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M.Sc. THESIS ON

REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION USING IRON COATED PUMICE

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TABLE OF CONTENTS

III

LIST OF FIGURES

LIST OF TABLES

LISTS OF ABBREVIATIONS

ASTM   American Society for Testing and Materials

CEC   Cation Exchange Capacity

Cr (III)   Trivalent Chromium

Cr (VI)   Hexavalent Chromium

DF   Dilution Factor

EPA   Environmental Protection Agency

ICP   Iron Coated Pumice

FTIR   Fourier Transform Infrared Spectroscopy

STDV   Standard Deviation

USEPA   United State Environmental Protection Agency

UV-Visible   Ultraviolet Visible Spectrophotometry

VPum   Volcanic Pumices

WHO   World Health Organization

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ABSTRACT

In this study, iron-coated pumice (ICP) was investigated as adsorbent for the removal of Cr (VI). The study employed a batch method to investigate the efficiency of the adsorbent. Parameters that influence adsorption such as: contact time, pH, adsorbent dose, and initial concentration of Cr (VI) have been studied. Optimum parameters for the adsorption of 10 mg/ L Cr (VI) were found to be: pH: 2, adsorbent dose: 10 g/L, and contact time: 4 h. A estimated adsorption capacity of 0.27 mg/L was found at optimal conditions using the Lagmuir adsorption isotherm model prediction. The results of kinetic models showed that the pseudo-second-order kinetic model was found to correlate well to the experimental data. Iron coated pumice is a good and cheap adsorbent with high potential for the adsorption and removal of chromium from contaminated water sources and could therefore serve as effective and efficient material for treating drinking water. In addition, it will help to enable people to use environmentally friendly and easily operational methods in developing countries as alternatives of advanced technologies.

KEYWORDS*: Adsorption, chromium (VI), Pumice, Iron coated pumice, Isotherm, adsorption kinetic.*

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1. INTRODUCTION

1.1 Background of the study

In aquatic systems, chromium can be mainly found as Cr (III) and Cr (VI). These two oxidation states have different chemical, biological and environmental properties. The abundant ratio of Cr (VI) and Cr (III) depends on many effects, such as the redox potential, pH, the presence of oxidizing and reducing compounds, the kinetics of the redox reactions, and the total chromium concentration [1]. Community concerns with chromium are mostly connected to hexavalent compounds, since these are toxic to humans, animals, plants and microorganisms [2]. Cr (VI) species, having movable and powerful oxidant characters, are known as mutagen and potential carcinogenic [3]. In humans, Cr (VI) mostly affects skin, liver, kidney and respiratory organs, resulting in a variety of diseases such as dermatitis, hepatic and renal tubular necrosis, bronchitis, perforation of the nasal septum and bronchogenic carcinoma [4]. Two major sources of Cr (VI) contamination are sludge-treated soil [5] and uncontrolled disposal of wastes [6]. In most developing countries such as Ethiopia, the last is believed to be the major source for chromium pollution in water bodies, since land application of sludge has not been widely practiced [7–9]. The chromium electroplating treatment and tanning industries are the largest sources of Cr (VI) emissions to the environment [10].

Chromium and its compounds are widely used in chromate preparation, electroplating and leather tanning [10], paint and pigments [11], dyeing [12], wood preservatives [13], textile and steel fabrication [14] industries. These industries may release large quantities of toxic metal wastewater effluents above the permissible limit. However, the maximum exit Cr (VI) concentration based on USEPA (United State Environmental Protection Agency) guidelines for portable water is 0.05 mg/L and the United Nation Food and Agricultural Organization recommended maximum level for irrigation water is 0.1 mg/L [15]. The World Health Organization (WHO) has also set the maximum permissible level of 0.05 mg/L for Cr (VI) in drinking water [16].

In general, several treatment technologies have been reported to remove Cr (VI) from water and waste water such as chemical-reduction precipitation, reverse osmosis, ion exchange and electrolysis, solvent extraction and evaporation. However, these methods are not widely used primarily because of their high running costs and inefficiency or failure to treat large volume of waste water [17] and high metal concentrations are the most common [18]. Therefore, the need exists for a purification strategy that is simple, effective and low cost. In this way, adsorption appears as a highly promising alternative to treat such polluted waters. Because of this most of the time more economical means such as adsorption for the removal to toxic metals have been applied [17].

A variety of materials are used as adsorbents for Cr (VI) and various studies have been published documenting its adsorption on natural and commercial materials [19-21]. From the light of these studies adsorption arises as a healthy and multipurpose method that could solve the problems of mud handling and reduce the purification system more economically sound, especially if low cost adsorbents are used. Among natural materials having better features to be used as low- cost adsorbents of heavy metals are volcanic rocks include pumice (Vpum) deposits originate in areas with young volcanic fields. This rock is abundant in many parts of the world including Ethiopia [22]. The potential of volcanic pumice to remove both cationic and anionic ions from aqueous systems has been reported [23-26]. However, the practical applicability of natural pumice is limited due to low efficiency Cr (VI) adsorption [27].

Coating and impregnation of natural adsorbents with some inorganic chemicals enhances their sorption capacity [28, 29]. For instance, aluminum oxide modified pumice was found to be effective for removal of fluoride from drinking water [29]. Pumice coating with iron or manganese improves its As (V) adsorption capacity [30]. A higher As (V) removal efficiency of Aluminum-coated Zeolite compared to aluminum-coated pumice also reported [28]. The studies on the adsorptive removal of Cr (VI) by using pumice is reported in the literature [27]. However, the preliminary tests, in this study revealed that they exhibited poor Cr (VI) adsorption. Therefore, the aim of this study was to investigate iron coated pumice and evaluate Cr (VI) removal efficiency.

1.2 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, various literatures devised different conventional and advanced methods such as chemical precipitation, electrochemical reduction 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 contaminated water using natural and modified adsorbents. Therefore, in this study, a highly applicable adsorbent in the removal of highly toxic chromium (VI) from aqueous solution using iron modified pumice which is locally available with modifications.

1.3 Objectives of the study

1.3.1 General Objective

❖ To investigate the removal of Cr (VI) from aqueous solution by using Iron-coated pumice.

1.3.2 Specific Objectives

➢ To determine the adsorption efficiency and capacity of Iron-coated pumice adsorbents
➢ To optimizes Cr(VI) adsorption parameters such as contact time, pH, adsorbent dose, and initial concentration.
➢ To assess the kinetic and equilibrium isotherm models of the adsorption of Cr (VI) onto the adsorbent.

1.4 Significance of the study

In this study, Iron coated pumice was evaluated for their efficiency and suitability as part of the effort to find less costly and environmentally friendly adsorbents. Successful outcomes of this research would be beneficial to many peoples in Ethiopia and other parts of the world who are suffering from excess Cr (VI) in their drinking waters.

