

**JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCE
DEPARTMENT OF CHEMISTRY**



**ADSORPTION STUDY OF Cr (VI) FROM AQUEOUS SOLUTION
USING Fe (III)-MODIFIED DIATOMITE**

**JANUARY, 2020
JIMMA, ETHIOPIA**

**ADSORPTION STUDY OF Cr (VI) FROM AQUEOUS SOLUTION
USING Fe (III)-MODIFIED DIATOMITE**

BY

ADUGNA HUNDESA

ADVISORS: FEKADU MELAK (PhD)

CO-ADVISOR: ABEBE DIRO (MSc)

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Title: Adsorption Study of Cr (VI) From Aqueous Solution Using Fe (III)-Modified Diatomite

Approved by board of Examiners

External Examiner	Signature	Date
_____	_____	_____
Internal Examiner		
_____	_____	_____
Advisors		
<u>Fekadu Melak (PhD)</u>	_____	_____
<u>Abebe Diro (MSc)</u>	_____	_____
Department Head		
<u>Ephrem Tilahun</u>	_____	_____

January, 2020
Jimma, Ethiopia

DECLARATION

I declare that the work in the thesis entitled Adsorption Study of Cr (VI) from Aqueous Solution using Fe (III)-diatomite was performed by me in the Department of Chemistry under the supervision of Dr. Fekadu Melak. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university

Name

Signature

Date

A dugna Hundesa

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List of Abbreviation

FDMA	Iron (III) modified diatomite
UV-VIS	Ultraviolet visible spectrophotometer
FT-IR	Fourier transforms infrared spectrophotometer
C_{eq}	Equilibrium concentration in mg/L
K	Capacity of the adsorbent
q_e	Amount of adsorbate adsorbed at equilibrium in mg/g
K_L	Langmuir constant in L/mg
R_L	Dimensionless separation factor
WHO	World Health Organization
USEPA	United States Environmental Protection Agency
R^2	correlation coefficient

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Abstract

This study investigated the effectiveness of Fe (III)-modified diatomite in removing hexavalent chromium from aqueous solution as a low cost adsorbent under various conditions. Batch mode experiments were conducted to study the effects of pH, contact time, adsorbent dose, and initial concentration of adsorbate on the adsorption of hexavalent chromium. Adsorption equilibrium was achieved after a contact time of 150 min. Hexavalent chromium adsorption was significantly dependent on solution pH, and the optimum adsorption was observed at pH 2. Equilibrium isotherm data were analyzed by the Langmuir and Freundlich models. Results indicated that adsorption process obeys Freundlich isotherm model better than Langmuir. An estimated maximum adsorption capacity of 1.96 mg/g was observed using Fe (III)-diatomite adsorbent at optimal conditions of the batch experiment.

Keywords: hexavalent chromium, Fe (III)-diatomite, Adsorption, Equilibrium isotherms.

1. INTRODUCTION

The quality of surface water and ground water is continuously deteriorating due to rapid increase in population and industrial growth all over the world. The use of metals in industrial and other processes have introduced high amounts of toxic heavy metals into the environment [1, 2]. High consumptions, frequent disposal and replacement of disposable items are generating diverse types of metallic wastes. These wastes are regularly discharged into the environment and thus are poisoning the environment [3]. Most heavy metals are extremely toxic, seriously harming all forms of life including human beings when exceeding their tolerance levels [4, 5]. Heavy metals are also not biodegradable and tend to accumulate in living organisms [6].

The presence of heavy metals in drinking water sources and in edible agricultural crops can be harmful to human. Heavy metals are highly toxic and they can damage nerves, liver, bones and also can block functional groups of vital enzymes. The major sources of heavy metals in water and soil are the effluents discharged from many industrial processes [7]. A number of industries such as plastic, leather tanning, electroplating, metal processing, paint manufacturing, steel fabrication and fertilizer, and ceramics etc. discharge heavy metals as waste. These led to contamination of fresh water resources and marine environment. One of these heavy metals known as chromium. Chromium can be mainly found as hexavalent and trivalent forms. Hexavalent chromium compounds are toxic, carcinogenic (having the potential to cause cancer), and mutagenic and even cause lung cancer [8, 9]. Chromium, which is on the top priority list of toxic pollutants defined by the US Environmental Protection Agency (EPA) are found to be exists in nature mainly in two oxidation states +3 and +6. Cr (VI) compounds are more toxic than Cr (III) compounds because of their high solubility in water and consequently high mobility. The trivalent chromium is relatively non-toxic and in fact an essential trace nutrient in the human diet, but the hexavalent chromium is very toxic [10]. As an example, US regulations have set the 0.050 mg/L of Cr (VI) and the USEPA Drinking Water regulations limit the total chromium in drinking water to <0.1 mg/L [5]. Concentration of Cr (VI) in drinking water that is allowable is 0.05 mg/L according to world health organization (WHO).

Hexavalent chromium compounds are widely used in leather tanning, electroplating, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile and steel fabrication industries.

Elimination of heavy metals in particular Cr (VI) from water/wastewater is the critical topic of many researchers [11]. The undesirable effects of Cr (VI) can be avoided by treating the effluents prior to discharge into water streams. Different conventional methods such as chemical precipitation, filtration, chemical oxidation and reduction, reverse osmosis, evaporation techniques, electrochemical and ion exchange methods are generally recommended for Cr (VI) removal from the environment [12]. However, these methods are cost effective and generate a variety of secondary pollutants [13]. Also, these techniques have low efficiency and inapplicability to a wide range of pollutants [14]. And these methods have also major disadvantage such as incomplete metal removal, utilization of expensive equipment and monitoring system requirements, high reagent or energy requirements and generation of toxic sludge or other waste products that require disposal.

Adsorption has been found to be superior to other techniques for water treatment in terms of initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants and does not produce harmful substances like most processes [15, 16]. Therefore, recently removal of heavy metal-contaminated aqueous solutions by using different adsorbents such as green sands [17], iron slag [18, 19], fly ash [20, 21] and waste iron [22], agricultural byproducts like hazelnut shell, orange peel, rice husk, pecan shells, jackfruit, activated carbon [23-25] and potato peels charcoal [26] were applied. Interestingly, algal biomass from *Spirogyra* species [27], *Chlorella Vulgaris* [28], *Ulva Lactuca* [29, 30], *Oedogonium* and *Nostoc* species [31] showed efficient absorbing capacity.

In the present work, the Cr (VI) adsorption capacity of Fe (III)-diatomite was studied as an adsorbent material. In more details, metal adsorption isotherms, kinetic model, the effect of initial metal concentration, contact time, adsorbent dosage, pH of Fe (III)-diatomite removal has been studied by batch experiments.

