the efficiencies of the adsorbents for this real sample, the solutions were diluted by taking 100µL in 50 mL volumetric flask and analyzed using AAS.

6.2.13. Statistical analysis

Triplicate measures were considered during the determination of Cr (VI) ion using AAS and the obtained results were analyzed by averaging the values. The curve fittings of the data obtained were performed using Microcal Origin 8.0 software.

7. Results and Discussion

In this batch adsorption experiment, different parameters such as effect of pH, adsorbents dose, initial chromium (VI) ion concentration, contact time and temperature were studied in order to determine the efficiencies of adsorbents to remove chromium both from aqueous solution and wastewater. The data collected from these studies is used to describe the responsible adsorption isotherm models and to assess the kinetic and thermodynamic of the adsorption of chromium (VI) onto some selected local adsorbents. The specific surface areas of the adsorbents were also determined.

7.1. Specific surface area

The specific surface area of adsorbent is the ratio of its surface area to its mass and the measured surface area is mainly based on the amount of surface exposed particles. The extent of adsorption is usually relative to specific surface area of adsorbent available [92]. The surface areas (S_A) of the adsorbents (m^2/g) that were determined by the methylene blue adsorption method are shown in Table (2) below and the results obtained revealed that the adsorption capacity of the adsorbents increases with increasing specific surface area as reported in various studies [93, 94].

Table 2: Determined specific surface areas of the adsorbents (m^2/g)

Adsorbents	Surface area (m^2g^{-1})
US	6.25
ACS	33.07
UA	5.04
ACA	8.36
UP	3.67
ACP	3.92

7.2. Effect of pH on adsorption of Cr (VI)

Solution pH is one of the most important parameter that affects adsorption of metal ions by influencing the surface properties of the adsorbents and ionic forms of the chromium solutions [95]. The pH of the chromium solutions were adjusted before and after adding adsorbents and its optimization was carried out by studying the extent of removal of Cr (VI) by a fixed mass (0.5 g) of the adsorbents from 30 mL of 10 mg/L solutions of the Cr (VI) ion in the pH range of 1-9 at 25 °C for 180 min. As it is shown in Figure 1 and 2, maximum adsorption was observed at pH 1 for all of untreated adsorbents (i.e., sawdust = 98.18%, avocado kernel seed = 96.35% and papaya peel = 94.58%) and activated carbon of sawdust (i.e., 99.71%). But for activated carbon of avocado kernel seed at pH 2 was 98.42% and for activated carbon of papaya peel at pH 3 was 95.85%.

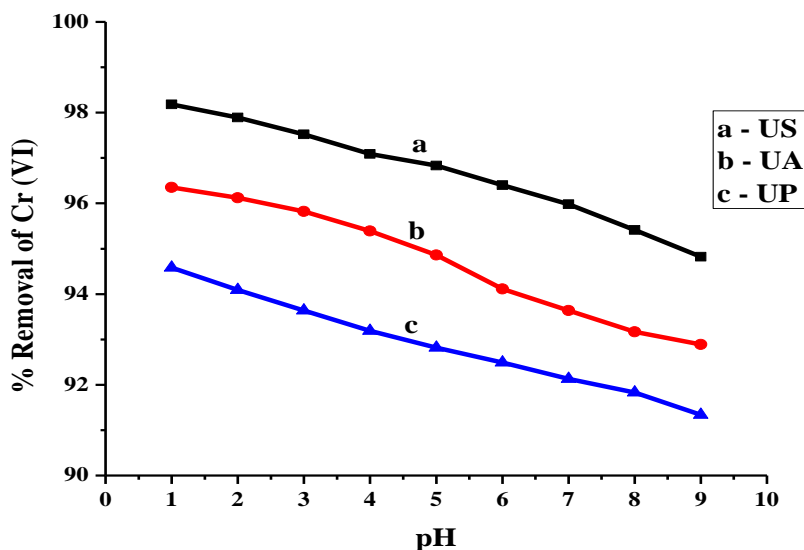


Figure 1: Effect of pH on adsorption of Cr (VI) onto US, UA and UP ([Cr (VI)]:10 mg/L, pH: 1-9, shaking speed: 200 rpm, adsorbents dose: 0.5 g, contact time: 180 min and temperature: 25 °C).

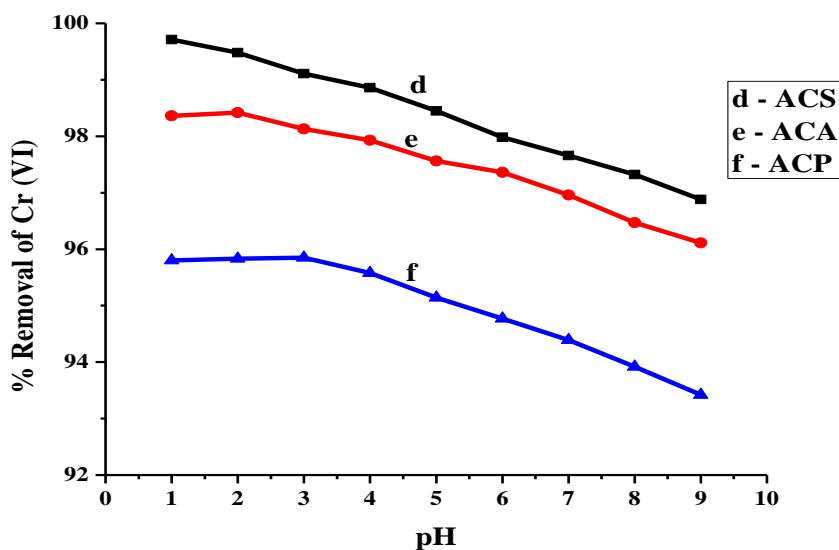


Figure 2: Effect of pH for adsorption of Cr (VI) onto ACS, ACA and ACP ([Cr (VI)]:10 mg/L, pH: 1-9, shaking speed: 200 rpm, adsorbents dose: 0.5 g, contact time: 180 min and temperature: 25 °C).

It was found that adsorption efficiencies of adsorbents were slightly decreased from lower pH values to higher ones. Similar trends were also reported by other investigators [54, 96]. More adsorption at acidic pH indicates that the lower pH results in an increase in H^+ ions on the adsorbents surface that results in significantly strong electrostatic attraction between positively charged adsorbents surface and chromate ions [86]. Lower adsorption of Cr (VI) at maximum pH values may be due to the dual competition of both the chromate anions and OH^- to be adsorbed on the surface of the adsorbents of which OH^- predominates. The favorable effect at low pH can be attributed to the neutralization of negative charges on the surface of the adsorbents by excess hydrogen ions, there by facilitating the diffusion of the hydrogen chromate ion ($HCrO_4^-$) and its subsequent adsorption, because $HCrO_4^-$ is the dominant anionic form of Cr (VI) at lower pH [97].

At pH 1, the chromium ions exist in the form of H_2CrO_4 , while in the pH range of 1-6 different forms of chromium ions such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ coexist of which $HCrO_4^-$ predominates. As pH increases this form shifts to CrO_4^{2-} and $Cr_2O_7^{2-}$.

Chromium exists in different oxidation states and the stability of these forms depends upon the pH of the system [98]. Thus it was found that removal of Cr (VI) ions from solution was strongly dependent up on pH values and in view of these observations, the values of pH (for US, UA, UP & ACS: 1, ACA: 2 & ACP: 3) was taken as the optimum pH for further experimental studies.

7.3. Effect of adsorbents dose

Adsorbents dose variation experiment is one of the significant parts of the study that determines the capacity of adsorbents for a given initial concentration of Cr (VI) at the operating circumstances. Thus the experiments were carried out under the conditions described earlier and varying adsorbents dose only from the range 0.1-0.7 g at 25 °C because of operational cost. The effect of adsorbents dose on the adsorption of chromium (VI) by those adsorbents are shown in Figure 3 and 4 below.

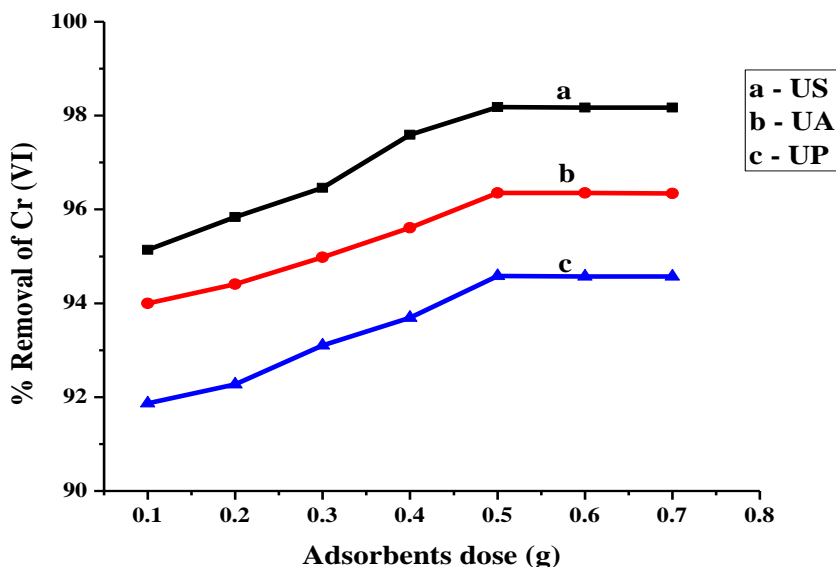


Figure 3: Effect of dose on the removal efficiencies of US, UA and UP ([Cr (VI)]: 10 mg/L, pH: 1 for all, shaking speed: 200 rpm, contact time: 180 min and temperature: 25 °C).