2. LITERATURE REVIEW

2.1 Chemistry of chromium

In aqueous systems, the chromium can be mainly found as Cr (III) and Cr (VI). At low concentrations Cr (III) can be considered a bioelement since it plays an important role in the metabolism of plants and animals. On the contrary, Cr (VI) is hazardous due to its strong oxidizing capacity and it can be adsorbed through the skin. As reported, exposure to excessive amounts of Cr (VI) may cause dermatitis, diarrhea, hemorrhaging and cancer in the digestive tract and lungs [31]. Hexavalent chromium can form several species, found as chromate, CrO_4^{2-}, Hydrogen chromate, $HCrO_4^-$ or dichromate, $Cr_2O_7^{-2}$, depending on both pH of the medium and total Cr (VI) concentration. $HCrO_4^-$ species is more stable in aqueous solution up to 7 beyond which it decreases. H_2CrO_4 species also stable within the low pH range but its concentration decreases sharply in aqueous solution with increasing pH. CrO_4^{2-} is stable in higher pH. Due to this, governments apply enhanced regulation for chromium species. In Croatia, the upper limit for the discharge of Cr (VI) into inland surface waters and public drainage systems is 0.1 mg L^{-1} [32].

2.2 Occurrence of Chromium

Chromium is a naturally occurring element present in water, sediments, rocks, soils, plants, animals, and volcanic emissions [33]. Chromium is usually originated from geogenic petroleum sources [34,35]. The most important ore of chromium is chromite ($FeCr_2O_4$). Less common sources include crocoite, $PbCrO_4$, and chrome ochre, Cr_2O_3. Cr (III) is a bioelement found as amorphous Fe (III), Cr (VI) hydroxides, and chromite, $FeCr_2O_4(s)$ in rock and soil. Naturally there are a great differences of Cr concentrations in soils and rocks. Shales, suspended river material, and soils with fine grain sediments have the lowest concentrations [36].

2.3 Food

Food contains chromium at concentrations ranging from <10 to 1300 μg/kg [37,38]. Highest concentrations have been found in meat, fish, fruit, and vegetables [37]. Utensils used in the preparation of food may contribute to chromium levels. The daily chromium requirement for adults is estimated to be 0.5–2 μg of absorbable Cr (III). If a fractional absorption value of 25% for "biologically incorporated" Cr (III) in food is assumed, this is provided by a daily dietary intake of 2–8 μg of Cr (III), equivalent to 0.03–0.13 μg of Cr (III) per kg of body weight per day for a 60-kg adult [39].

2 4. Total exposure and relative contribution of drinking-water

Mean chromium intakes from food and water range from 52 to 943 μg/day [40]. The estimated total intake of chromium from air, water, and food by the general population in the United Kingdom is in the range 78–106 μg/day. Food contributed 93–98% of the total intake and water 1.9–7%. In the Netherlands, the estimated mean daily chromium intake is 100 μg, with a range of 50–200 μg [41]. In general, food appears to be the major source of intake. Drinking-water intake however, contribute substantially when total chromium levels are above 25 μg/litre.

2.5 Sources of hexavalent chromium

In addition to natural sources, hexavalent chromium enters drinking water sources through discharges of effluents from leather tanning industries [35], Chromate chemicals that are used as rust inhibitors in cooling towers, particulate matter delivered during manufacture and use of metal chromates, chromic acid smog from the plating industries, waste from the manufacture of steel and other alloys, bricks in furnaces, dyes and pigments, and effluents from wood preserving are also considered as sources of Cr [42]. Not surprisingly, communities near chromium waste disposal sites or chromium manufacturing and processing plants are at particular risk of exposure. Probably the most impacted people are workers exposed on the job.

2.6 Human health effects of hexavalent chromium

Heavy metals normally occurring in nature are not harmful to our environment because they are only present in very small amounts [43]. However, if the levels of these metals are higher than the recommended limits, their roles may change to a negative impact on the environment and health of human being. It may damage adrenals, livers and lungs. Exposure to Cr (VI) may also cause dermatitis, ulcer, destruction of mucus of nose and cancer of the stomachs [44]. Due to its cancer and mutation causing potential, it has been classified as a group I carcinogen [45]. Hexavalent chromium is a carcinogen and a reproductive toxicant for humans. Exposure to hexavalent chromium occurs through breathing, ingestion, and contact with the skin. Although most of the known health impacts are related to inhalation, there is now strong data linking ingestion of hexavalent chromium, such as through drinking water, to severe health effects. In addition to cancer and reproductive harm, short and long-term exposures can lead to eye and respiratory irritation, asthma attacks, nasal ulcers, dermal burns, anemia, acute gastroenteritis, vertigo, gastrointestinal hemorrhage, convulsions, ulcers, and damage or failure of the liver and kidneys [46,47].

In Ethiopia, literatures are indicating the presence of hexavalent chromium in surface waters such as streams and rivers nearby leather industries. In the water bodies of Ethiopian rift-valley lakes, in six rivers (their inflows), and in effluents from two factories Cr was reported to occur in ranges between 0.104 and 0.121 mg/L [48]. Cr(VI) concentrations have been shown to exceed the Ethiopian drinking water standard (ES261:2001 or CES 58-2013) of 0.05 mg/L and the maximum permissible level set by the WHO. An example is the pollution of surface water reported in Addis Ababa [49], where chromium is present above background level due to the uncontrolled disposal of wastes, especially tannery wastes, and insufficient waste management strategies.

2.7 Adsorption

The adsorption involves two types of forces physical and chemical adsorption.

Physisorption: The adsorbates is bound to the surfaces by relatively weak vander waals forces, which are similar to the molecular force of cohesion and are involved in the condensation of vapors into liquids.

Chemisorption: involves exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. The bond formed between the adsorbate and it thus much stronger than in the physisorption.

The importance of adsorption is seen in the need for choosing effective adsorbent for choosing effective adsorbent for the purification needed. The determination of adsorption capacity is a necessary advantage for selecting adsorbent [50].

Adsorption is mostly used physical method to remove or lower the concentration of large amount of dissolved organics or inorganic pollutants in effluent [51]. On the other hand, 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 concentrate at the surfaces of a solid. The phenomenon of the enrichment of chemicals substances at the surface of a solid is called adsorption. All adsorption processes are dependent on solid-liquid equilibria and on mass transfer rates [52]. 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 [17].

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 batch. From a process systems point of

view, the key feature that differentiates continuous process from batch and semi-batch processes is that continuous processes have a steady state, whereas batch and semi-batch processes do not [53].

3. MATERIALS AND METHODS

3.1 Chemicals and Materials

3.1.1 Chemicals

All chemicals and analytical graded reagents were used. The chemicals used for this study were: potassium dichromate, $K_2Cr_2O_7$ (99.5%, FINKEM, England), Nitric acid, HNO_3 (69-72% was obtained from research lab fine chemical industries, Mumbai, India), $FeCl_2.6H_2O$. Acetone, $(CH_3)_2CO$ (99.5%), 1,5-diphenylcarbozide, $C_6H_5-NH.NH)_2CO$ (98% BDH laboratory supplies, poole, BH_{15} ITD, England), sodium hydroxide, NaOH (98%) and hydrochloric acid was obtained from Wardle chemical Ltd (Birmingham, England). Distilled water was used for dilution of sample and standard solutions prior to adsorption and rinsing glass were and sample bottles.

3.1.2 Materials

The materials used for this study were: standard sieves (model DSCO 1674, JPG, 0.075-0.425 mm, UK), volumetric flasks, beakers, measuring cylinder, glass rod, hot plate, droppers, Whatman filter paper, micro pipette, mortar and pestle were used for crushing plastic bottle and adsorbents so on were used during solution preparation and / or adsorbent preparation at target analyzes or by optimize parameter.