1.1. Statement of the Problem

Along with the economic growth, increasing number of population and increasing use of industrial product, untreated wastewater produced industrially also increased. Industries of tanneries, metal plating, mining, etc. discharge several contaminated heavy metals like chromium into their aqueous waste streams [32, 33]. Many industries involve chemical reactions and mechanical changes, which use a lot of water. It generates waste most of the time in developing countries, which discharged in to the rivers or other water areas and open field land areas. It could have adverse effect on the environment and human if it not properly managed due to the presence of dangerous chemical and elements such as chromium, sulfur, etc. [34]. Chromium is not biodegradable and tends to bio-accumulate in living organisms causing serious disease and disorders. Efficient methods of chromium removal from wastewater are important to attain environmental quality standards.

Adsorption has been identified as one of the most promising method for removal of Cr (VI) from wastewater [35]. Different conventional methods are generally recommended for Cr (VI) removal. However, these methods face drawbacks as cost incompatibility, sludge production, and removal inefficiency. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost adsorbent. Therefore, it is necessary to developing an inexpensive and efficient adsorbent material that easily available in large quantity and economically feasible to treat the wastes effluent from different industries. Diatomite is a type of adsorbent with large specific area, high adsorption capacity, and good mechanical properties, broadly utilized in wastewater treatment [36]. Therefore, the main focus of this study is to assess the adsorption capacity of modified diatomite by iron (III) for Cr (VI) removal and the suitability of diatomite as alternative adsorbent.

1.2. Objective

1.2.1. General Objective

To assess the efficiency and/ or capacity of Fe (III)-diatomite for the removal of Cr (VI) from aqueous solution.

1.2.2 Specific Objectives

- To prepare modified Fe (III)-diatomite from iron (III) and commercial diatomite.
- To characterize the prepared adsorbent.
- To optimize the effects of pH, time, initial concentration of Cr (VI) and adsorbent dosage on the adsorption efficiency of modified diatomite.
- To describe adsorption capacity based on adsorption isotherm
- To compare the modified diatomite with pure diatomite.

1.3 Significance of the Study

Investigation of removal of hexavalent chromium from aqueous solution using on modified diatomite, is useful

- It will give the implication to reduce the level of Cr (VI) from water/waste water from industries.
- To motivate industries in the use of modified diatomite may be from beer industries in the filtration of yeasts, and other industries which released hexavalent chromium to the environment, as economical and technically feasible adsorbent.
- It will help as baseline to researchers in the use of modified diatomite for Cr (VI) removal.

2. LITERATURE REVIEW

2.1 Environmental Pollution

Environmental pollution, which arises from the development of modern industrial activities, is one of the most significant problems of the country. Most industrialists try to discharge their wastewater effluents inadequately treated or totally untreated, directly to rivers or nearby water bodies, and land without considering the level of damage it may bring to local community. Different industries discharge their wastes containing different heavy metals into the environment such as mining; energy and fuel production; electroplating; atomic energy installation and Leather manufacturing industry, etc. The most important technologies for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies, which include chemical precipitation, ion exchange, membrane separation, coagulation-flocculation, and adsorption. Adsorption is a well-established and powerful technique for treating the industrial effluents. In comparison with conventional technology methods adsorption process, appeared to be preferable in terms of its efficiency, simplicity of design/operation, and the ease with which it can be applied in its application in the removal of heavy metals in wastewater [37].

2.2 Chromium and its Impact on Environments and Health

Chromium compounds are widely used in many industries, resulting in disposal of large amounts chromium ions into the environment. Chromium contamination of soil and water is a major environmental problem. The toxicity of chromium varies greatly among a wide variety of chromium compounds, its oxidation state and its solubility in water [38]. Chromium occurs in the environment primarily in two valence states, trivalent chromium, Cr (III) and hexavalent chromium, Cr (VI). Cr (III) is considered to be an essential dietary element to the human and mammals while Cr (VI) is highly toxic and possesses mutagenic and carcinogenic activity [39, 40]. Chromium contamination may occur in the natural environment or due to industrial processes. However, it is human-caused chromium contamination that has recently been the focus of much scientific discussion, regulatory concern, and legal posturing. Chromium contamination of water bodies is the questions that continue to arise regarding the safety of the drinking water supply. Chromium from anthropogenic sources is commonly released as Cr-bearing liquid or solid wastes which may contain any combination of Cr (III) or Cr (VI) with

various solubility. The concentration of Cr in discharged effluents depend mainly on the amount and state of Cr compounds utilized in the industrial process, on the pH, and on the presence of other organic and inorganic processing wastes.

One of the most important Cr (VI) discharge to aqueous environments is derived from industrial waste streams such as pigment manufacturing, wood preservation, leather tanning and waste disposal sites leakage [41, 42]. At present several methods are available which are applicable for the removal of Cr (VI) from water [43]. Many of these techniques have their own drawbacks and suffer from their constraints. However, adsorption is the most popular, promising and versatile technique for the treatment of contaminated waters and thus, it has gained much attention of the researches [44, 45].

2.3 Adsorbent

The most commonly used adsorbent is activated carbon and it generally has high metal adsorption capacity. Although activated carbon is effective in the removal of metal ions from wastewater, it is expensive and requires chelating agents to enhance its performance, thus increasing treatment cost [46]. For the past two decades, researchers have focused on using low-cost, efficient sorbents for heavy metal adsorption. Furthermore, the sorption behavior of several natural materials and waste products has also been investigated [47]. Now a day, there are study results available on research carried out on the treatment of heavy metals of different sources using agricultural wastes, industrial by products and natural substances as adsorbents [48].

Diatomite is a siliceous sedimentary rock composed of an amorphous form of silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) containing a small amount of microcrystalline material. The silica surface contains silanol groups that spread over the matrix of silica [49]. The silanol group is an active one which tends to react with many polar organic compounds and various functional groups [50]. It has a unique combination of physical and chemical properties such as high porosity, high permeability, small particle size, large surface area, and low thermal conductivity [51]. This material is of great interest and has several uses such as: purification of drinking water, adsorbent of the pesticides, manufacture of antibiotics, some pharmaceutical syrups and its qualified like friendly material with to respect the environment [52]. The choice of this material was indicated to us by the fact

that: it is very abundant; it has a adsorptive affinity towards the heavy metals [53, 54], and organic molecules [55, 56].