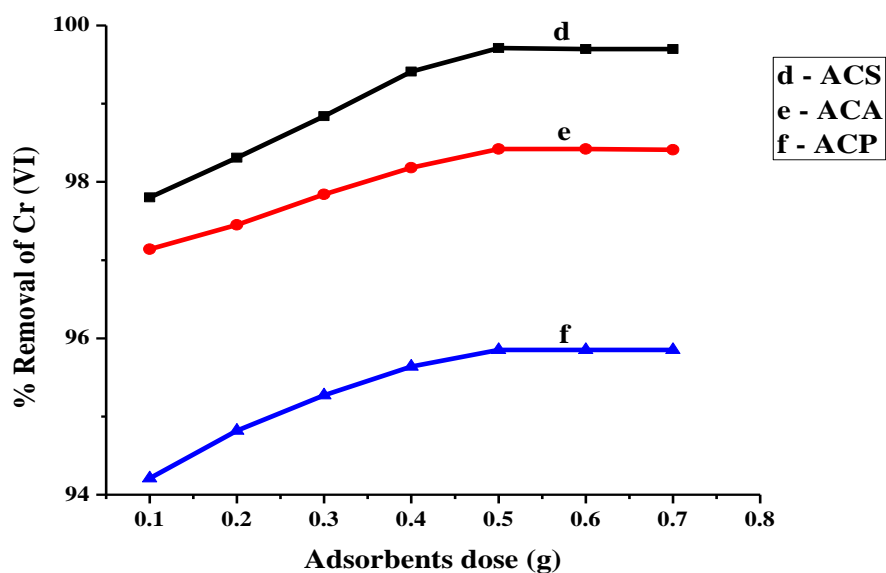


Figure 4: Effect of dose on the removal efficiencies of ACS, ACA and ACP ([Cr (VI)]: 10 mg/L, pH: 1, 2 and 3 for ACS, ACA and ACP respectively, shaking speed: 200 rpm, contact time: 180 min and temperature: 25 °C).

As it is illustrated in Figure 3 and 4, the Cr (VI) removal efficiencies increases with increase in adsorbents dose and reach a saturation level at high doses (i.e., starting from 0.5 g of the adsorbents) for both of untreated and activated carbon adsorbents. The increase of removal efficiencies with increase of adsorbents mass until 0.5 g is because contact surface of adsorbents particle increase for adsorbate and it would be more probable for HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions to be adsorbed on adsorption sites and also the remained constant removal efficiencies at adsorbents quantities higher than 0.5 g is probably because of the resistance to mass transfer of Cr (VI) from bulk liquid to the surface of the solids [99].

Various reasons have been also suggested to explain the steady in adsorption efficiencies at maximum adsorbents dose including availability of solute, electrostatic interaction and interference between binding sites [100]. Explicitly stated the number of adsorption sites per unit mass of an adsorbents remains constant or in other words the effective surface area of adsorbents decreases. Similar results have been reported in the study on adsorption of Cr (VI) and Ni (II) [97, 101].

7.4. Effect of initial chromium (VI) concentration

The uptake of chromium on untreated and activated carbon adsorbents was studied at optimal pH values, the adsorbents dose of 0.5 g, shaking speed (200 rpm), contact time (180 min) and temperature of 25 °C. The initial chromium concentrations studied were (5, 10, 20, 30, 40 and 50 mg/L) and the percentage of sorption is given in the following Figures.

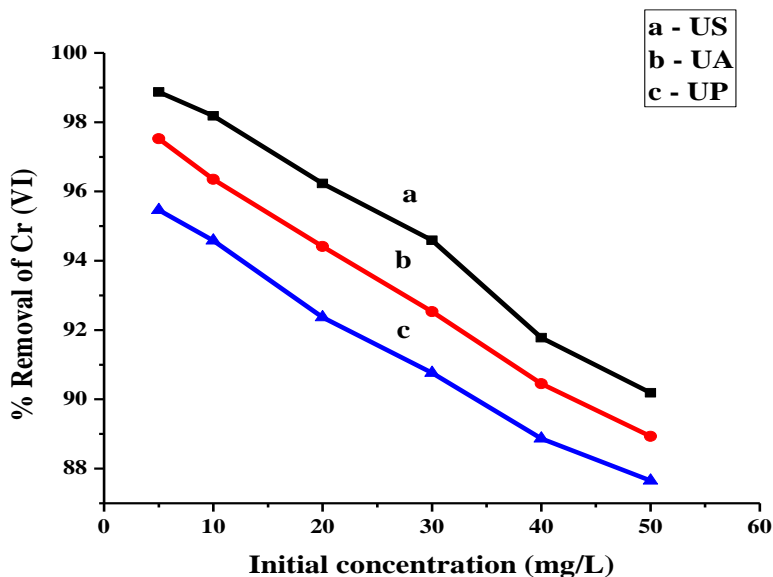


Figure 5: Effect of initial concentration on the removal of Cr (VI) by US, UA and UP (pH: 1 for all, shaking speed: 200 rpm, adsorbents dose: 0.5 g, contact time: 180 min and temperature: 25 °C).

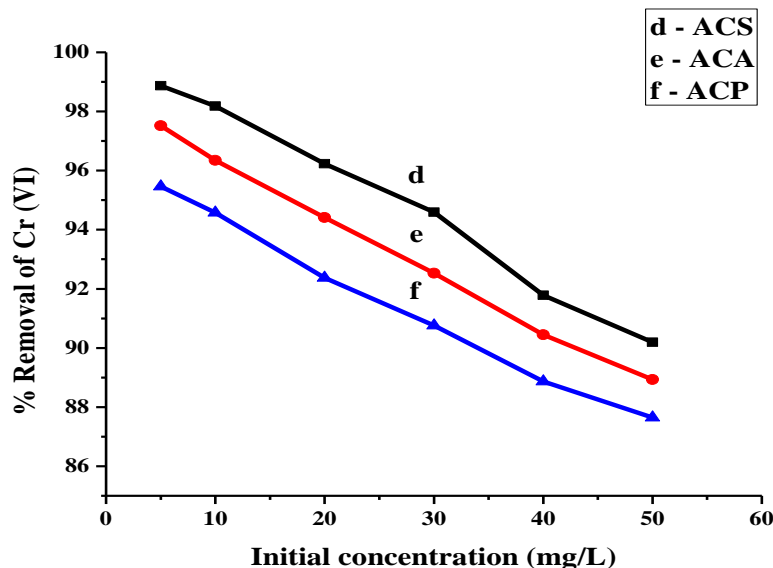


Figure 6: Effect of initial concentration on the removal of Cr (VI) by ACS, ACA and ACP (pH: 1, 2 and 3 for ACS, ACA and ACP respectively, shaking speed: 200 rpm, adsorbents dose: 0.5 g, contact time: 180 min and temperature: 25 °C).

As it is shown in Figure 5 and 6, the effect of initial chromium (VI) concentration on the removal efficiencies of adsorbents were determined and the percentage of Cr (VI) ions adsorption was decreased with increasing initial concentration from 5-50 mg/L. This is because at lower concentration there are sufficient active sites that the sorbate can easily occupy. However, at higher concentrations, active sorption sites are not sufficiently available for the sorbate to occupy. Hence, Cr (VI) ions were not completely adsorbed from solutions due to the saturation of binding sites. In addition, the electrostatic repulsion between negative charges of adsorbate ions results in the decrease of the adsorption percentage [97]. These results are consistent with other investigators work [102].

7.5. Effect of contact time

One of the most important parameter that the amount of metal ion adsorbed depends also is that the contact time taken for adsorption equilibrium to be established which should be as small as possible so that it can be used to remove contaminants in lesser time. Thus, for removal of pollutants, one looks to adsorbents that showing fast adsorption kinetic. The time dependent behavior of Cr (VI) uptake adsorption onto the adsorbents was measured by

varying the contact time in the range of 10-180 minutes and the following results were obtained.

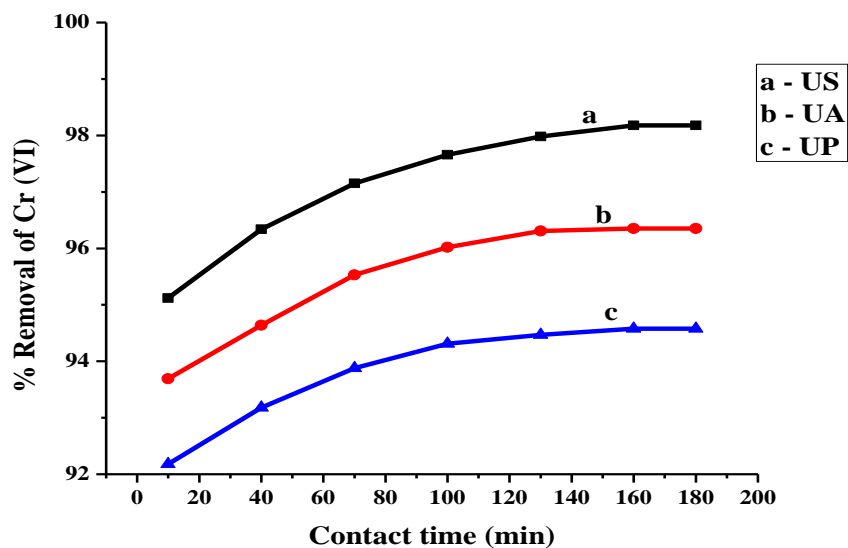


Figure 7: Effect of contact time on the Cr (VI) removal by US, UA and UP ([Cr (VI)]: 5 mg/L, pH: 1 for all and shaking speed: 200 rpm, adsorbents dose: 0.5 g and temperature: 25 °C).