3.1.3 Instruments

The instruments used for this study were: oven (model GENLAB WLDNES, England), pH meter was measured using Sci-net 353 ATC pH meter based $pH/mv/C^0$ Bench meter and glass pH electrode were obtained from Sci-net group, Electronic balance that can measure up to 110 g (model KERN ABJ-NMLABS-N) for measuring of masses. A single Beam colorimeter (JENWAY 6051, UK) was used for the adsorption of Cr (VI). All apparatus was washed with detergents using tap water and finally, rinsed with distilled water. After washing the apparatus used for solution preparation were soaked in 10% HNO_3 for 24 hours followed by rinsing with distilled water, dried in oven and kept in clear places until analysis time.

3.3 Methods

3.3.1 Preparation of stock solution

The stock solution containing 1000 mg/L of Cr (VI) was prepared in volumetric flask by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$, 99.9%) in 1000 mL distilled water. Then stock solution containing 100 mg/L of Cr(VI) was prepared in volumetric flask by dissolving 50 mL of stock solution in 500 mL of distilled water. A series of standard solution, of 0.05, 0.1, 0.2, 0.4, 0.8 and 1.6 mg/L were prepared in 100 mL volumetric flask by dilution of the working solution for the calibration of the Calorimeter. The working solutions containing 2 mg/L Cr(VI) was also prepared again in volumetric flasks by dissolving 20 mL from 100 mg/L in 1000 mL by adjusting the resulting solution to desired pH using 0.1M HCl or 0.1M NaOH, the volume of solution was adjusted to the mark by adding more distilled water.

3.4. Adsorbent preparation

3.4.1. Preparation of unmodified adsorbents

The rock sample of pumice was collected from volcanic cones of the main rift valley, Ethiopia. The collected adsorbent samples were washed repeatedly with distilled water to remove any dust and water-soluble impurities. The rock sample was then dried at 55 ^{0}C for 48 h in the oven to evaporate the remaining water [54, 55]. Then, the dried adsorbent was crushed in a mortar and pestles, sieved into mesh size fraction fine (0.125-0.425 mm) following the American Society for testing and materials (ASTMD 422) soil textural classification system [25,56].

3.4.2. Preparation of Iron-Coated Pumice (ICP)

The coating of iron oxide onto pumice was carried out according to the method used by Tsegaye with slight modification [57]. A 150 mL of 0.25 M $FeCl_2.6H_2O$ was added to completely soak in to 50 g of the dried pumice (0.125-0.425 mm) in a beaker. The mixture was shaken in thermostatic water bath shaker for 6 h at 150 rpm in 50 ^{0}C. Then, the pumice was decanted and dried in an oven at 70 ^{0}C for 12 h. The dried pumice was subsequently soaked in 1M NaOH to neutralize it and complete the coating process. Then, the iron coated pumice was drained and

dried in an oven at 75^{0}C. The coated sample was washed several times with deionized waters, dried at 75 ^{0}C for 48 h and stored for Cr (VI) adsorption studies.

3.5 Batch adsorption study

Depending on the parameters under study, the contact time, pH, adsorbents dose and initial Cr(VI) concentration were varied to study the adsorption efficiencies. The Batch adsorption studies were carried out using 70 mL of plastic bottles. A specific amount of dry iron -coated pumice was added to 25 mL of a Cr(VI) solution having a desired pH value. The initial pH was adjusted using 0.1M NaOH or 0.1M HCl and afterwards the bottles were tightly closed. Then, the bottles were agitated at a speed of 150 rmp in thermostatic water bath shaker at 25 $\pm$1 ^{0}C for an equilibrium time. The residue was filtered after the equilibrium time was completed. The aqueous phase was filtered after the equilibrium time was completed. The aqueous phase was filtered through Whatman filter paper and the final concentration of chromium left in the filtrates was analyzed using single beam colorimeter spectrophotometer [39]. 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 [29, 57].

$$\% \text{ Removal of Cr(VI)} = \frac{(C_o - C_f)}{C_o} X100 \tag{1}$$

Where C_o and C_f (mg/L) are the initial and final concentration of Cr(VI) ion respectively.

To calculate the adsorbents removal efficiencies, the following step wise formulas were used.

$$\text{Dilution factors (} D_f) = V_f / V_i \tag{2}$$

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

$$C_o = D_f C_e \tag{3}$$

The amount of equilibrium adsorption, q_e (mg/g), was calculated using the formula.

$$q_e = \frac{(C_o - C_e)V}{m} \tag{4}$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations Cr(VI) ions in solution respectively. V is the volume of the solution (L) and m is the mass of the adsorbent (g).

The amount of adsorption at time t, q_t (mg/g), was calculated using the following equation.

$$q_t = \frac{(C_o - C_t)V}{m} \tag{5}$$

where C_t (mg/L) is the liquid phase concentrations at any time t, C_o (mg/L) is the initial concentration of the Cr(VI) ions in solution.

3.5.1 Effect of pH

The effect of pH on adsorption of metal ion was studied between pH 2 - 8. This was done by using 10g of iron coated adsorbents with 2 mg/L concentration of Cr(VI) ion solution in 1 L plastic bottle. The pH of each solution was adjusted to the desire values by drop wise addition of 0.1M HCl and /or 0.1M NaOH.

The bottle, containing the mixture were kept in a thermostatic water bath shaker and shaken at 150 rpm and 25 ± 1 ^{0}C. The adsorbents were removed from the solution by filtration. The residual chromium ion concentration left in these filtrate solutions was analyzed. Then the pH at which maximum adsorption occurred was taken as the optimum pH.

3.5.2 Effect of contact time

The adsorption of Cr(VI) ions by iron coated pumices was studied at various time intervals. This was done by weighing of 10 g of each adsorbent into plastic bottles containing 1 L of 2 mg/L of Cr(VI) ion solutions at the optimized pH and the bottles were shaken in thermostatic water bath shaker at 150 rpm at 25 ± 1 ^{0}C for various periods of time. The solutions in the bottles were filtered at different time intervals from the first to the last bottle. The filtrates were then taken for analysis using a Colorimetric spectrophotometer.

3.5.3 Effect of adsorbent dose

The adsorption of Cr(VI) ion by iron-coated pumice at different adsorbent doses in the range of 1–20 mg/L and Cr(VI) concentration of 10 mg/L was investigated. This was done by adding 1, 2, 5, 8, 10 and 20 g/L of the adsorbents into each bottle of 2 mg/L Cr(VI) by keeping other parameter constant (at optimal pH, contact time). The bottle, were kept in a thermostatic water bath and shaken at 150 rpm and a temperature of $25\pm1\ ^0C$, after adsorption time was completed the adsorbents were removed from the solution by filtration and the concentration of residual metal ion in each solution was analyzed using Colorimetric spectrophotometer.

3.5.4 Effect of initial Cr (VI) ion concentration

In order to determine the effect of initial chromium (VI) concentration on the adsorption, the batch adsorption study was carried out using a concentration range of 2 to 20 mg/L. This was done by using 10 g of the adsorbents into each of the plastic bottles and 1L of Cr(VI) ion solution at optimum pH and contact time. The bottles were kept in thermostatic water bath and shaken at 150 rpm and $25 \pm 1\ ^0C$. 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 colorimetry.