The physicochemical properties of diatomite as reported by [57] are given in Table 1

Table 1:The physicochemical properties of diatomite

Parameters	Value
Moisture content, %	80
Water retention, %	182
Specific gravity, g/mL	1.9
pH	7.3

2.4 Adsorption Processes

Adsorption is a unit process that occurs when a vapour or liquid solute collects on the open surface of a solid or a liquid (adsorbent), forming a molecular or atomic layer thick film (the adsorbate). Adsorption method is considered to be one of the preferable methods for the removal of Cr (VI) or other metal ions from aqueous solution due to its significant advantage such as; low operational cost, widely applicable and creates relatively low sludge [58]. This solves the problems of sludge disposal and renders the system more economically viable especially if low cost adsorbents are used [59]

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature. Different adsorption isotherms are Freundlich, Langmuir and BET theory.

2.4.1. Basic Adsorption Isotherms

2.4.1.1. Freundlich Adsorption Isotherm

Freundlich adsorption isotherm is an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. The Freundlich equation was applied to describe the analytical results on the adsorption. It is represented by the equation Eq (1) [60].

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

Where C_{eq} is the equilibrium concentration (mg/L), x/m is the amount adsorbed per unit mass of Fe (III)-diatomite, n is the indication of favorability and K is the capacity of the adsorbent. Plotting $\log q_e$ vs. $\log C_e$ gives a straight line with a slope of $1/n$ and $\log K_f$ is the intercept. Freundlich isotherm correctly established the relationship of adsorption with pressure at lower values; it failed to predict value of adsorption at higher pressure.

2.4.1.2 Langmuir Adsorption Isotherm

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at the site. The phenomenon of adsorption is essentially an attraction of adsorbate molecules to an adsorbent surface. The preferential concentration of molecules in the proximity of a surface arises because the surface forces of an adsorbent solid are unsaturated. Both repulsive and attractive forces become balanced when adsorption occurs. Adsorption is nearly always an exothermic process.

The Langmuir model is given by following Eq (2)

$$C_e / q_e = 1/q_m K_L + C_e / q_m \text{----- (2)}$$

where, C_e is the equilibrium concentration mg/L, q_e is the amount of Cr(VI) adsorbed at equilibrium (mg/g) and q_m is q_e for a complete monolayer (mg/g); K_L is sorption equilibrium constant (L/mg). A plot of C_e/q_e versus C_e is straight line of slope $1/q_m$ and an intercept of $1/K_L q_m$ [61, 62]. The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation factor, R_L , defined by Eq. (3).

$$R_L = 1 / (1 + K_L C_e) \text{----- (3)}$$

The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$.

Adsorption processes can be classified as either physical adsorption (van der Waals adsorption) or chemisorptions (activated adsorption) depending on the type of forces between the adsorbate and the adsorbent.

2.4.2 Physisorption (Physical Adsorption)

In physical adsorption the individuality of the adsorbate and the adsorbent are preserved. The resulting adsorption is like condensation, which is exothermic and thus is accompanied by the release of heat. Physical adsorption occurs quickly and may be mono-molecular (unimolecular) layer or monolayer, or 2, 3 or more layers thick (multi-molecular). As physical adsorption takes place, it begins as monolayer. It can then become multi-layer, and then, if the pores are close to the size of the molecules, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the maximum capacity of a porous adsorbent can be more related to the pore volume than to the surface area.

2.4.3 Chemisorption (Chemical adsorption)

In contrast it involves the formation of chemical bonds between the adsorbate and adsorbent is a monolayer, often with a release of heat much larger than the heat of condensation. Chemisorptions from a gas generally takes place only at temperatures greater than 200°C, and may be slow and irreversible.

3. MATERIALS AND METHODS

3.1. Chemicals and Materials

3.1.1 Chemicals and Reagents

The chemicals used for this study were analytical grade of: potassium dichromate, (K_2CrO_7 BDH, England), acetone, ($(CH_3)_2CO$) (99%) (Sigma Aldrich, USA), ferric chloride hexa-hydrate ($FeCl_3 \cdot 6H_2O$, (99%), diatomite (DB, Brand name), hydrochloric acid, (HCl) (Riedel-de Haen, Germany) aqueous solution (37% V/V), distilled water, sodium hydroxide, (NaOH), (BDH, England) and sulphuric acid, (H_2SO_4) (RANKEM, India), 1, 5-diphenylcarbozide (98%) (Merck, Germany). Standard solutions for adsorption experiments were prepared by a series of dilution of the stock solution. All chemicals for this research were used without any treatment.

3.1.2. Materials and Instruments

The following materials were used for this work. Crucible, pH meter (HANNA instruments, pH 211), Electronic balance (ADAM AFP-110L), Volumetric flask, Measuring cylinder, Mortar and pestle, Oven (Model GENLAB WIDNES, England), Thermostatic water bath (Model Grant GLS400, England), Sieve (300 μm), double beam UV-Vs spectrophotometer (Model analytik Jena Aspect UV), and Fourier transforms infrared (FT-IR) spectrophotometer (Spectrum 65 FT-IR, Perkin Elmer model).

3.2. Experimental

3.2.1 Adsorbent Preparation

Firstly, 20 g of diatomite (80 mesh) was immersed in 300 ml 6M NaOH solution at 90°C for 2 h to partially dissolve ($SiO_2 \cdot nH_2O$) [63]. The 2.42 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 500 mL of distilled water and it was immediately added to the mixture. Then, the mixture was exposed to air for 24 h and discarded the supernatant and afterwards dried in an oven at 105°C for 24 h [64, 65]. Finally, the samples were grinded and then sieved into mesh size fraction fine (300 micrometer) and stored for further study. The prepared sample was named as Fe (III)-diatomite. The surface of diatomite and Fe (III)-diatomite was observed by using a Fourier transforms infrared (FT-IR) spectrophotometer.

3.2.2. Preparation of Adsorbate

Stock solutions of Cr(VI) with a concentration of 1000 mg/L were prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) (analytical grade) in 1 L distilled water. The working solutions with different concentrations of the metal ions were prepared by appropriate dilutions of the stock solution with distilled water before used. Thermostated Water bath (Model Grant GLS400, England) was used as the medium for the process.

The concentration before and after adsorption of each Cr (VI) was determined using double beam UV-Vs spectrophotometer at 548 nm.

3.2.3. Characterization of the Adsorbent

FT-IR spectra of the adsorbent before and after Cr (VI) adsorption were recorded at 400-4000 cm^{-1} wave number range using a Spectrum 65, Perkin Elmer model FT-IR spectrophotometer to determine the surface functional groups of prepared modified diatomite.

3.3. Adsorption Study

The adsorption study was carried out using variable concentration of Cr (VI) under 10 g/L adsorbent dose, pH of conducted at 25 °C and at equilibrium time in a thermo stated water bath. The residual Cr (VI) was analyzed using double beam UV-Vs spectrophotometer at 548 nm. All experiments were carried out doublet, and the concentrations given are average values. Before each measurement, the instruments were calibrated with standard solutions.