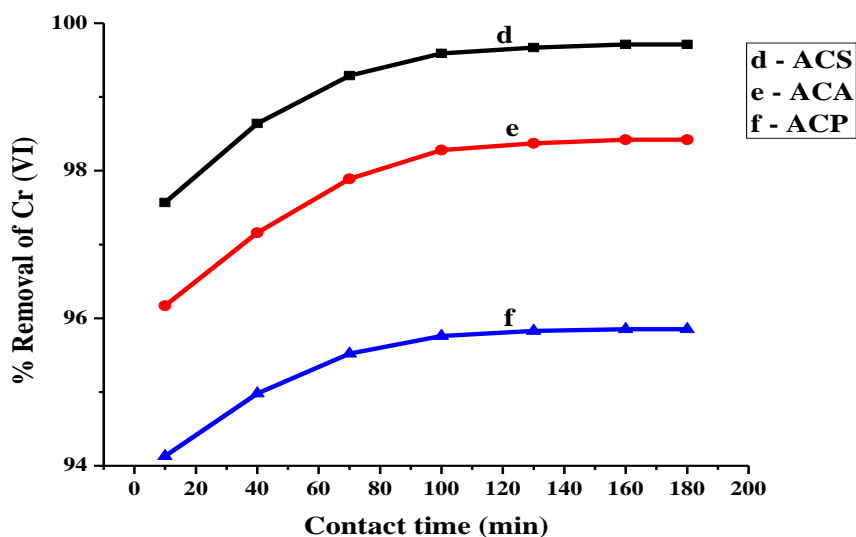


Figure 8: Effect of contact time on Cr (VI) removal by ACS, ACA and ACP ([Cr (VI): 5 mg/L, pH: 1, 2 and 3 for ACS, ACA and ACP respectively, shaking speed: 200 rpm, adsorbents dose: 0.5 g and temperature: 25 °C).

The adsorption efficiencies of Cr (VI) removal by these adsorbents found to increase with increase in contact time and maximum percentages of adsorption occurred at 160 min as indicated in Figure 7 and 8 for all of the adsorbents and thereafter, it becomes constant. The initial rapid rate of adsorption may be due to the availability of the vacant surfaces of the adsorbents for anionic Cr (VI) species removal present in the solution. The later slow adsorption rate could be due to the electrostatic hindrance caused by already adsorbed adsorbate species and the slow pore diffusion of the ions [103]. In general, by the time adsorption involves a surface reaction process, the initial rate of adsorption is fast. Then a slower adsorption would follow as the available adsorption sites which are slowly decreased. This is due to the fact that a huge number of unoccupied surface sites are available for adsorption during the initial stage and after ascend of time the remaining unoccupied surface site are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [104]. Then from the results obtained the optimum contact time for adsorption onto adsorbents was fixed to be 160 min.

7.6. Effect of temperature

Temperature is an important parameter to determine the thermodynamic of adsorption process. Accordingly, because of high operational cost, the percentage of Cr (VI) adsorption was performed as a function of temperature only in the range of 20 °C-45 °C onto both untreated and activated carbon adsorbents and the results obtained are presented in Figure 9 and 10.

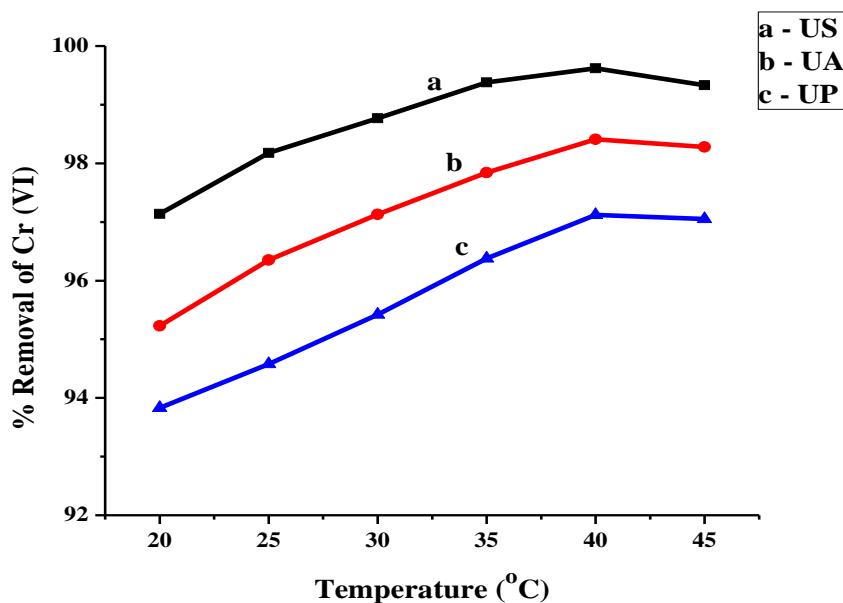


Figure 9: Effect of temperature on Cr (VI) removal by US, UA and UP ([Cr (VI): 5 mg/L, pH: 1 for all, shaking speed: 200 rpm, adsorbents dose: 0.5 g, contact time: 160 min).

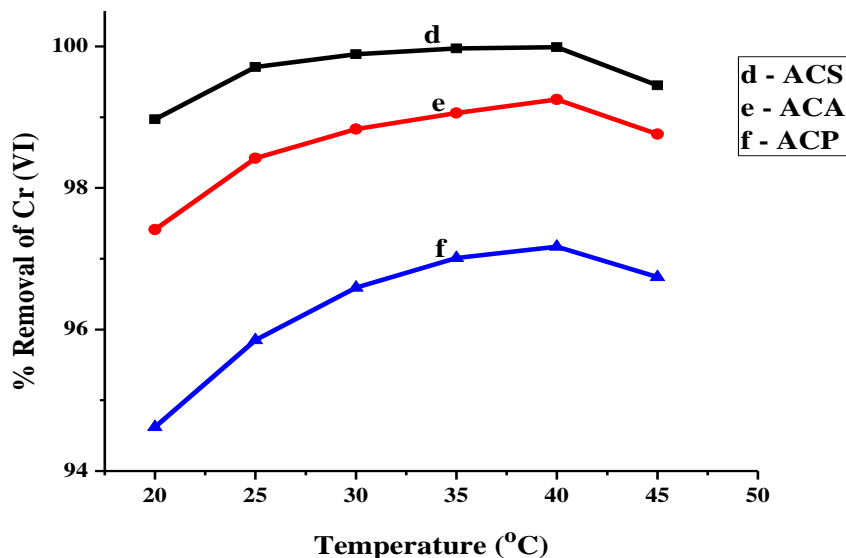


Figure 10: Effect of temperature on chromium (VI) removal by ACS, ACA and ACP ([Cr (VI): 5 mg/L, pH: 1, 2 and 3 for ACS, ACA and ACP respectively, shaking speed: 200 rpm, adsorbents dose: 0.5 g, contact time: 160 min).

The percent removal of Cr (VI) was generally increased with increase of temperature from 20 °C-40 °C and shown decreasing after 40 °C when the other conditions were kept constant. It was observed that the adsorption efficiencies increased from 98.18% to 99.24% for US, 96.35% to 97.22% for UA, 94.58% to 95.44% for UP and 99.71% to 99.98% for ACS, 98.42% to 99.50% for ACA and 95.85% to 96.34% for ACP as the temperature was increased from 25 °C to 40 °C. The enhancement in the adsorption efficiencies for some range of temperature may be due to the chemical interaction between adsorbate and adsorbents, creation of some new adsorption sites or the increased rate of intraparticle diffusion of Cr (VI) ions into the pores of the adsorbents at higher temperatures. The decrease in percentage of adsorption after temperature of 40 °C may be due to desorption caused by an increase of the available thermal energy that may damage the active binding sites of adsorbents. Higher temperature induces higher mobility of the adsorbate causing desorption [105, 106].

7.7. Adsorption isotherm 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 [97]. The adsorption capacity and also the performance of the adsorbents were usually predicted from equilibrium sorption isotherm [107]. It also reported that adsorption isotherm is very useful in choosing the best adsorbent for adsorption or purification need. Several models describe the process of adsorption. Although many theories of adsorption have been put forward to explain the phenomena of adsorption, the isotherms of Langmuir and Freundlich have been widely used by several researchers [38].

The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbents and it represents the equilibrium distribution of metal ions between the solid and liquid phases. The basic assumption of the Langmuir adsorption process is the formation of a monolayer for adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbents surface, i.e. the adsorptive sites (surface of untreated and activated carbon adsorbents) are made up of small heterogeneous adsorption patches that are homogeneous in themselves. The activation of adsorption sites takes place, leading to increased adsorption probably through the surface exchange mechanism [106].

The linear forms of the Langmuir and Freundlich isotherms are represented by the equations (6) and (7):

Langmuir isotherm equation:

$$C_e / q_e = 1/ K_L Q_m + (1/ Q_m) C_e \quad (6)$$

Where q_e is the amount of Cr (VI) ion adsorbed (mg/g) at equilibrium, C_e is the equilibrium concentration of the adsorbate (mg/L) (i.e., the concentration of Cr (VI) ion left after adsorption), Q_m and K_L is Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg) respectively.