3.6 Adsorption kinetic studies

Kinetics study can determine the equilibrium time needed for adsorption of Cr(VI) from aqueous solution. Adsorption is necessary to know the rate of adsorption for design and evaluates the adsorbents in removing chromium. In order to evaluate the kinetic parameters, pseudo first order, pseudo second order and intra particle diffusion models were implemented [58].

The Pseudo first order equation is

$$\text{Log } (q_e\text{-}q_t) = \log q_e - \frac{K_1}{2.303}t \tag{6}$$

Where q_e and q_t are the amount of Cr(VI) ion adsorbed on adsorbent at equilibrium and at time t, respectively (mg/g), and K_1 is the rate constant of the first order adsorption (min^{-1}).

The plot of Log(q_e-q_t) versus t will give a straight line and the value of K_1 can be calculated from the slope of the graph [59].

The pseudo- second order kinetic model equation is given as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

If the pseudo second order kinetics is applicable to the system, then the plot of $\dfrac{t}{q_t}$ versus t of equation 7 given a linear relationship with $1/q_e$ and $1/K_2 q_e^2$ as a slope and intercept, respectively. The value of q_e and K_2 can be calculated from the slope and intercept. The pseudo second-order kinetic model has been successfully applied to several adsorption systems as reported by [60].

3.7 Adsorption isotherms

Adsorption isotherm indicates how the adsorbed molecules distribute between the liquid and solid phase when adsorption process reaches an equilibrium states [61]. The adsorption capacity and performance of the adsorbents were usually predicted from equilibrium sorption isotherm [62]. Several models describe the process of adsorption, the most common being used are the Langmuir and Freundlich models.

The Langmuir isotherm model is based on the assumption that there are a finite number of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for the adsorption of a mono molecular layer and there is no interaction between adsorbed molecules. A well-known linear form of the Langmuir equation can be expressed as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{9}$$

Where q_e is the amount of chromium ion adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), C_o is the highest initial Cr(VI) concentration and q_m and K_L Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg). According to equation above, when the adsorption obeys the Langmuir equation, a plot of C_e/q_e versus C_e should be a straight line with a slope of $1/q_m$ and intercept $1/q_m K_L$. This is important

15

characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L, which is defined as:

$$R_L = \frac{1}{1 + K_L C_O}$$
(10)

The R_L values indicate the type of adsorption as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [63].

The Freudlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbates on the adsorbent surface also increases and correspondingly, the sorption energy exponentially decreases on completion of the sorption centers of the adsorbent. The well-known expression for Freundlich model is given as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$
(11)

$$q_e = K_f C_e^{1/n}$$
(12)

$$slope = \frac{1}{n}$$
(13)

$$\text{int } ercept = \log K_f$$
(14)

Where qe is the amount adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, 1/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). The value of K_f and 1/n can be obtained from the slope and intercept of the plot of log q_e against log Ce. Value of K_f and 1/n can be obtained from the slope and intercept of the plot of log q_e against log Ce.1/n ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface [64].

3.8 Statistical Analysis

Triplicate samples were used during the determination of Cr(VI) ion using colorimeter and the obtained results were analyzed by averaging the value. The curve fitting of data obtained were performed using origin 8.0 software.

4. RESULTS AND DISCUSSION

In this batch adsorption experiment, different parameters such as effect of contact time, pH, adsorbents dose and initial concentration were studied in order to determine the efficiencies of the adsorbents to removes chromium from aqueous solution. The data collected from these studies is used to describe the responsible adsorption isotherm models and to assess the kinetic of the adsorption of hexavalent chromium.

4.1 FTIR Analysis for Cr (VI) adsorption

Fourier Transform Infrared Analysis (FTIR) study was carried out to identify the functional groups presents in the adsorbents in the range of 400-4000 cm^{-1} wavenumber. The adsorption capacity depends upon porosity as well as chemical reactivity of functional groups at the adsorbent surface [65]. The FTIR spectra of iron coated pumice before and after adsorption of Cr (VI) were used to determine vibrational frequency changes of the functional groups in the adsorbents. The spectra were plotted using the same scale on the transmittance axis for the adsorbents before and after adsorption. The spectra of the adsorbents show number of adsorption peaks, indicating the complex nature of the adsorbents, as shown in fig. 1.
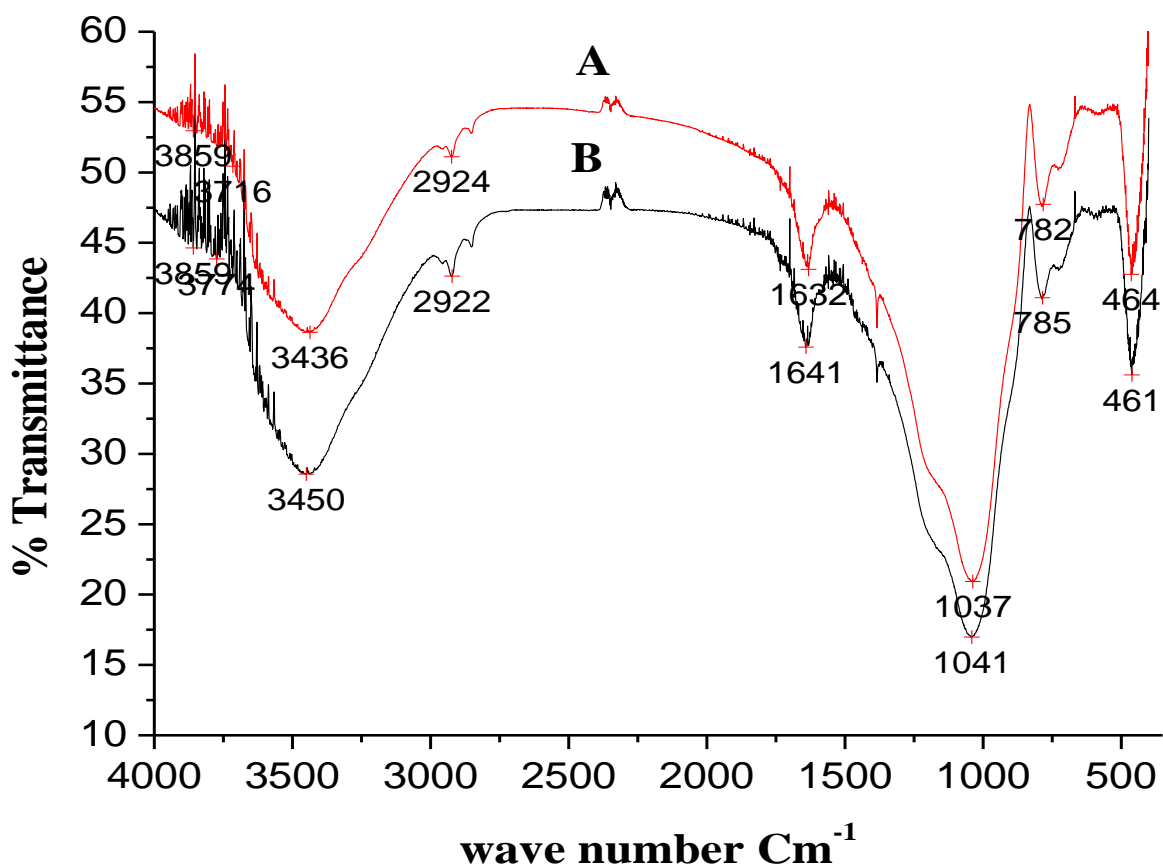
Figure 1: FTIR Spectra of (A) before and (B) after adsorption of iron coated pumices.