The amount of adsorption at a given time, t , q_t (mg/g) and the amount of equilibrium adsorption, q_e (mg/g), will be calculated using the following relation [63].

$$q_t = \frac{(C_o - C_t)V}{W} \text{-----(6)}$$

Where C_t (mg/L) is the liquid phase concentrations of metal ion at any, C_o (mg/L) is the initial concentration of the metal ion in solution. V is the volume of the solution (L) and W is the mass of dry adsorbent (g).

The amount of equilibrium adsorption, q_e (mg /g), will be calculated using the formula [66]

$$q_e = \frac{(C_o - C_e)V}{W} \text{-----(7)}$$

Where C_o and C_e (mg/L) are the liquid-phase concentrations of Cr (VI) ions initially and at equilibrium. The percentage adsorption Cr (VI) solution will be calculated by using the following equation [67].

$$\% \text{adsorption} = \frac{(C_o - C_e) \times 100}{C_o} \text{-----(8)}$$

Where C_o and C_e (mg/L) are the initial and equilibrium concentrations of the Cr (VI) ion in solutions.

3.3.1 Effect of Contact Time on Adsorption

The adsorptions of the Cr (VI) by Fe (III)-diatomite were studied at various time intervals (30-360 min.) and at a concentration of 5 mg/L. This was done by weighing 10 g/L Fe (III)-diatomite into each conical flask and 0.02 L of 5 mg/L of Cr (VI) ion solutions at optimal pH was introduced into it. The waste was left in a thermostatic water bath and shaken at 150 rpm on 25°C for varying periods of time. The solution in the thermostatic water bath was decanted at different time intervals from the first to the thermostatic water bath. The mixtures were filtered immediately through Whatman filter (pore size 2.5 µm) and the concentration of residual metal ion in each solution was determined using double beam UV-Vs spectrophotometer. The amount of metal ions adsorbed was calculated for each sample.

3.3.2 Effect of pH on Adsorption

The effect of pH on the adsorption of the Cr (VI) was done by contacting 10 g/L of modified diatomite with 0.02 L of 5 mg/L Cr (VI) ion solutions in a conical flask within buffer solution ranging from pH 2 to 7. The pH of each solution was adjusted by the desire value by drop wise addition of 0.1 M HCl and/or 0.1 M NaOH. The conical flask containing the mixture were left in a thermostatic water bath and shaken at 150 rpm and 25 °C for 150 min. The mixtures were filtered immediately through filter paper and filtrate was analyzed for final chromium concentration using spectrophotometer. The optimum pH was determined as the pH with the highest adsorption of each metal ion.

3.3.3 Effect of Adsorbent Dose on Adsorption

The adsorption of Cr (VI) by modified diatomite at different adsorbent doses (1.0 –16 g/L) and at chromium concentration of 5 mg/L is investigated. This was done by weighing 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0 and 16 g /L of modified diatomite into each conical flask and 0.02 L of 5 mg/L of Cr (VI) ion solutions at optimal pH and contact time. The flasks were left in a thermostat water bath and shaken at 150 rpm on 25°C. The modified diatomite was removed from the solution and the concentration of residual metal ion in each solution was determined using double beam UV-Vs spectrophotometer.

3.3.4. Effect of Initial Concentration on Adsorption

Batch adsorption study of Cr (VI) ion was carried out using a concentration range of 5 to 25 mg/L. This was done by introducing 10 g/L of the modified diatomite into each of the conical flask employed and 20 mL of Cr (VI) ion solutions at optimal pH and contact time. The flask were left in a thermo stated water bath and shaken at 150 rpm and 25 °C. Modified diatomite was removed from the solution and the concentration of residual metal ion in each solution was determined using double beam UV-Vs spectrophotometer.

4. RESULT AND DISCUSSION

4.1. Characterization of the Adsorbent

The FT-IR spectra were obtained in order to analyze the mechanism of the Cr (VI) adsorption and identify functional groups on the surface of modified adsorbent.

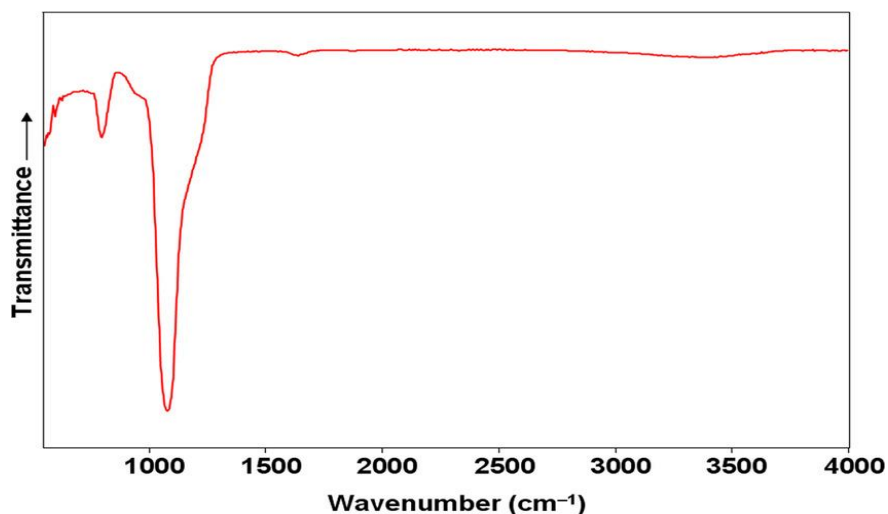


Figure 1: FT- IR spectra of raw diatomite

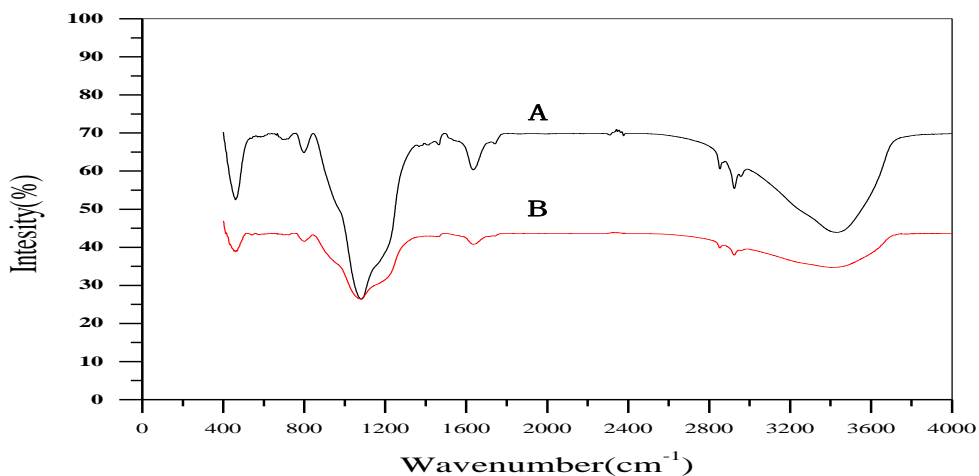


Figure 2: FT-IR spectra of FMDA before (A) and after (B) adsorption of Cr (VI)