Freundlich isotherm equation:

$$\text{Log } q_e = \log K_F + 1/n \log C_e \quad (7)$$

Where q_e is the amount of Cr (VI) ion adsorbed (mg/g) at equilibrium, K_F is the Freundlich constant, n is the heterogeneity factor which is related to the capacity and intensity of the adsorption and C_e is the equilibrium concentration (mg/L). Value of $1/n$ ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface. The isotherm constants of Langmuir and Freundlich were calculated from the slope and intercept of the plots of C_e / q_e versus C_e and $\log q_e$ versus $\log C_e$ respectively [105].

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L , known as the separation factor, as given by equation (8):

$$R_L = 1 / (1 + K_L C_o) \quad (8)$$

Where K_L is Langmuir constant and C_o is the highest initial Cr (VI) ion concentration (mg/L) (i.e., concentration of Cr (VI) ion before adsorption). The value of R_L provides information as to whether the adsorption is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [108].

In this study, adsorption equilibrium data were fitted to the Langmuir and Freundlich isotherms. However, the experimental data were found to fit well to the Freundlich isotherm as indicated by the higher, R^2 , values (Table 3 and Figure 11-22).

Table 3: Results of isotherm models for the adsorption of Cr (VI) ions onto untreated and activated carbon adsorbents at a temperature of 25 °C.

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants			R_L at 50 mg/L
	Q_m	K_L	R^2	K_F	n	R^2	
US	16.03	3.0303	0.968	1.2823	2.049	0.996	0.0066
ACS	27.93	2.801	0.957	1.6032	2.849	0.968	0.0071
UA	10.08	3.367	0.963	1.0162	1.724	0.998	0.0059
ACA	17.67	2.967	0.971	0.5559	1.219	0.992	0.0067
UP	7.16	3.861	0.966	0.8109	1.508	0.997	0.0052
ACP	9.86	3.322	0.980	0.8872	1.672	0.988	0.0060

The Freundlich constant, n , is a measure of the deviation of the adsorption from linearity. The adsorption is linear if the value of n is equal to unity. If the value of n is less than unity, it implies that the adsorption process is unfavorable and if the value of n is more than unity, adsorption is favorable [109]. In the present study, the values of n at equilibrium were more than unity, this suggesting that the adsorption process is favorable. Besides, the values of the dimensionless factor, R_L , were between 0 and 1. This also suggested a favorable adsorption between adsorbents and Cr (VI) ion.

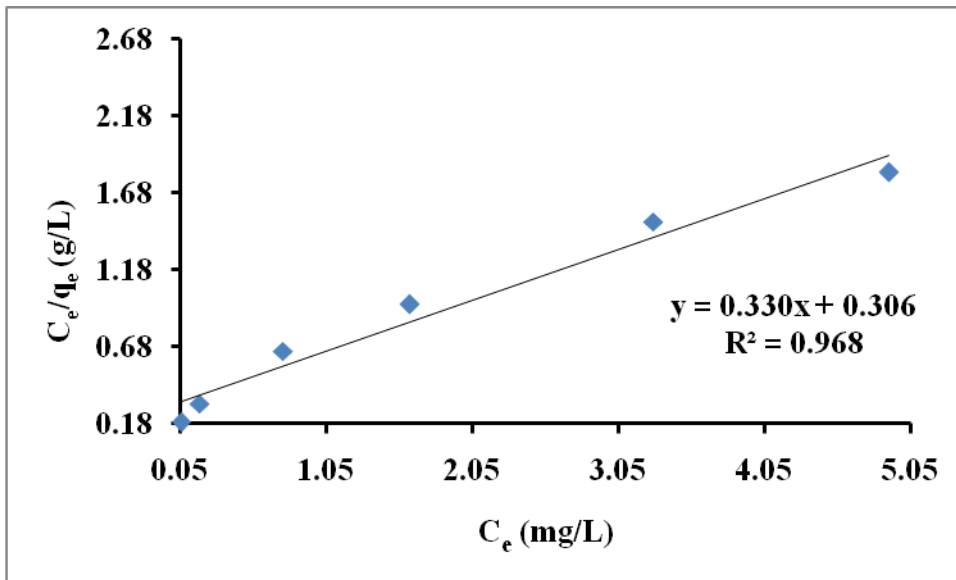


Figure 11: Langmuir plot of chromium (VI) loaded onto US (pH: 1; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

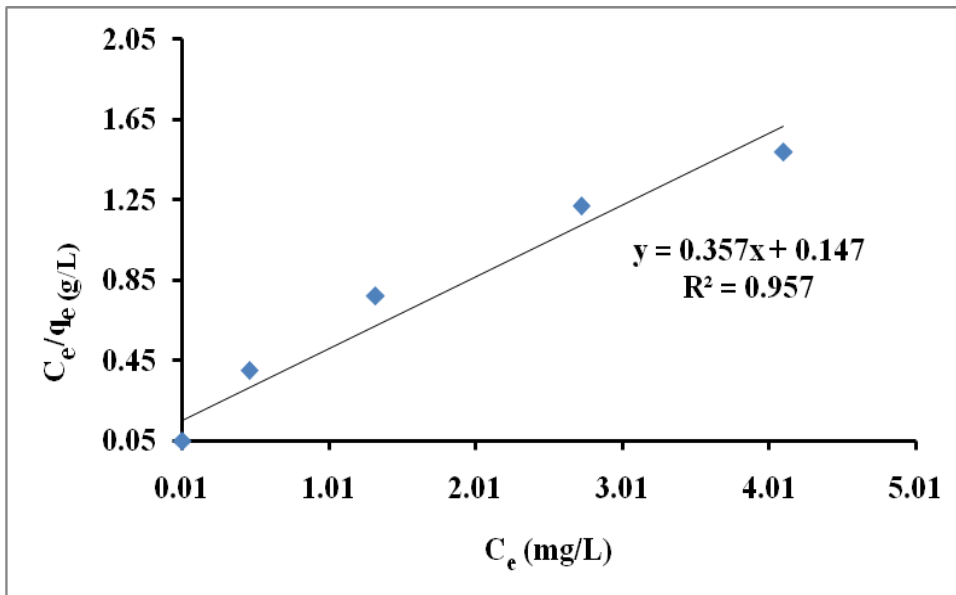


Figure 12: Langmuir plot of chromium (VI) loaded onto ACS (pH: 1; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

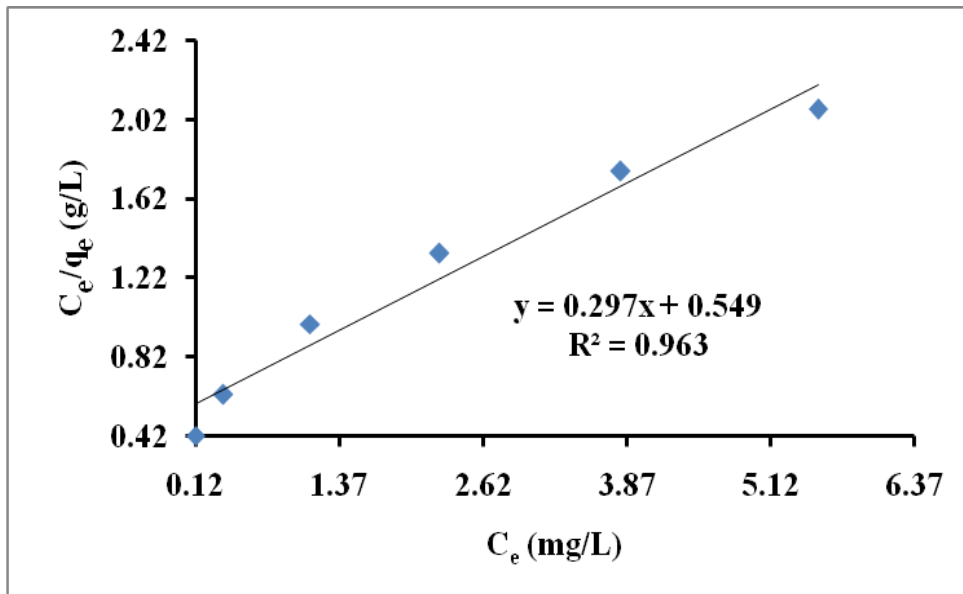


Figure 13: Langmuir plot of chromium (VI) loaded onto UA (pH: 1; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

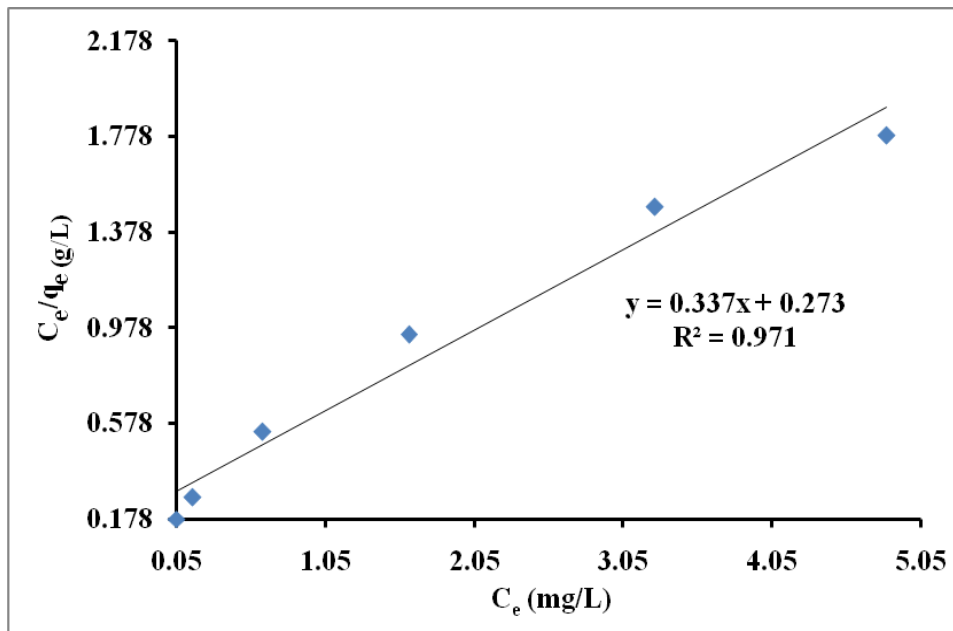


Figure 14: Langmuir plot of chromium (VI) loaded onto ACA (pH: 2; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