In ICP, the adsorption peak around 3400 cm^{-1} indicates hydroxyl group (-OH) through water molecules was responsible for the binding of Cr (VI) ions onto the adsorbents. The peaks observed at 2922-2924 cm^{-1} can be assigned to the C-H stretching vibration of the (-CH$_2$-) group and the peak around 1632 cm^{-1} carbonyl group. It was found that C-N stretch 1041 cm^{-1} were also responsible for the effective removal of Cr (VI) ions [66]. For the samples, the band of Fe-O at 464 cm^{-1} and Si-O at 692-790 cm^{-1} observed were functional groups representing each peak [67].

4.2. Effect of contact time

In this experiment, except contact time all parameters such as effect of pH (2), adsorbent dose 10 g/L and initial chromium concentration (2 mg/L), were kept constant. The effect of contact time on chromium adsorption efficiency is shown in Fig.2 below.
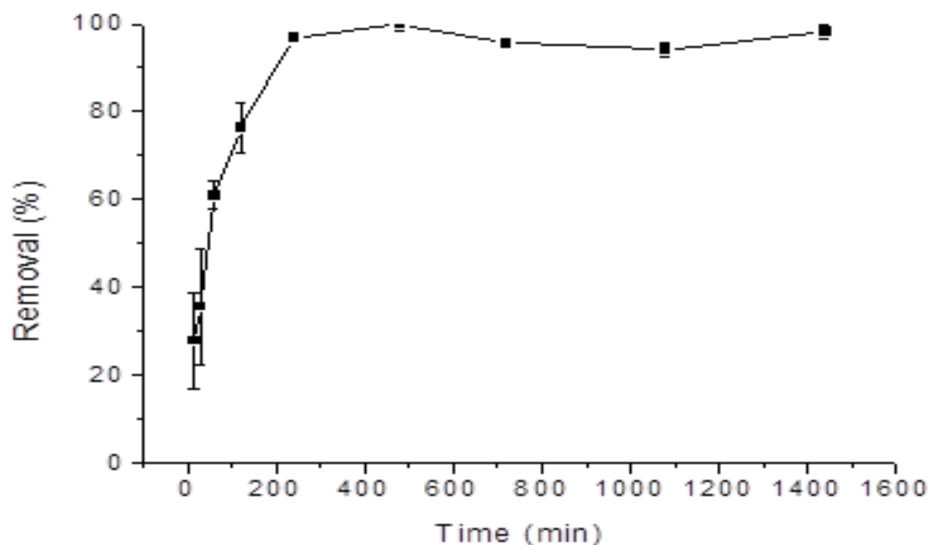

Figure 2: Effect of contact time on adsorption of Cr(VI) by ICP (Initial concentration of Cr(VI) 2 mg/L, adsorbent dose 10 g/L, pH 2, and temperature 25 ± 1 ^{o}C).

The Cr(VI) removal efficiency of iron-coated pumice was found to be increase up to 4 hours and then after it becomes remained constant. There was no significant change in equilibrium concentration after 4 hours up to 24 hours which means after 4 hours, the adsorption phase reached equilibrium. Therefore, 4 hours was selected as equilibrium time and used in next optimization. The high rate of removal at initial stage may be due to the fact that initially all adsorption sites were vacant of adsorbents for anionic Cr(VI) removal present in the solution, and the solute concentration gradient in the first parts of the solution was high. Later, the chromium uptake rate by adsorbent decreased significantly, due to the decrease in number of adsorption sites, electrostatic hindrance caused by already adsorbed adsorbent species and slow pore diffusion of the ions [68]. After increased of time the remaining unoccupied surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulky phases [61].

20

4.3 Effect of pH

The pH of the aqueous solution is an important parameter that affects the adsorption of Cr(VI) ions by surface properties of the adsorbents. The pH Cr(VI) solutions were adjusted before adding adsorbents and its optimization was carried out using a fixed 10 g/L of the adsorbents dose and 2 mg/L solutions of the Cr(VI) ions in the pH range of 1-8 at 25 °C for 4 hours.
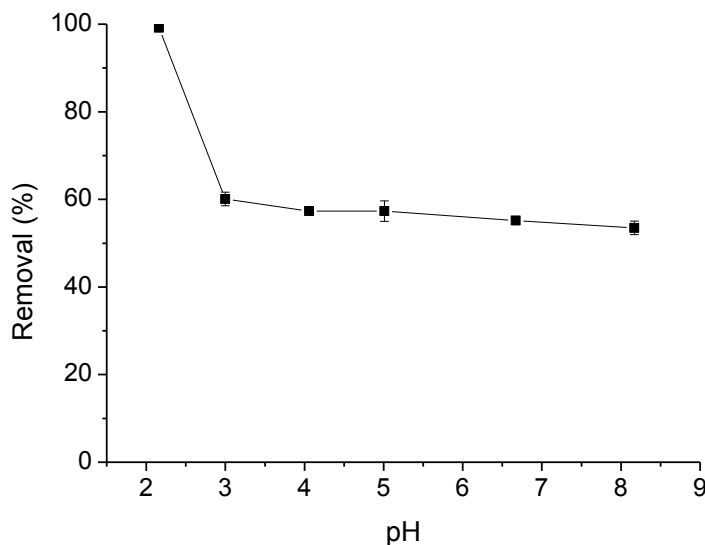

Figure 3: Effect of pH on adsorption of Cr(VI) by ICP (contact time 4h, Initial concentration of Cr(VI) ion 2 mg/L, adsorbent dose 10 g/L, shaking speed 150 rpm and temperature 25±1 °C).

As shown in Figure 3, the pH of the solution in which adsorption is taking places has a significant effect on the adsorption efficiency of the adsorbent, maximum adsorption was found to be 99% for ICP at pH 2. The selection of this low pH has important features for the actual pH value of industrial effluents such as tannery effluent (at pH 2) [67, 69], electroplating effluent (at pH 2.2) [70], chromium plating effluent (at pH 1) [71] and the experimental studies reported in the literature [72–74]. It was found that adsorption efficiencies of adsorbents were slightly decreased from lower values to higher ones. Similar trends were also reported by other literatures [75,76].