FT-IR spectra of the raw diatomite, Fe (III)-modified diatomite and Cr (VI) loaded were shown in Figure 1 and 2 (A & B) respectively. The adsorbent materials showed the following bands for raw diatomite before modification. As shown in Figure 1 the broad peak at the 3450 cm⁻¹ is due to the stretching vibration of adsorbed water-hydroxyl (O-H) and the peaks in the region

1670– 1550 cm^{-1} were attributed to the bending vibrations of the adsorbed water-hydroxyl and surface hydroxyl groups. The stretching bands around 1100 cm^{-1} attributed to the stretching vibration of Si-O-Si and the absorption band at 990 cm^{-1} is attributed to asymmetric Si-O stretching vibration of bridging siloxane groups (Si-O-Si), which refers silicate materials that compose diatomite [68]. Changes in intensity and shift in the position of the peaks could be observed in FT-IR spectrum after Cr (VI) adsorption on Fe (III)-diatomite (Figure 2 B).

The broad absorption peak range 3600-3100 cm^{-1} may be assigned to asymmetrical and symmetrical O-H stretching vibration modes for water of hydration and the 1670-1600 cm^{-1} regions to O-H bending vibration modes [69]. The presence of SiO_2 is verified by adsorption bands at 1085 cm^{-1} of asymmetric Si-O-Si stretching vibrations, and Si-O-Si bending vibrations at 469 cm^{-1} [68]. The absorption band at 2320 cm^{-1} correspond the vibration of Si-H [70]. The absorption band at 1635 cm^{-1} correspond the vibration of $\text{Fe}(\text{OH})_3$ [71]. Figure 2 shows the FTIR spectra of Fe (III)-modified diatomite before and after adsorption of hexavalent chromium from aqueous solution. It clearly showed that after the adsorption of hexavalent chromium on Fe (III)-modified diatomite, there is a small shift in frequency values and some of the frequency regions were absent. This observation indicated the participation of adsorption of Hexavalent Chromium on Fe (III)-modified diatomite. In general, functional groups present in Fe (III)-modified diatomite are listed in the table below.

Table 2: Summery of available functional groups

Functional groups	Range of wave number (cm^{-1})	Unloaded	Loaded
OH stretching	3100-3600	3439	3495
Si-O-Si stretching	1050-1100	1085	1097
Si - O- Fe stretching	700 – 990	805	810

4.2. Effect of Contact Time

Contact time required for the maximum adsorption of Cr (VI) by modified diatomite was done by 5 mg/L of Cr (VI) and 0.20 g of adsorbent at pH 5.70. There is an increase of adsorption in initial stages of reaction as seen in curve.

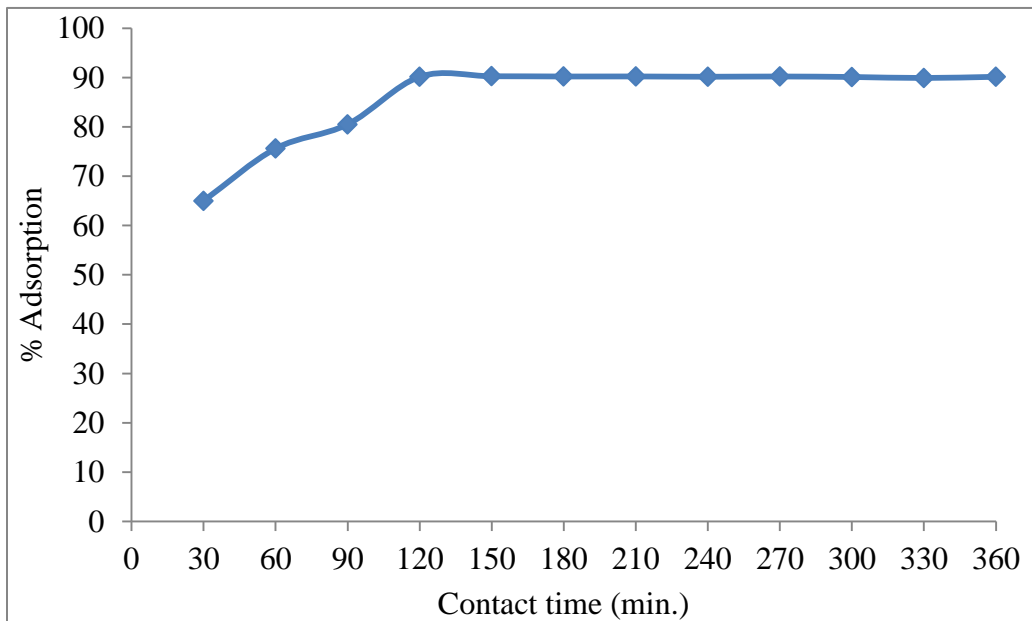


Figure 3 : Effect of contact time for adsorption of Cr (VI)

From the Figure 3, the results showed that chromium uptake is fast for the first 60-90 min. and thereafter, they proceeds at a slower rate and finally attains saturation. The initial fast reaction may be due to the increased number of vacant sites available at the initial stage; as a result there exist increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent. Generally, by the time adsorption involves a surface reaction process, the initial adsorption is fast. Then, a slower adsorption would follow as the available adsorption site which is gradually decreased. This is due to the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sited are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [72].

Maximum percentage of Cr (VI) adsorption occurs at 150 min after that the percentage adsorption remains uniform. Adsorption of Cr (VI) at this point is maximum, 90.25% for Cr (VI) in 5 mg/L of solution. Result shows the optimum contact time for adsorption on modified diatomite was fixed to be 150 for Cr (VI).

4.3. Effect of pH on Adsorption

The pH of the aqueous solution is an important parameter in the removal of metal ion by adsorption. The solution pH was varied from 2 to 7 at a temperature of 25 °C and 5 mg/L

concentration of Cr (VI) aqueous solution. The contact time has been fixed as 150 min for all the experiments.