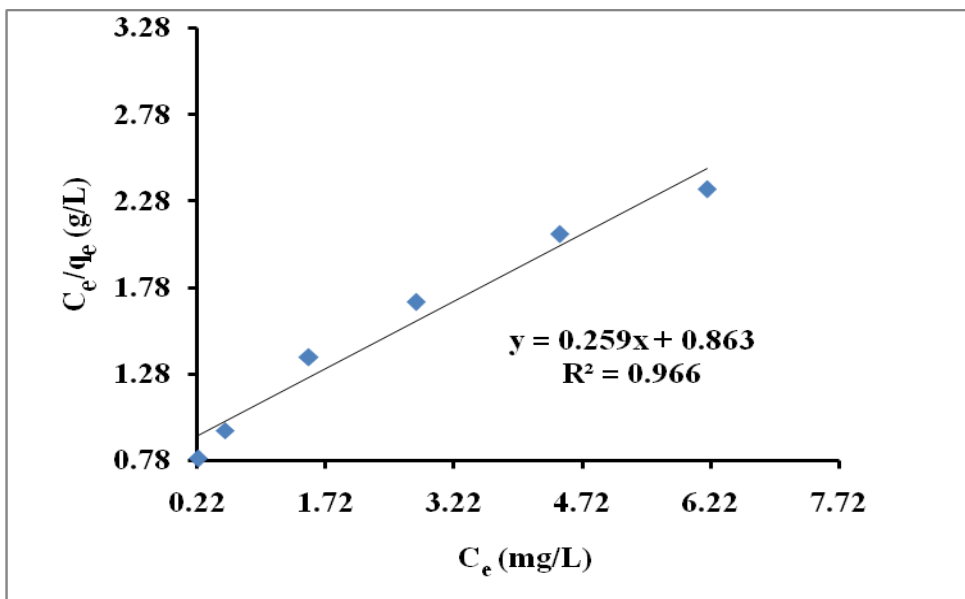


Figure 15: Langmuir plot of chromium (VI) loaded onto UP (pH: 1; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

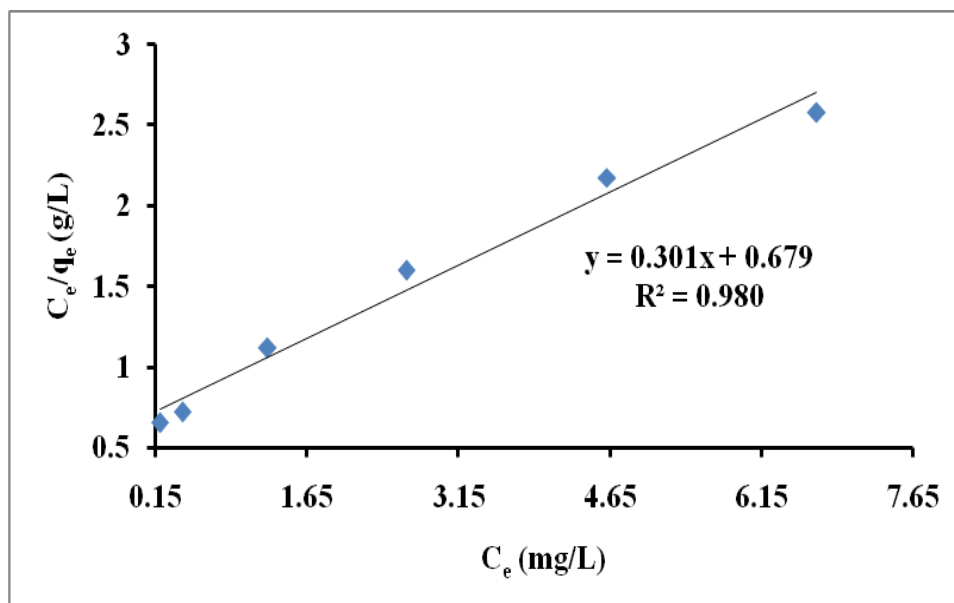


Figure 16: Langmuir plot of chromium (VI) loaded onto ACP (pH: 3; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

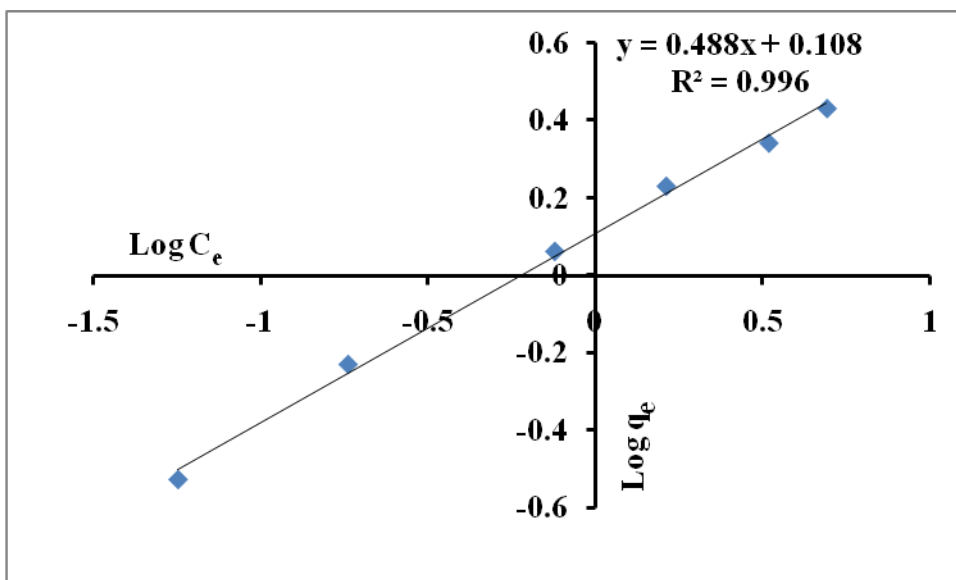


Figure 17: Freundlich plot of chromium (VI) loaded onto US (pH: 1; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

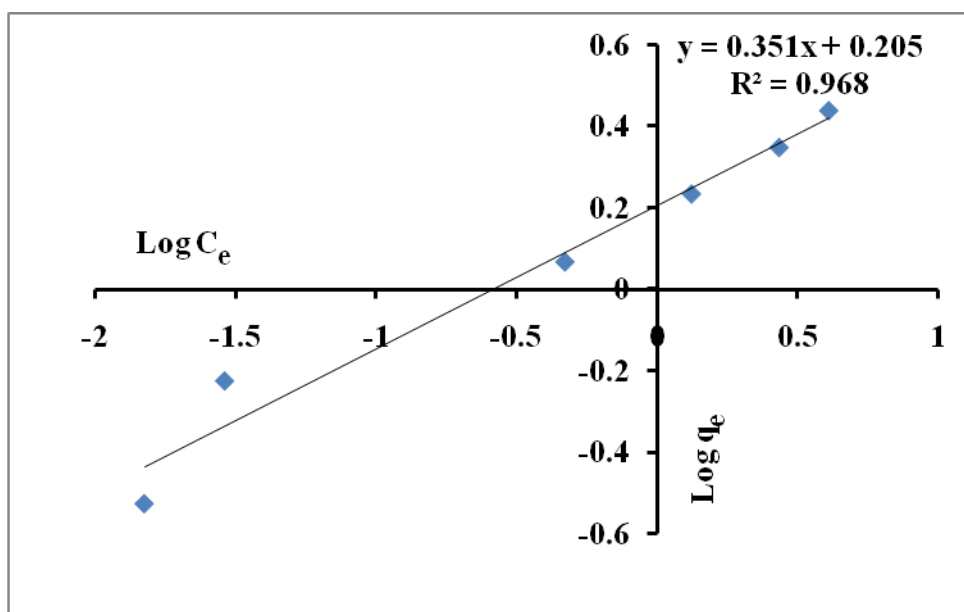


Figure 18: Freundlich plot of chromium (VI) loaded onto ACS (pH: 1; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