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 surfaces and chromate ions [78]. Lower adsorption of Cr(VI) at maximum pH values may be due to the dual competition of both the OH^- and chromate anions to be adsorbed on the surface of the adsorbents 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 [61]. Thus, it was found that removal of Cr(VI) ions from observations, the value of pH 2 was taken as the optimum pH for further experimental studies

4.4 Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of Cr(VI) was studied under the conditions described earlier and changing adsorbents dose only from the range of 1-20 g/L at 25 $^{\circ}$C. The results obtained are shown as percentage removal of Cr(VI) versus adsorbent dosage in Figure 4 below.
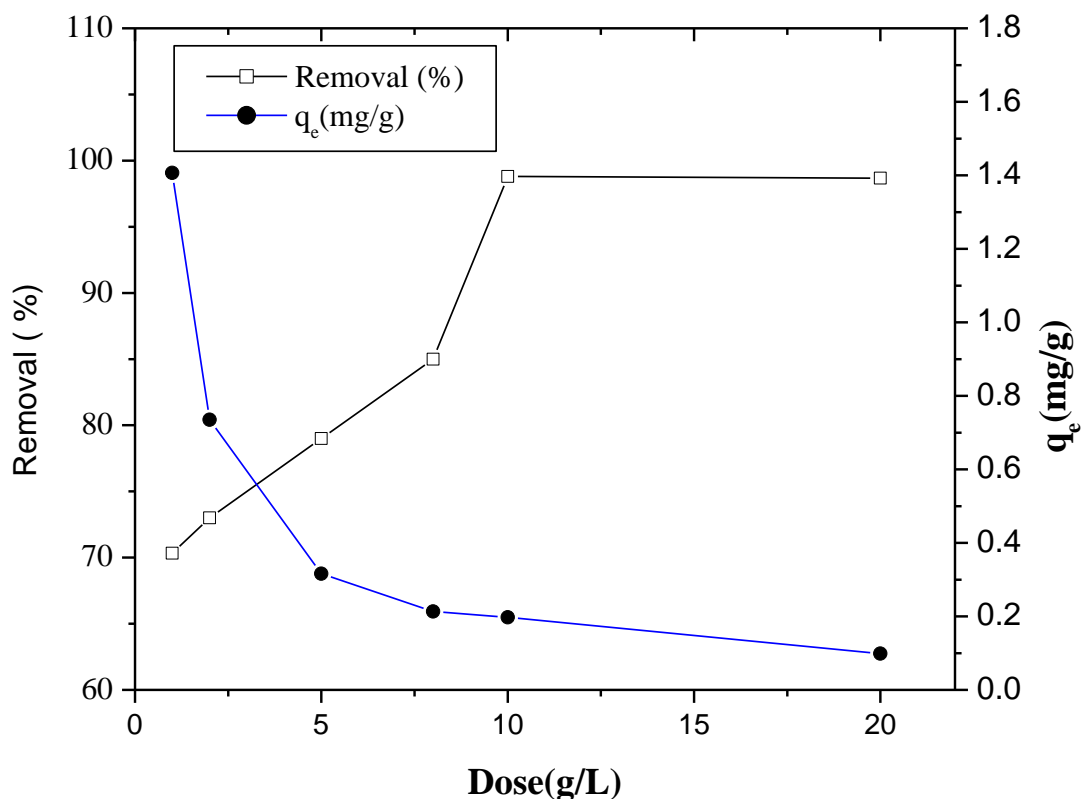
Figure 4: Effect of adsorbent dose on adsorption of Cr(VI) by ICP (contact time 4 h, pH 2,
Initial concentration of Cr(VI) ion .2 mg/L, shaking speed 150 rpm and temperature $25\pm1^{\circ}$C).

As shown in Figure 4, percentage of removal increases with increases with increasing in
adsorbent dose until 10 g/L is because of contact surface of adsorbent particle increase for
adsorbates. It might be due to high adsorption sites of the adsorbent for $HCrO_4^{2-}$ and $Cr_2O_7^{2-}$ ions
[78]. However, after 10 g/L of adsorbent dose, there was no significant change in percentage
removal because of the resistance to mass transfer of Cr(VI) from solution to surface of
adsorbents [79]. Similar results are reported in the study on adsorption of Cr(VI) and As (V)
[61,80].

4.5. Effect of initial concentration

The effect of adsorbate concentration was studied by using the initial concentration of Cr(VI) solution having 2, 3, 5, 8, 10, 15 and 20 mg/L at optimum contact time 4 hours, pH 2, adsorbents dose of 10 g/L, and temperature of 25 ± 1 ^{0}C. The results, obtained are shown in Figure below.
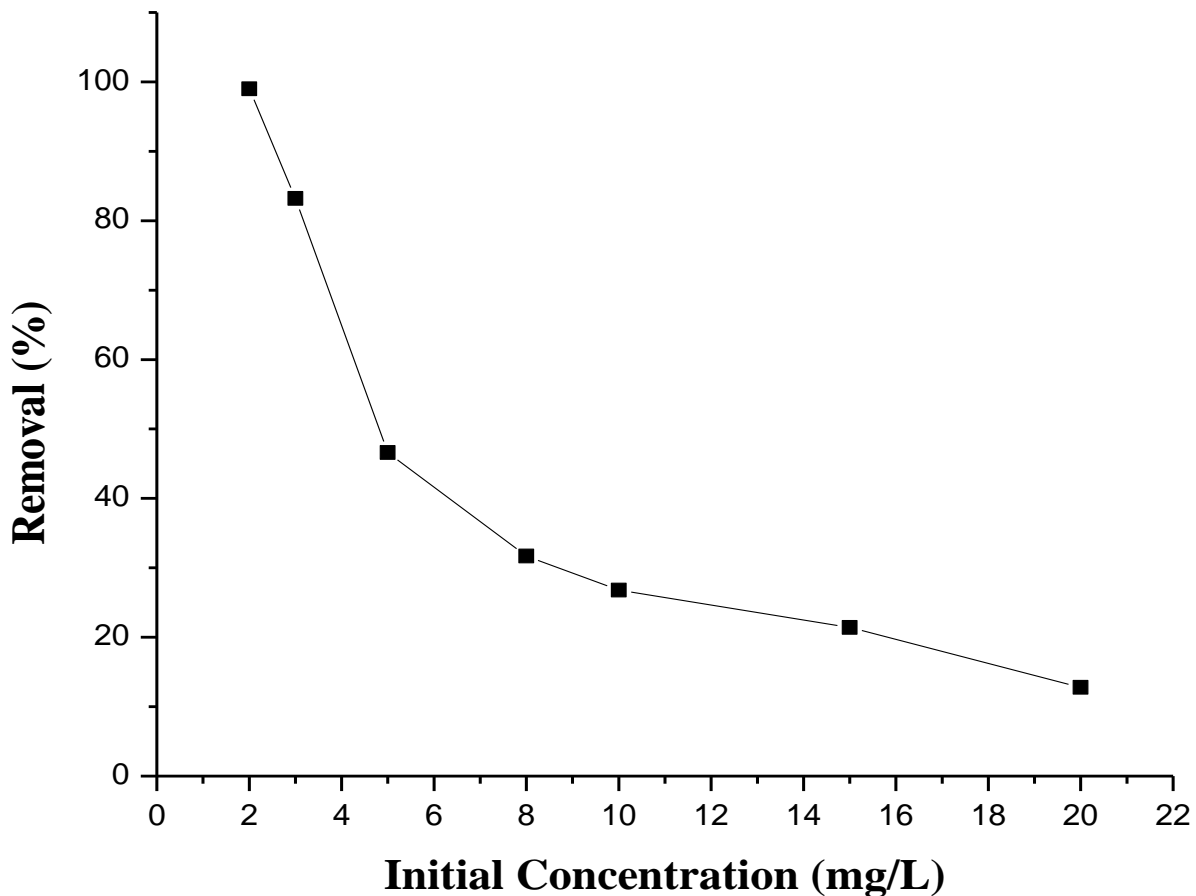

Figure 5*:* Effect of initial concentration on the removal of Cr(VI) by ICP (pH 2, contact time 4 **hrs,** adsorbents dose 10 g/L, shaking speed 150 rpm and temperature 25 ± 1 ^{o}C).