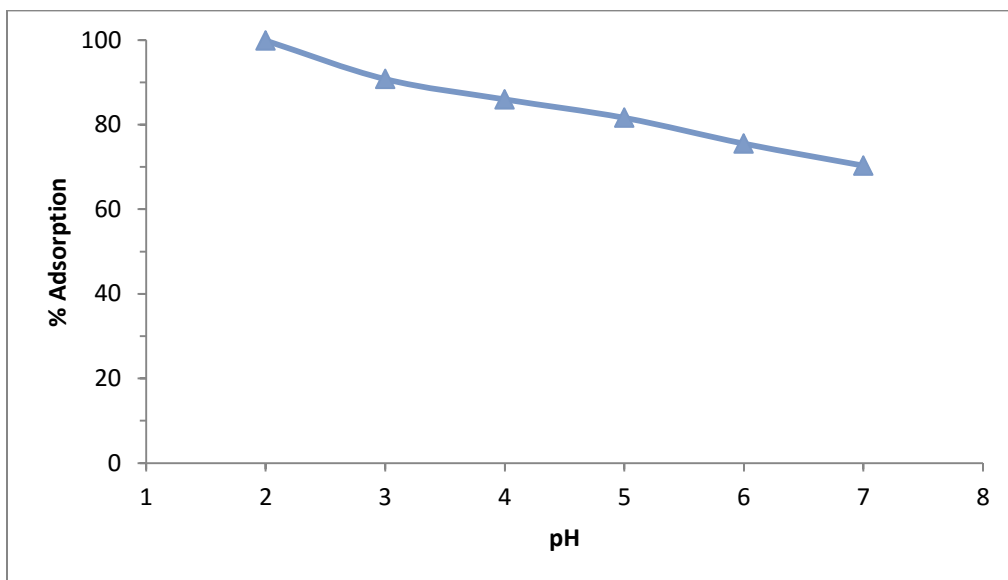


Figure 4: Effect of pH on adsorption of Cr (VI) onto modified diatomite. (Temperature 25 °C, adsorbent dose 10 g/L, concentration 5 mg/ L Cr (VI), time 150 min., and shaking speed 150 rpm)

Figure 4 show the effect of pH on the adsorption of Cr (VI) onto Fe (III)- modified diatomite. It can be seen in Figure 4 that the maximum of Cr (VI) adsorption (99.86%) occurs at the lowest pH value. It is well known that the dominant form of Cr (VI) at this pH is HCrO_4^- . The favorable effect of low pH can be attributed to the neutralization of negative charges on the surface of the adsorption by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions (HCrO_4^-) and their subsequent adsorption [74], HCrO_4^- is the dominant and ionic form of Cr (VI) at lower pH. Increasing the pH will shift the concentration of HCrO_4^- to the other forms; CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. Moreover, the surface of Fe (III)-diatomite becomes highly protonated under acidic conditions that favoured the adsorption of Cr (VI) in the anionic form [75]. The increase in pH value caused a decrease in protonation of the surface, which led to a decrease in the net positive surface potential of adsorbent. This decreased the electrostatic forces between adsorbent and adsorbate, leading to reduced adsorption capacity [76].

4.4. Effect of Adsorbent Dosage

The variation of the adsorbent dosage experiments is an important part of the study, because it

determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The dependence of Cr (VI) adsorption on dose was studied by varying the amount of adsorbents from 1 to 16 g/L, by keeping the other parameters (pH, contact time and initial concentration) constant.

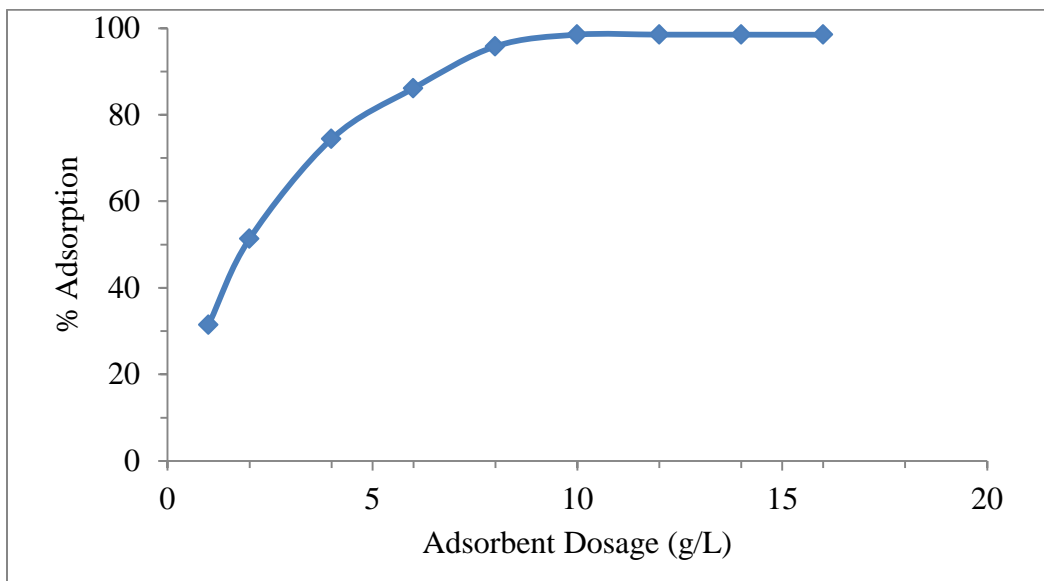


Figure 5: Effect of adsorbent dosage for adsorption of Cr (VI)

In Figure 5, the results showed that the percent adsorption increases from 31.49 to 98.51% for Cr (VI) with an increase in the dose of modified diatomite from 1.0 to 16.0 g/L and remained nearly constant at adsorbent quantities higher than 10 g/L. This is due to the greater availability of adsorption sites of adsorbent and thus making easier penetration of the Cr (VI) to the adsorption sites [73]. Since the quantity of Cr (VI) is constant, an increase in the amount of adsorbent above a quantity that can completely adsorb the available Cr (VI) had no apparent effect on further increasing the percent adsorption of Cr (VI). After an adsorbent dosage of 10 g/L Cr (VI) adsorption was not observed to increase significantly.

4.5. Effect of Metal ion Concentration on Adsorption

The effect of initial Cr (VI) concentration on the adsorption efficiency of Fe (III)-diatomite under optimum conditions of pH and contact time is shown in Figure 6.