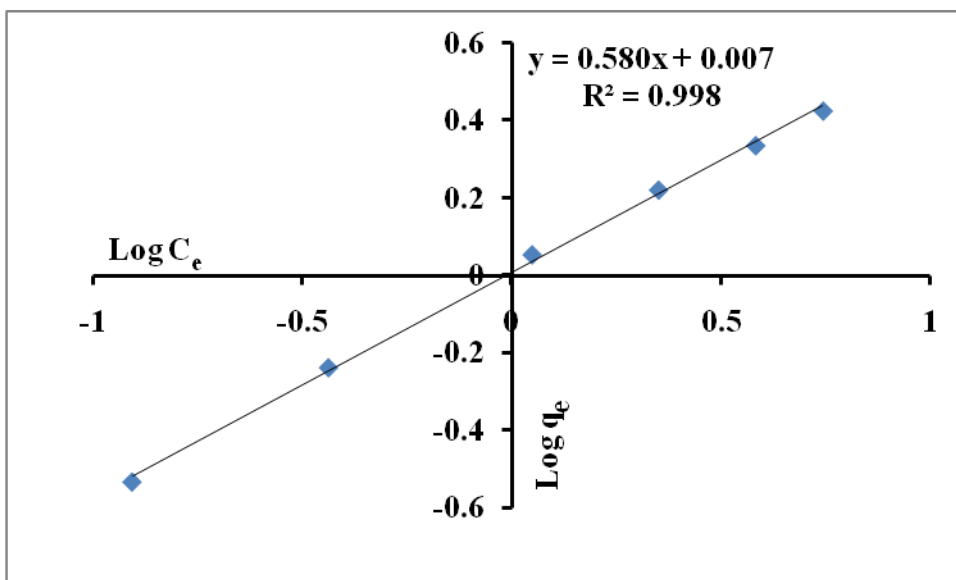


Figure 19: Freundlich plot of chromium (VI) loaded onto UA (pH: 1; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

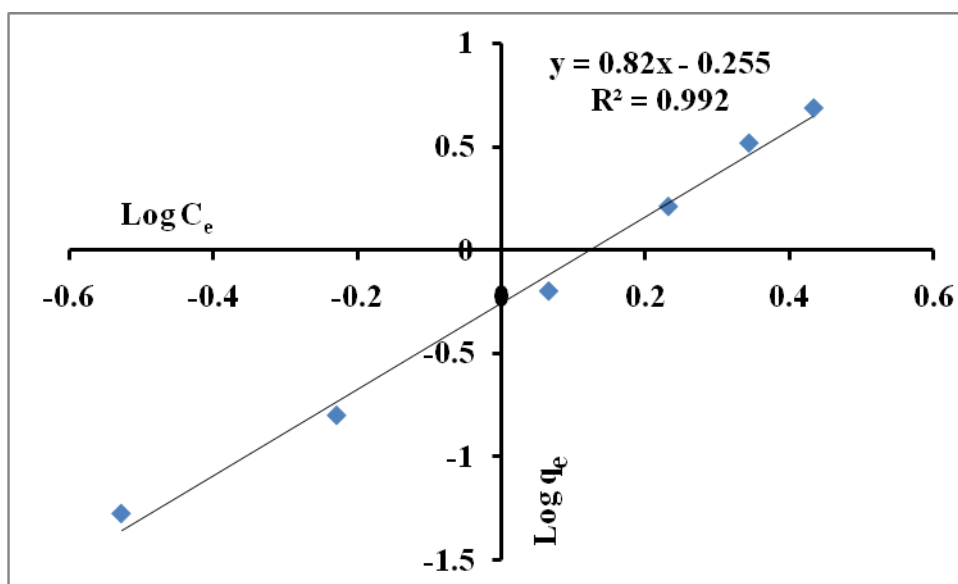


Figure 20: Freundlich plot of chromium (VI) loaded onto ACA (pH: 2; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

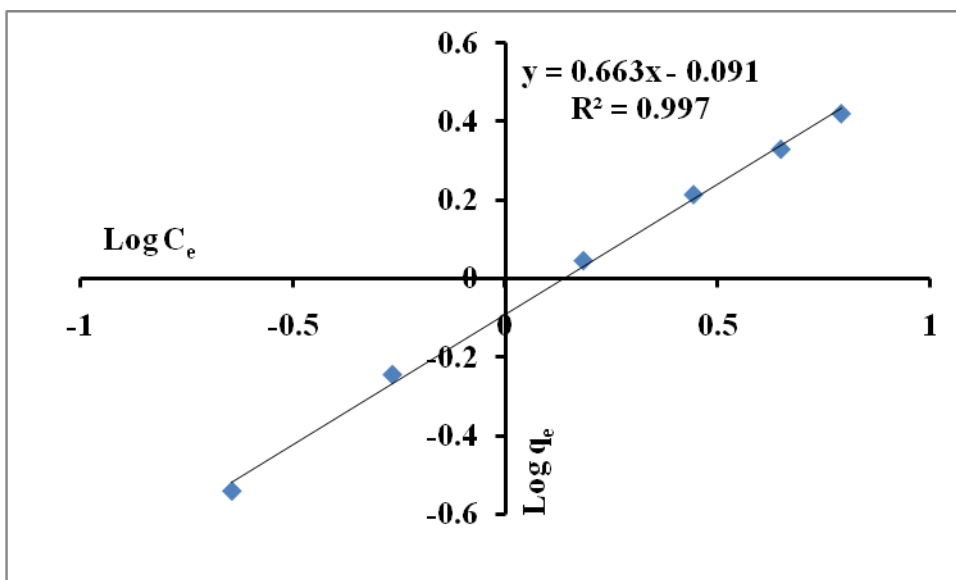


Figure 21: Freundlich plot of chromium (VI) loaded onto UP (pH: 1; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

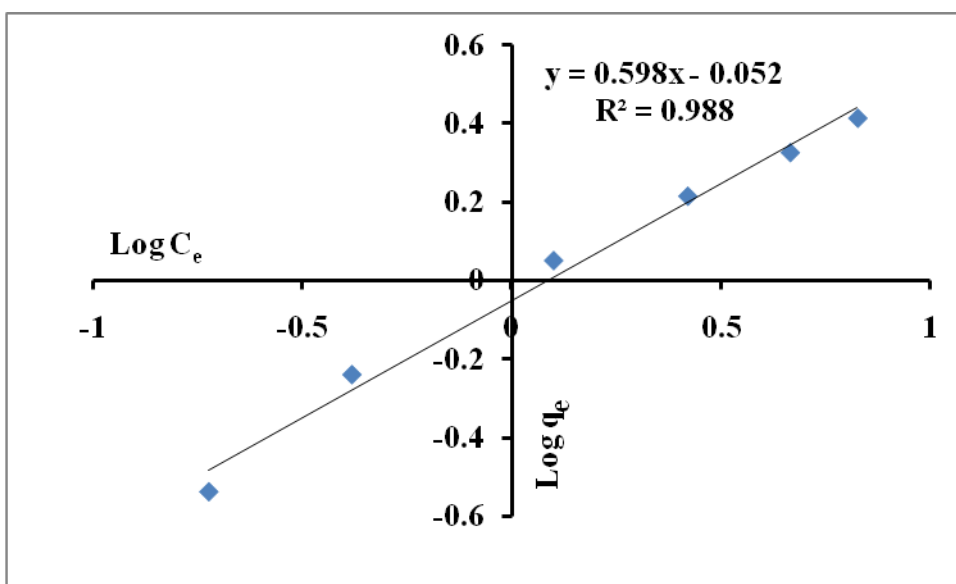


Figure 22: Freundlich plot of chromium (VI) loaded onto ACP (pH: 3; adsorbent dose: 0.5 g; shaking speed: 200 rpm; contact time: 180 min and temperature: 25 °C).

7.8. Adsorption kinetic study

A kinetic study can determine the equilibrium time required for the uptake of metals from a liquid solution. Various kinetic models can be suggested for an adsorption including the Lagergren pseudo-first order kinetic, pseudo-second order kinetic, liquid diffusion model and intraparticle diffusion model [110]. In many cases, the kinetics of adsorption by any biological material has been described by pseudo-first order kinetic to explain the mechanism of the adsorption process, as given by the Lagergren equation [111]. However, it has also been shown that a pseudo-second order approach can sometimes provide a better description of the adsorption kinetics [112].

The pseudo-first order equation is:

$$\text{Log } (q_e - q_t) = \log q_e - (K_1 / 2.303) t \quad (9)$$

The pseudo-second order equation is:

$$1/q_t = 1/K_2 q_e^2 + (1/q_e) t \quad (10)$$

Where: q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is the mass of metal at time t (min), K_1 the first-order reaction rate constant of adsorption (1/min) and K_2 the pseudo-second order rate constant of adsorption (mg/g min). The values of K_1 and q_e were calculated from the slope and intercept of the plot of $\log (q_e - q_t)$ versus t while the values of K_2 and q_e were evaluated from the intercept and slope of a plot of t / q_t versus t respectively [111].

The experimental results for the adsorption of Cr (VI) ions onto both types of adsorbents showed rapid initial adsorption rate followed by a slower rate. Initially, the adsorption sites are open and the metal ions interact easily with the sites and hence a higher rate of adsorption is observed. Moreover, the driving force for adsorption (the concentration difference between the bulk solution and the solid-liquid interface) is higher initially and this leads to a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of adsorbate into the interior of the adsorbents [113].

The two adsorption kinetic models mentioned above have been used to understand the adsorption kinetics and the correlation coefficient, R^2 , were calculated from these plots. The linearity of these plots indicates the applicability of the two models [84]. These pseudo-first order and pseudo-second order models were calculated by using equations (9) and (10). However, the correlation coefficient, R^2 , values showed that the pseudo-second order model fits better to the experimental data than the pseudo-first order model (Figure 23-26 and Table 4). Therefore, the more fitness described was based on the assumption that the rate limiting step may be physisorption due to the presence of weak forces of attraction between adsorbents and adsorbate. As reported by different investigators the pseudo second-order kinetic model has been successfully applied to several adsorption systems [114, 115].