As it is shown in Fig. 5, the percentage of adsorption decreased with increasing initial concentration from 2-20 mg/L. At lower concentrations, (2 mg/L) all chromium ions present in the solution would be adsorbed on the binding sites because of minimum competition among these chromium ions for the binding sites that the sorbate can easily occupy. At higher concentrations (20 mg/L) more Cr(VI) ions are not adsorbed in the solution because of the saturation of binding sites and active sites are not sufficiently available for the adsorbate to occupy. This appears due to the electrostatic repulsion between negative charges of adsorbate ions competing for available binding sites [51] of the adsorbents ions resulting in the decrease of the adsorption percentage [61].

4.6 Adsorption kinetic studies and data presentation

Table 1: Kinetic parameters for the adsorption of Cr(VI) by ICP at 25 ± 1 ^{o}C.

Pseudo-first order				Pseudo-second order		
q_e exp. (mg/g)	$q_e$cal.	k_1	R^2	$q_e$cal.	k_2	R^2
0.1939	-0.85226	92.6817	0.96253	0.1996	0.15344	0.99814

Kinetic study determines the rate of equilibrium time needed for the removal of Cr(VI) from aqueous solution. To know the reaction is fast or slow. In order to evaluate the kinetic parameters, pseudo first order, pseudo second order and intra particle diffusion models were used to analyze the experimental data [58]. The pseudo first order is given in equation (6).

Figure 6: Pseudo-first-order kinetic plot for the adsorption of Cr(VI) by ICP. (Cr (VI) 2 mg/L, pH 2, adsorbents dose 10 g/L, shaking speed, 150 rpm).
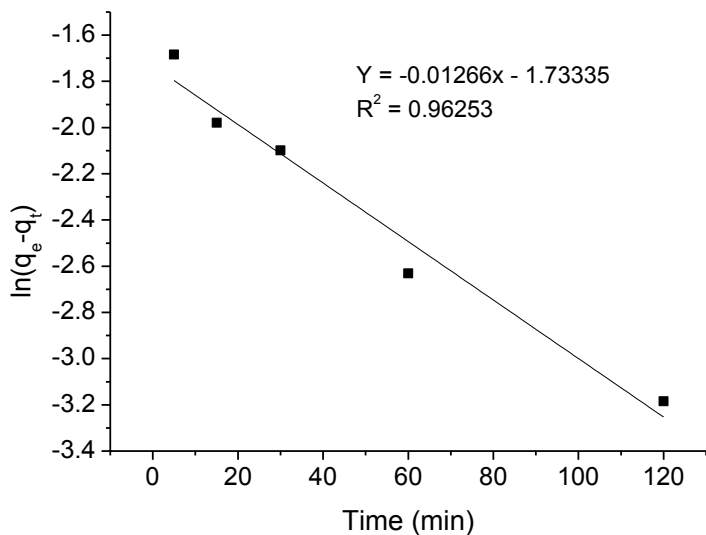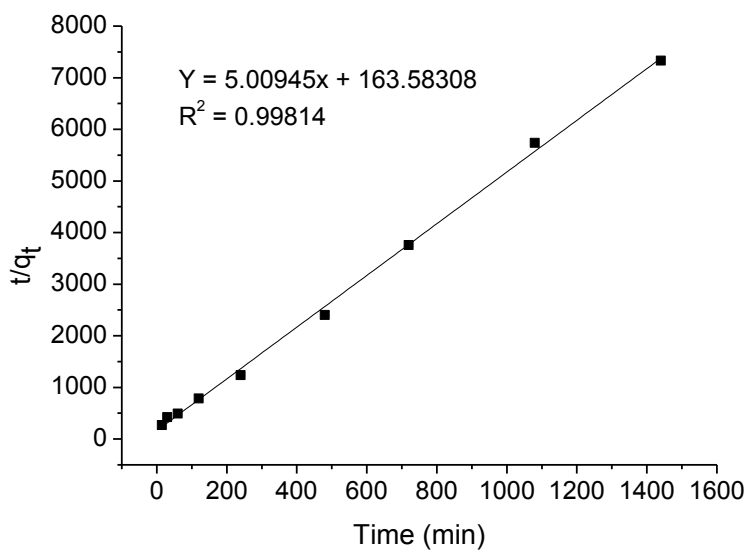

Figure 7: Pseudo-second-order kinetic plot for the adsorption of Cr(VI) by ICP. (Cr (VI) 2 mg/L, pH 2, adsorbents dose 10 g/L, shaking speed 150 rpm).

From the plots of log $(q_e$-$q_t)$ versus t, K_1 can be calculated from the slope and theoretical qe can be obtained from intercepts. The pseudo second order was given in equation (7). The linear plots of t/q_t versus t determine $1/qe$ as slope and $1/K_2q_e^2$ as intercepts. The correlation coefficients, R^2 for the second order kinetic model were almost fit better than pseudo first order for all the concentrations signifying the applicability of the model.it appeared that the system under study is more suitably described by pseudo second order kinetics which was based on the assumption that the rate limiting steps may be physisorption due to the presence of weak forces of attraction between adsorbent and adsorbate. The pseudo second-order kinetics model has been successfully applied to several adsorption systems as reported by [59]

The amount of Cr adsorbed per unit mass of adsorbent at time t, q_t, as a function of the square of the contact time, $t^{1/2}$ was examined using the intraparticle diffusion model which is based on the theory proposed by Weber and Morris given as

$$q_t = k_d \, t^{1/2} \tag{8}$$

where k_d (mg/g/min$^{1/2}$) is the intraparticle diffusion coefficient, was calculated from the slope of the linear portion of curves and C (mg/g). It is proportional to the boundary layer thickness. It is assumed that, the larger the intercept, the greater the contribution of the surface adsorption in the rate- controlling step.

Intra particle diffusion plays a significant role in controlling the kinetics of the adsorption process if the plot of qt versus $t^{1/2}$ yields a straight, K_d. If the line does not pass through the origin it is indicative of some degree of boundary layer control and this further show that the intra-particle diffusion is not the only rate limiting step, but other kinetic models may also control the rate of adsorption. Similar finding was reported by other researchers [61].
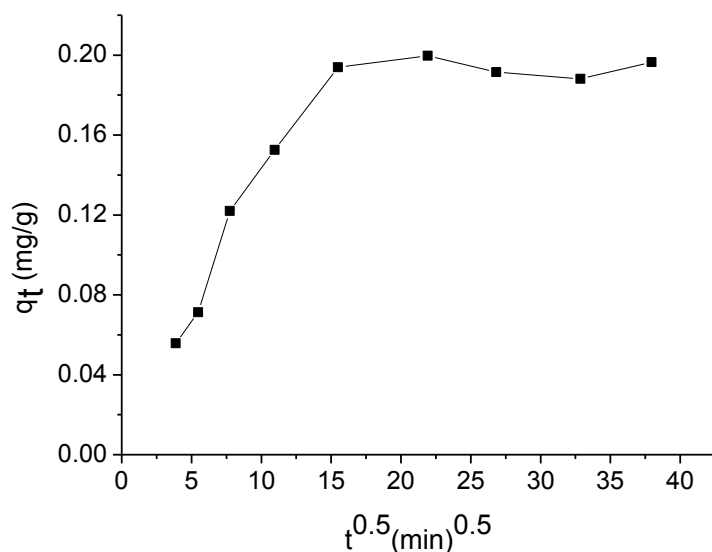
Figure 8: Intra-particle diffusion curve for adsorption of Cr(VI) by ICP at 25 ± 1 $^{\circ}$C. (Cr (VI) 2 mg/L, pH 2, adsorbents dose 10 g/L, shaking speed 150 rpm).