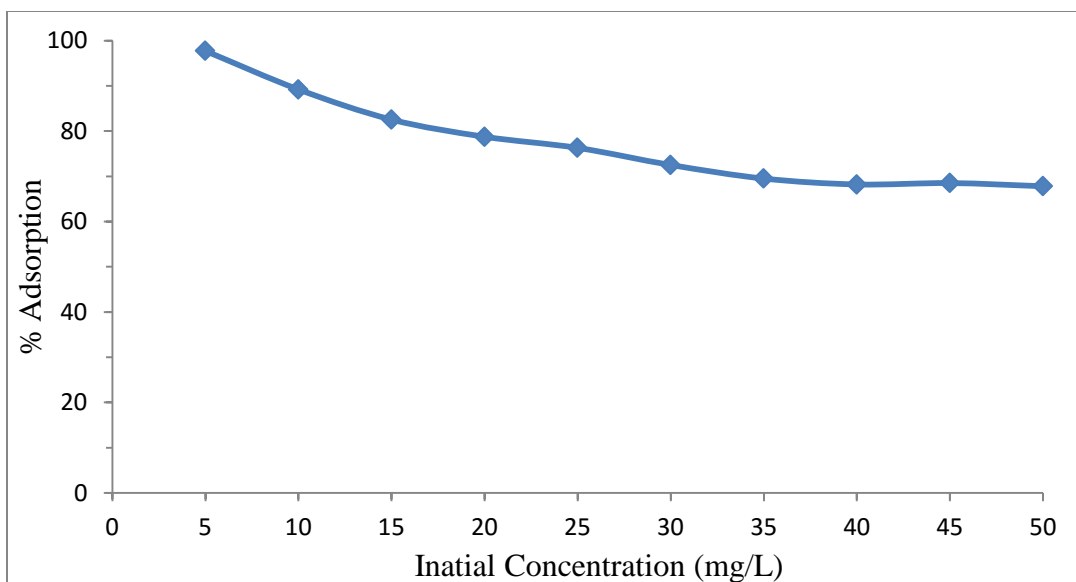


Figure 4: Effect of Initial metal ion concentration for adsorption efficiency of Cr (VI).

The adsorption efficiency decreased from 97.71-67.70% for Cr (VI) with increases initial concentration from 5 to 50 mg/L This is due to increase in number of metal ions competing for available binding sites and due to lack of binding sites for complexation at higher metal ion concentration. At lower concentration almost all the metal ions could interact with binding sites facilitating maximum adsorption at 5 mg/L concentration i.e. 97.71% for Fe (III)-diatomite. At higher concentration more chromium ions are left un-adsorbed in the solution due to saturation of adsorption sites [77]. But the solution reached equilibrium at 30 mg/L and after that the adsorption did not change significantly.

However, the adsorption capacity of Cr (VI) by Fe (III)-diatomite increases with an increasing the initial metal ion concentration. The adsorption capacity increases from 0.4885-1.96 mg/g for Cr (VI) for the first initial metal ion concentration increased from 5 to 25 mg/L but the solution reached equilibrium at 25 mg/L and after that the adsorption did not change significantly.

4.6. Adsorption Isotherms

An adsorption isotherm describes the relationship between the amounts of adsorbate which is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium [78]. According to the 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 place [79]. The adsorption isotherm of Cr (VI) onto the prepared Fe (III)-diatomite was

fitted by several well-known isotherms models, namely the Langmuir and Freundlich models, to assess their utility. Langmuir isotherm was based on the theory that the monolayer adsorption and assumes that the surface of sorbent was composed of amounts of homogeneous adsorption sites.

The Langmuir equation applied for adsorption equilibrium is as follows [80]:

$$C_e / q_e = 1/K_L q_m + C_e / q_m \text{ ----- (9)}$$

Where, K_L and q_m are constants related to the apparent energy of adsorption and the adsorption capacity, respectively q_e the amount adsorbed per unit mass of the adsorbent (mg/g) with an equilibrium concentration of C_e (mg/L). A plot of (C_e / q_e) vs. C_e was linear and the constants $1/q_m$ and $1/q_m k_L$ can be calculated from the slope and intercept of the plot. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given as:

$$R_L = 1/ (1+k_L C_o) \text{ ----- (10)}$$

Whereby k_L is the Langmuir constant and C_o is the initial concentration of the adsorbate in solution. $0 < R_L < 1$ indicates a favorable adsorption, linear ($R_L=1$), on the other hand, $R_L > 1$ makes the process unfavorable or irreversible ($R_L=0$). Furthermore, the values of the dimensionless factor, ($R_L = 0.038$), were between 0 and 1 which suggest a favorable adsorption between Fe (III)-diatomite and Hexavalent Chromium ion.

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption properties consisting of heterogeneous surface of the adsorbent. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption [81]. The linear form of Freundlich isotherm is:

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

Where q_e is the amount adsorbed at equilibrium (mg/g), K_f and n are 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 values of K_f and $1/n$ can be obtained from the slope and intercept of the plot of $\log q_e$ against $\log C_e$.