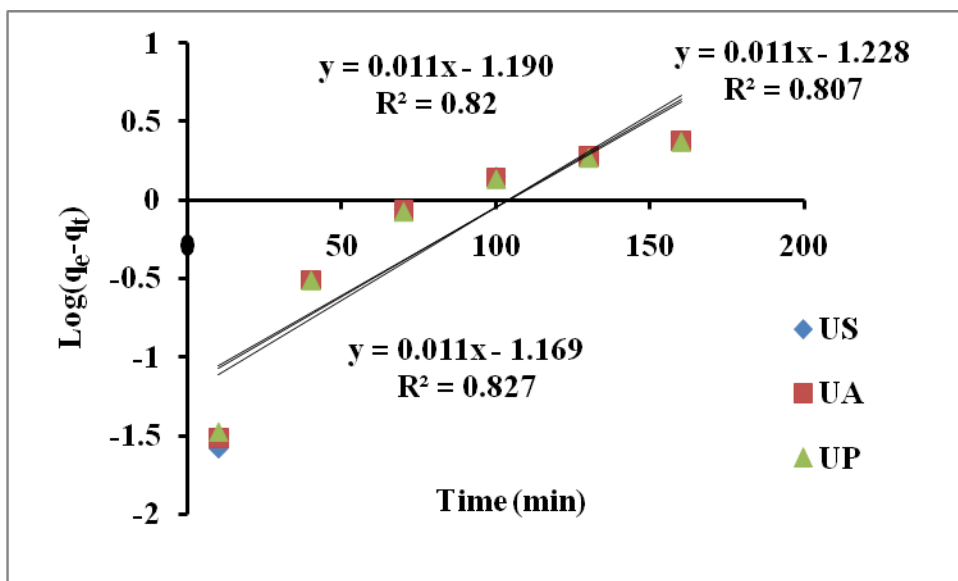


Figure 23: Pseudo-first order plot for Cr (VI) adsorption onto US, UA and UP ([Cr (VI)]: 5 mg/L; pH: 1; adsorbents dose: 0.5 g; shaking speed: 200 rpm and temperature: 25 °C).

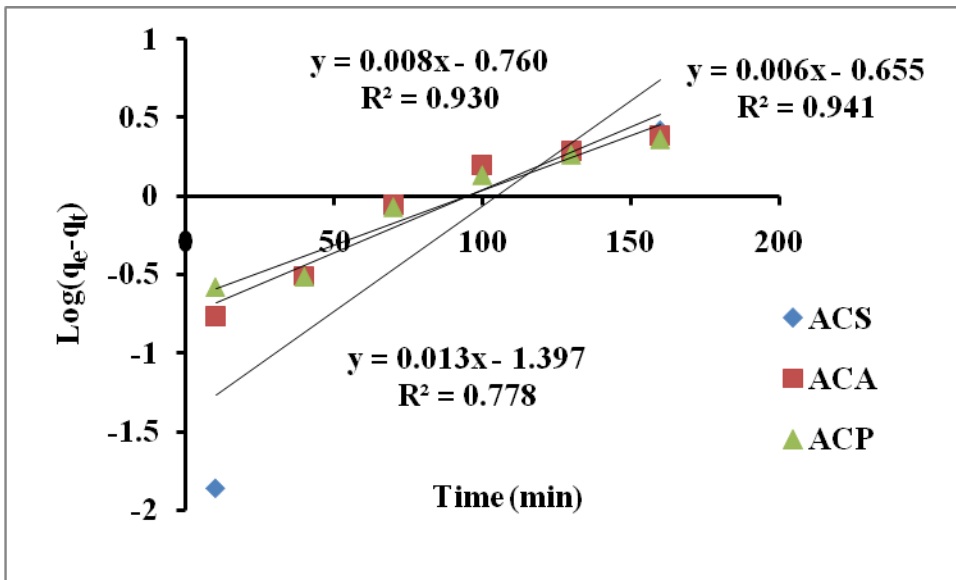


Figure 24: Pseudo-first order plot for Cr (VI) adsorption onto ACS, ACA and ACP ([Cr (VI)]: 5 mg/L; pH: 1, 2, and 3 for ACS, ACA and ACP respectively; adsorbents dose: 0.5 g; shaking speed: 200 rpm and temperature: 25 °C).

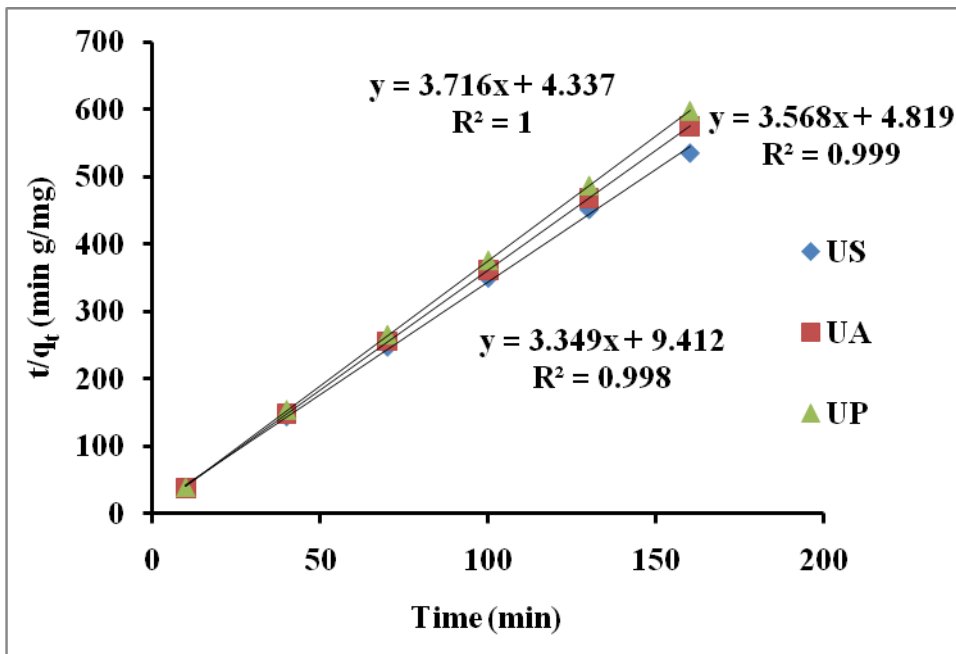


Figure 25: Pseudo-second order plot for Cr (VI) adsorption onto US, UA and UP ([Cr (VI)]: 5 mg/L; pH: 1; adsorbents dose: 0.5 g; shaking speed: 200 rpm and temperature: 25 °C).

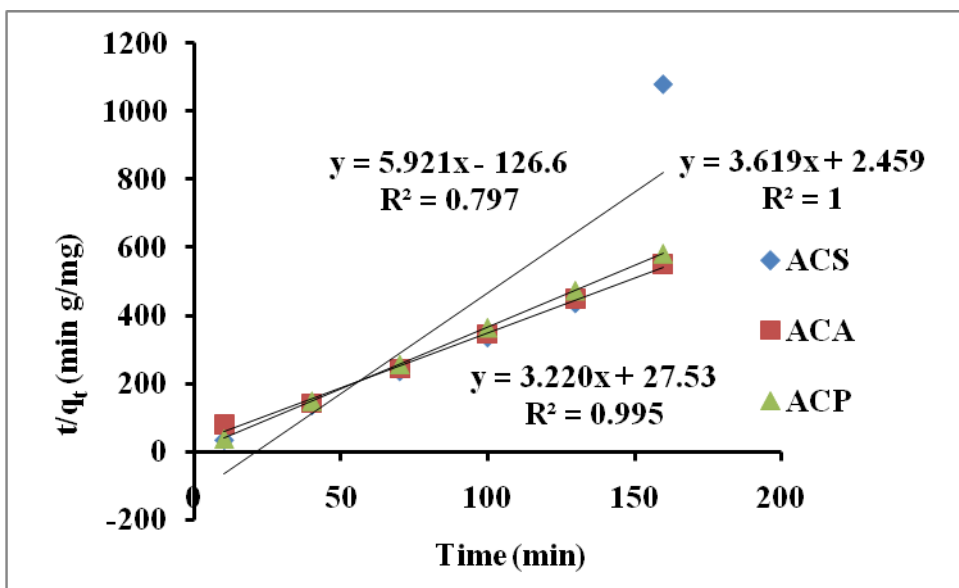


Figure 26: Pseudo-second order plot for Cr (VI) adsorption onto ACS, ACA and ACP ([Cr (VI)]: 5 mg/L; pH: 1, 2, and 3 for ACS, ACA and ACP respectively; adsorbents dose: 0.5 g; shaking speed: 200 rpm and temperature: 25 °C).

Table 4: The adsorption kinetic model rate constants for adsorption of Cr (VI) ions onto both untreated and activated carbon adsorbents at constant temperature of 25 °C.

Adsorbent	Pseudo-first order			Pseudo-second order		
	K_1	q_e	R^2	K_2	q_e	R^2
US	0.0253	0.0592	0.807	1.1916	0.2986	0.998
UA	0.0253	0.0646	0.820	2.6413	0.2803	0.999
UP	0.0253	0.0678	0.827	3.1837	0.2691	1.000
ACS	0.0299	0.0401	0.778	0.2768	0.1689	0.797
ACA	0.0184	0.1738	0.930	0.3106	0.3765	0.995
ACP	0.0138	0.2213	0.941	5.3276	0.2763	1.000

7.9. Adsorption thermodynamic study

The thermodynamic of an adsorption process can be obtained from a study of the influence of temperature on the process. They are necessary to conclude whether the process is spontaneous or not. Standard Gibb's free energy change, ΔG° , is the fundamental criteria of spontaneity.