The plots of intra-particle diffusion in Fig. 7 showed that, the line did not pass through the origin. This implied that the rate limiting process is not only governed by intra particle diffusion. Some other mechanism along intra particle diffusion was involved for the whole adsorption process. Similar finding was reported by other researchers [75].

4.6 Adsorption isotherms and experimental data

Several models have been used to describe experimental data for adsorption isotherms. Among these, the Langmuir and Freundlich isotherms are the most appropriate models for this study. According to Langmuir isotherm, adsorption occurs at homogenous sites and forms a monolayer. In other words, once adsorbate is attached to a site, no further adsorption can take places. The linear form of Langmuir isotherm equation is given in equation (9). The R_L essential characteristics of the Langmuir equation can be expressed in terms of dimensionless factors, R_L which is given in equation (10). The R_L values indicates the types of adsorption is irreversible if $R_L =0$, favorable if $0< R_L<1$, linear if $R_L=1$ and unfavorable if $R_L>1$. The obtained values of R_L are with range of (0-1), suggesting favorable equilibrium adsorption of iron coated pumice [63].

In this study, the experimental data of iron coated pumice were fitted well to the Langmuir isotherm as indicated by the higher, R^2, values (Table 2 and Figure 8-9)
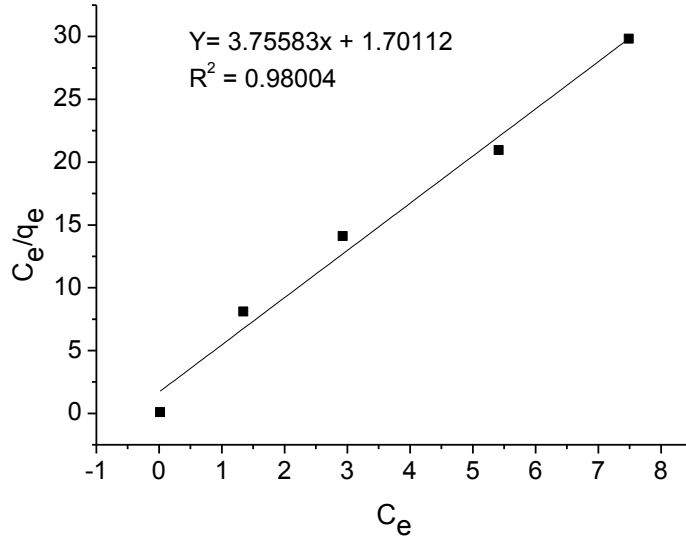

Figure 9: Langmuir isotherm plot of Cr(VI) on ICP ICP (pH: 2; adsorbent dose: 10 g/L; shaking speed: 150 rpm; contact time: 4 h).
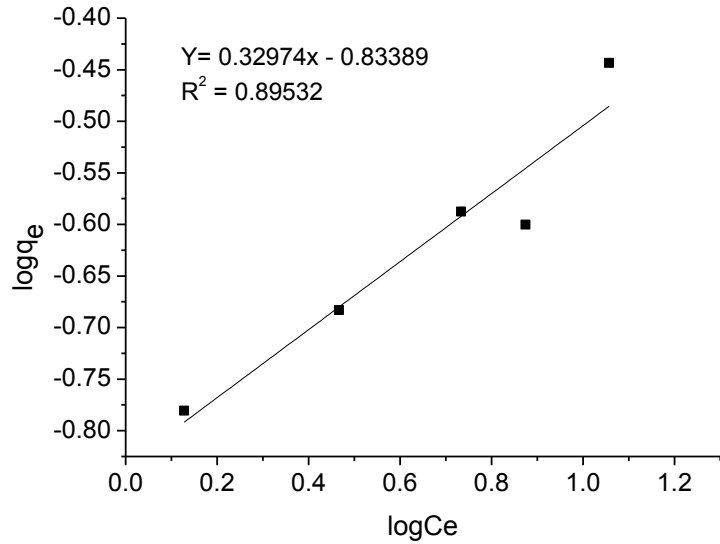

Figure 10: Freundlich isotherm plot of Cr(VI) on ICP. ICP (pH: 2; adsorbent dose: 10 g/L; shaking speed: 150 rpm; contact time: 4 h).

The research attempted to analyzed the above mentioned parameters at $25\pm1^{\circ}$C. The correlation coefficients, R^2 were calculated by fitting the experimental equilibrium data for Cr(VI) ion by iron coated pumices using Langmuir and Freundlich isotherms as shown in Table 2.

Table 2: Results of isotherm models for the adsorption of Cr(VI) by ICP at $25\pm1^{\circ}$C.

Langmuir isotherm			Freundlich isotherm			R_L at 20 mg/L
q_m (mg/g)	K_L	R^2	K_f	1/n	R^2	
0.26625	2.20786	0.98004	9.48×10^{-18}	0.330	0.89532	0.0221

4. 8 Comparison of chromium (VI) adsorption capacities of various adsorbents

Capacities of the adsorbents used in this investigation compared with those of others reported in the literature and the values of adsorption capacity as presented in Table 3. The experimental data of the present investigation were compared with reported values. Results of investigation revealed that the adsorbents have high adsorption capacity than almost all adsorbents. The difference in adsorption capacity of iron coated pumices with those previously reported could be due to the type of adsorbents, pH and the difference in experimental conditions on the removal of Cr(VI).

Table 3: Comparison of iron coated pumices with others.

Adsorbents	Capacity qm(mg/g)	pH	References
Rice bran	0.069	2	83
Sawdust	0.229	2	84
Pine leaves	0.277	2	84
Raw race brain	0.07	2	85
Iron coated pumices	0.27	2	This study

5. CONCLUSION

In this study, adsorption efficiencies of iron coated pumice toward the removal of Cr(VI) in aqueous solution was investigated. The adsorption of Cr(VI) was found to be dependent on contact time, the pH of the system, adsorbent dose and initial concentration of Cr(VI). Maximum uptake of Cr (VI) was obtained at adsorbent dosage of 10g/L and adsorption equilibrium attained with 2h. The best results being obtained at pH 2. The maximum adsorption capacity (q_{max}) was obtained 0.27mg/L. The adsorption equilibrium data obtained for removal of Cr(VI) ion onto the adsorbents studied showed best fit to the Langmuir isotherm. The adsorption kinetic data fitted a pseudo-second-order model well. Iron coated pumice is a good and cheap adsorbent with high potential for the adsorption and removal of chromium from contaminated water sources and could therefore serve as effective and efficient material for treating drinking water. In addition, it will help to enable people to use environmentally friendly and easily operational methods in developing countries as alternatives of advanced technologies.

6. RECOMMENDATION

Column and pilot scale (follow-up) study is important to implement this promising adsorbent for the real application. The interference and speciation consideration of chromium should be investigated.

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