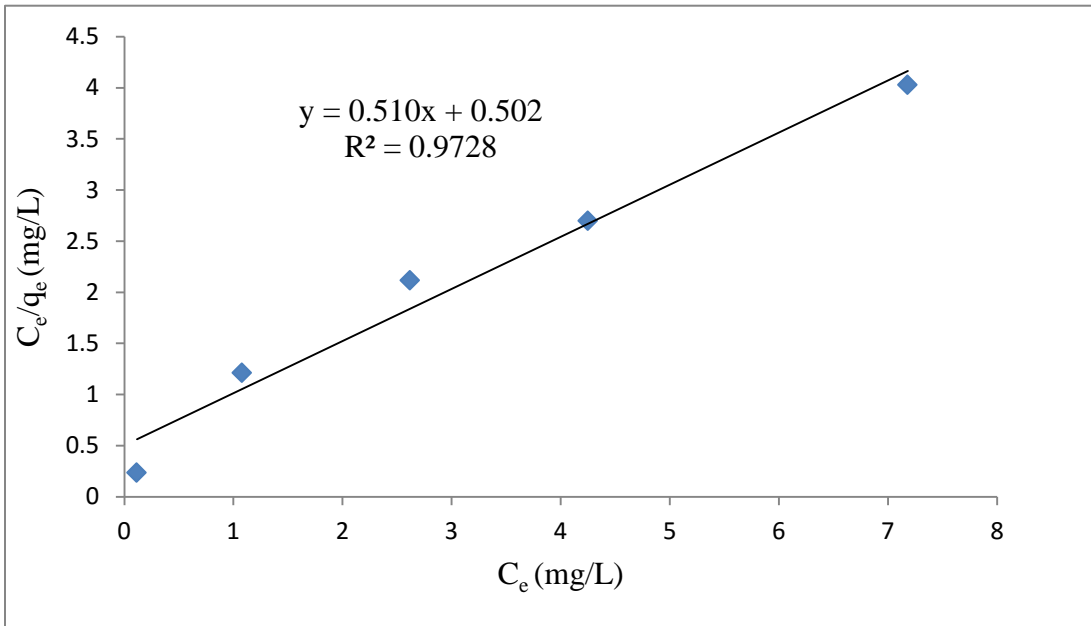


Figure 5: Langmuir adsorption isotherm of Cr (VI) onto Fe (III)-diatomite

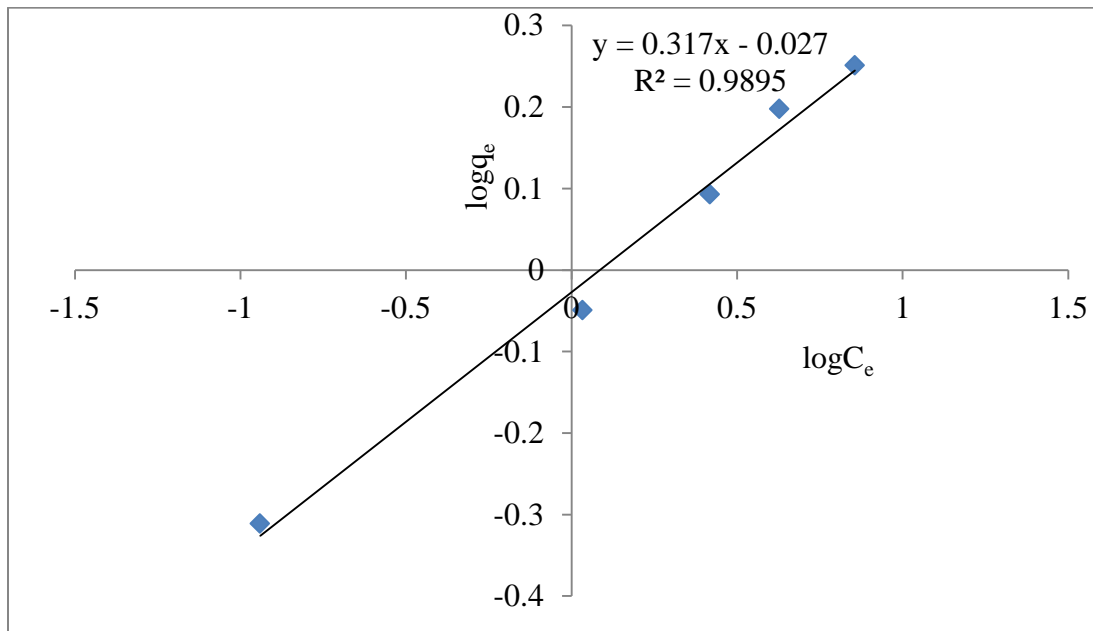


Figure 6: Freundlich adsorption isotherm of Cr (VI) onto Fe (III)-diatomite

The curves of the linear transforms of Langmuir and Freundlich obtained are presented in Figure 7 and Figure 8 respectively and the various parameters calculated are summarized in Table 3.

As the parameters shown in Table 3, Compared with Langmuir isotherm ($R^2=0.9728$), Freundlich isotherm ($R^2=0.9895$) model was better fitted to describe the adsorption characteristics of Cr (VI) on Fe (III)-diatomite. The fact that the Freundlich model is a good fit to the experimental adsorption data suggests physical adsorption as well as a heterogeneous distribution of active sites on the Fe (III)-diatomite surface. The other Freundlich constant, n , is a measure of the deviation of the adsorption from linearity. If the value of n is equal to unity, the adsorption is linear. If the value of n is below unity, it implies that the adsorption process is unfavorable, and if the value of n is above unity, adsorption is favorable [82]. In the present study, the value of ($n=3.15$) at equilibrium was above unity, suggesting favorable adsorption.

Table 3: Langmuir and Freundlich parameters for the adsorption of Cr (VI) onto Fe (III)-diatomite

Langmuir Isothermal				Freundlich Isothermal		
$q_m(\text{mg/g})$	$k_L(\text{L/mg})$	R_L	R^2	$k_f(\text{mg/g})$	n	R^2
1.96	1.02	0.038	0.9728	0.940	3.15	0.9895

4.7. Comparison of Cr (VI) Adsorption with Different Adsorbents

The adsorption capacity of the adsorbents for the adsorption Cr (VI) has been compared with those of others reported in the literature and the values of adsorption capacity as presented in Table 4. The experimental data of the present investigation were compared with reported values. Results of our investigation revealed that Fe (III)-diatomite has the highest percent adsorption and adsorption capacity.

Table 4: Comparison of adsorption capacities of Cr (VI) with various adsorbents.

Adsorbents	Initial Cr(VI) concentration (mg/L)	pH	Adsorption capacity (mg/g)	Reference
Activated rice husk carbon	10	2	0.8	[83]
Peanut shell	100	2	8.31	[84]
Activated alumina	10	4	1.6	[83]
Sawdust	5	2	0.229	[85]
Wood sawdust	150	2	4.87	[86]
Kaolinite	50	4.6	6.1	[87]
Fertilizer industry waste	100	2	15.24	[88]
Diatomite	10	4	0.402	[65]
Coconut shell carbon	25	4	10.88	[89]
Fe(III)-diatomite	25	2	1.96	This study

The adsorption capacity of the adsorbents for the adsorption of Cr (VI) has been compared with those of others reported in the literature and the values of adsorption capacity as presented in Table 4. The experimental data of the present investigation were compared with reported values. Results of our investigation revealed that FMDA has the highest percent adsorption and adsorption capacity.

5. Conclusion and Recommendation

5.1. Conclusion

In this paper, Fe (III) was utilized to coat on the surface of diatomite for the efficient removal of Cr (VI). The results illustrated that the prepared adsorbent showed a high efficiency in adsorption of Cr (VI). The maximum Cr (VI) removal capacity was found to be 1.96 mg/g for the studied concentration ranges at pH 2 and temperature of 25 °C for 150 min. study. Both Freundlich and Langmuir models were used to fit the data and estimate model parameters but the overall data is better fitted by Freundlich isotherm at the studied temperature, reflecting surface heterogeneity of Fe (III)-diatomite. Finally Fe (III)-diatomite, an inexpensive and easily available material, can be an alternative for more costly adsorbents used for Cr (VI) ions removal in wastewater treatment processes

5.2. Recommendation

- Adsorbent prepared from diatomite had been shown to have the potential in removing Cr (VI) ions from aqueous solution. Further investigate its effectiveness and on the application of the adsorbent to remove other heavy metal ions from synthetic and actual waste water.
- The regeneration and reusability of the adsorbent, desorption should be conducted using surfactant acid or base.
- Column adsorption should be study for further investigation of its effectiveness.

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