The standard Gibb's energy change can be computed using the equation:

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

Where: R is universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature in K (Kelvin) and K_c is the thermodynamic equilibrium constant.

The equilibrium constant K_c can be evaluated at each temperature using the relationship:

$$K_c = C_{Ae} / C_e \quad (12)$$

Where: C_{Ae} and C_e is the amount of Cr (VI) ion adsorbed on solid phase at equilibrium and the equilibrium concentration (i.e., concentration of Cr (VI) left in solution after adsorption) in mg/L respectively.

Other thermodynamic parameters such as standard enthalpy change (ΔH°) and standard entropy change (ΔS°) can be calculated using the equation:

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT \quad (13)$$

ΔH° and ΔS° can be obtained from the slope and intercept of the plot of $\ln k_c$ versus $1/T$.

Standard enthalpy change (ΔH°) is used to identify whether the adsorption process is exothermic or endothermic. But standard entropy change determines the disorder of the adsorption at solid-liquid interface [116].

These thermodynamic parameters of the adsorption process were calculated using equations 11-13 above and the calculated values of these parameters is given in Table 5.

Table 5: Thermodynamic parameter results for the adsorption of Cr (VI) ions onto untreated and activated carbon adsorbents at different temperatures.

Adsorbent	ΔH° (kJmol ⁻¹)	ΔS° (kJmol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)					
			293 K	298 K	303 K	308 K	313 K	318 K
US	-57.616	0.22082	-6.83	-8.12	-9.27	-11.2	-12.7	-11.4
UA	-36.898	0.14483	-5.48	-6.29	-7.05	-7.93	-8.89	-8.82
UP	-28.999	0.11498	-4.78	-5.22	-5.78	-6.53	-7.27	-7.03
ACS	-67.102	0.26879	-9.41	-12.7	-15.4	-18.9	-22.2	-11.9
ACA	-28.409	0.12321	-7.08	-8.48	-9.39	-10.1	-10.9	-9.71
ACP	-18.349	0.08132	-5.15	-5.95	-6.59	-7.05	-7.32	-7.04

The negative values of the standard Gibb's energy change (ΔG°) indicate that the feasibility and spontaneous nature of the adsorption process but the negative values of the standard enthalpy change (ΔH°) indicate that the adsorption process was exothermic in nature and a given amount of heat is evolved during the binding of chromium (VI) ions on the surface of adsorbents. The positive values of the standard entropy change (ΔS°) show the increased randomness at solid-liquid interfaces during the adsorption of metal ions onto both untreated and activated carbon adsorbents. Furthermore, it is also suggest that the positive values of entropy indicate that there are some structural changes in the adsorbate and adsorbents [106, 117].

7.10. Adsorption efficiencies of adsorbents on real sample

The efficiencies of both untreated and activated carbon adsorbents toward the removal of chromium were also tested using wastewater which had pH 4.95 and 4085 mg/L initial chromium concentration. Adsorption experiments on this real sample were carried out at three different pH values: at pH 1 (i.e., the optimum pH for US, UA, UP and ACS) and at pH 2 and 3 (i.e., the optimum pH for ACA and ACP respectively). Because of the chromium concentration (4085 mg/L) initially in the effluent was high in order to study the efficiencies

of the adsorbents for this real sample, the solutions were diluted in 50 mL volumetric flask by taking 100 μ L from the solutions filtered for analysis and analyzed using AAS.

To calculate the adsorbents removal efficiencies, the following step wise formulas were used [87, 118].

$$\text{Dilution factor (D)} = V_f/V_i \quad (14)$$

Where V_f is volume of volumetric flask used for dilution and V_i volume of solution taken to be diluted from the filtered solution after adsorption time was completed.

$$C_o = DC_e \quad (15)$$

Where C_o is initial concentration (mg/L) of chromium in the wastewater, D is dilution factor and C_e is the final concentration (mg/L) of chromium left in the diluted wastewater solution.

$$C_f = DC_e \quad (16)$$

Where D is dilution factor, C_f is final concentration (mg/L) of chromium left in the solutions which were not diluted after adsorption time was completed and C_e is the equilibrium concentration (mg/L) (i.e., the final concentration of chromium left in the diluted solutions other than diluted wastewater). Then the removal efficiencies of adsorbents were calculated using the formula:

$$\%Cr \text{ (VI) removal} = [(C_o - C_f) \times 100]/C_o \quad (17)$$

Where C_o is initial concentration (mg/L) of chromium in the wastewater and C_f is final concentration (mg/L) of chromium left in the solutions which were not diluted after adsorption time was completed.

As the chromium concentration in the effluent was high, the adsorption analyses by AAS were carried out after diluting 500 times. Even after diluting the effluent solution, it was still very concentrated. That is why percent adsorptions tabulated (Table 6) below seem small and the final concentration of chromium were high in case of all adsorbents. So that to bring its concentration into the World Health Organization (WHO) standard of chromium (VI) concentration (0.05 mg/L) in drinkable water, the effluent should be diluted 81700 times before discarding into the environment.

Table 6: Percent removal of chromium from the real sample solution

Adsorbent	Initial conc.(mg/L)	Final conc.(mg/L)	% Removal
US	4085	2687	34.22
UA	4085	3277.5	19.77
UP	4085	3990.5	2.31
ACS	4085	2216	45.75
ACA	4085	2411.5	40.97
ACP	4085	3318.5	18.76

7.11. Comparison of chromium (VI) adsorption capacities of various adsorbents

The adsorptive capacities of the adsorbents used in this work have been compared with other adsorbents reported in the literature as having been examined for the removal of Cr (VI) under similar conditions to those employed in the present work. These have been tabulated in Table (7) below. Thus from the results it is clearly seen that the investigated adsorbents exhibited considerably higher adsorption capacities.

Table 7: Summary of Chromium (VI) adsorption capacities of different adsorbents

Adsorbents	Q _m (mg/g)	References
Rice bran	0.069	[47]
Cooked waste tea	30.39	[48]
Potato peel waste	8.012	[49]
Pre-boiled sunflower stem	4.9	[50]
Formaldehyde treated sunflower	3.6	[50]
Granular activated carbon (GAC)	7.0	[73]
Char of South African Coal (CSAC)	0.3	[73]
Bael fruit (<i>Aegle marmelos correa</i>) shell	17.27	[76]
Untreated juniperus procera Sawdust (US)	16.03	This work
Untreated Avocado kernel seeds (UA)	10.08	This work
Untreated Papaya peels (UP)	7.16	This work
Activated Carbon of juniperus procera Sawdust (ACS)	27.93	This work
Activated Carbon of Avocado kernel seeds (ACA)	17.67	This work
Activated Carbon of Papaya peels (ACP)	9.86	This work

8. Conclusion and Recommendation

In this study, different locally available adsorbents have been tested for their effectiveness in removing Cr (VI) both from aqueous solution and wastewater. Effects of different parameters such as pH, amount of adsorbents, initial concentration, contact time and temperature were investigated for these selected six adsorbents. The specific surface areas of all of the adsorbents were also determined using methylene blue adsorption method.

The adsorption equilibrium data obtained for removal of Cr (VI) ion onto all kinds of adsorbents were fitted into the Langmuir and Freundlich adsorption isotherms. However, the experimental data for the adsorption process were well fitted to the Freundlich adsorption model relative to the fit of the Langmuir adsorption isotherm model into both untreated and activated carbon adsorbents. The adsorption kinetic data were modeled using the pseudo-first order and pseudo-second order kinetic equations. It was shown that the pseudo-second kinetic order model is suitable for describing the adsorption system than the pseudo-first order model. Different thermodynamic parameters (ΔG° , ΔH° , and ΔS°) have also been evaluated and it has been found that the adsorption was feasible, spontaneous and exothermic in nature. The positive values of the entropy change suggest that the increased randomness at solid-liquid interfaces during the adsorption of metal ion onto adsorbents and also indicate that there are some structural changes in the adsorbate and adsorbents.

The efficiencies of untreated and activated carbon adsorbents (US, UA, UP, ACS, ACA, and ACP) toward the removal of hexavalent chromium were also examined using aqueous Cr (VI) solution and tannery waste effluent and it was found that as they have capacity to remove chromium from both kinds of solutions. But the very important aim is not to dispose chromium into the environment.

Adsorption as a means of remediation technique of heavy metals removal from wastewater has long been studied and different adsorbents were investigated for their removal efficiencies that leading to the development of efficient and economical sorbents. Through process the low cost agricultural waste by-products have been known to be better candidates due to their availability and capacity. This work has also focused on evaluating adsorption efficiencies of various low-cost locally available adsorbents. Therefore, this study will help

to enable people to use these adsorbents environmentally friendly and in easily operational methods in developing countries as alternatives of advanced technologies. Moreover, the study initiates the community to due attention for chemicals disposed nearby the water.

However, the future studies should focus on applicability of these adsorbents to the real situation where large volume of waste effluent is being discharged and also desorption experiments should carry out in order to recover chromium from the adsorbed surface. Additionally, the impact of other ions in the wastewater on the removal efficiencies should also be studied as the real waste effluents composed of a number of other ions.

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