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M.Sc. THESIS ON

ADSORPTIVE REMOVAL OF Cr(VI) FROM AQUEOUS SOLUTION USING POLYACRYLAMIDE MODIFIED DIATOMITE

By

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We, the undersigned, member of the Board of Examiners of the final open defense by **TEKLU DEGEFA** have read and evaluated his/her thesis entitled **"Adsorptive Removal of Cr(VI) From Aqueous Solution Using Polyacrylamide Modified Diatomite"** and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree Master of Science in **Chemistry (Analytical)**.

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Abstract

Chromium (VI) is a highly toxic metal ion found in the priority list of pollutants. In this study, synthesized Polyacrylamide (PAM) modified diatomite adsorbent was investigated for removal of Cr(VI) from aqueous solution. The functional groups on the adsorbent that incorporated before and after for adsorption of Cr(VI) were studied by Fourier transform infrared spectroscopy (FT-IR). Batch adsorption studies were employed to assess the effects of various parameters such as contact time, pH, adsorbent dose and initial Cr(VI) concentration on adsorption of Cr(VI) by PAM modified diatomite. It was found that the removal efficiency of chromium (VI) increased with increased contact time and adsorbent dose and decreased with increased in pH and initial Cr(VI) concentration. The adsorption process was optimal at pH 2. The adsorption capacity of the adsorbent was found to be 2.0 mg/g at optimum conditions using the Langmuir adsorption isotherm model prediction. The isotherm equilibrium data was well fitted to Langmuir isotherm model than Ferudlich isotherm model with a correlation coefficient of 0.998. It is found that, PAM modified diatomite is a promising adsorbent to reduce Cr(VI) ions in water/ wastewater media.

Keywords: *Chromium(VI), adsorption, Batch mode, Polyacrylamide*

Table of Contents

Contents **Pages**

List of Tables

List of Figures

ABBREVIATIONS / ACRONYMS

DE	Diatomaceous Earth
DCP	Diphenylcarbazide
EC	European Commission
EPA	Environmental Protection Agency
EU	European Union
FT-IR	Fourier Transform Infrared
IARC	International Agency for Research on Cancer
MCL	Maximum Contaminant Level
PAMs	Polyacrylamides
USEPA	United State Environmental Protection Agency
WHO	World Health Organization

1. INTRODUCTION

Water is the most essential substance to human life and ecosystem. It is required for a number of purposes ranging from drinking, irrigation, industrial, construction, etc [1].With increasing in industrialization and development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals waste-water are directly or indirectly discharged into hydrosphere causing water pollution, especially in developing countries [2]. In Ethiopia large amount of waste products from industries are discharged directly into water sources without any treatment. In most cases, industries do not treat their wastes unless it contains recyclable products which could be reprocessed or sold to generate additional income [3]. Improper treatment and effluent discharge from industries in to the water bodies creates harmful effects to the aquatic flora and fauna, following which it ends up in the food chain and affecting humans too [4].

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 [2]. The most common heavy metals being discharged from industrial activities and processes are lead, chromium, cadmium, copper, nickel, zinc, arsenic and mercury [5]. Among these various kinds of heavy metal ions, chromium (Cr) appears to be the foremost typical heavy metal pollutant, that exists widely in the effluents produced from metal plating, tannery, textile industries and chemical manufacturing [6].

Chromium occurs in nature in two relatively stable oxidation states, as chromium (III) and chromium (VI). Chromium (III) is essential for living organisms, plays an important role in metabolic processes by enhancing the activity of certain enzymes and stimulates the synthesis of cholesterol and fatty acids [7]. However, Cr(VI) is an effective mutagen and potential carcinogen with high fluidity in soil and aquatic systems, is soluble in almost the whole pH range, has greater mobility and 500 times more toxic than Cr(III) [8]. It may be exist in various forms such as CrO_4^{2}, $HCrO_4^-$ and $Cr_2O_7^{2-}$ depending on the pH and the concentration of chromium [8].

Acute exposure to Cr(VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhaging, and respiratory problems. It damages the gastrointestinal tract, causes skin changes, hinders the photosynthetic apparatus as well as has mutagenic and teratogenic impact on organisms [9]. It is also toxic to all life forms and considered as a priority pollutant that the International Agency for Research on Cancer (IARC) has classified inhaled Cr(VI) as a human carcinogen [10]. Hexavalent chromium is broadly used in industrial sectors like electroplating, leather, metal finishing, mining, metal cleansing, pigments, wood preservation and chemical manufacturing [11]. The World Health Organization (WHO) recognized as all Cr(VI) compounds are strong oxidizing agents "carcinogenic to humans (Group 1)" and set maximum contaminant limits for surface water of 0.1 mg/L, and the permissible limit is 0.05 mg/L for potable water [12, 13]. The U.S. Environmental Protection Agency (USEPA) has categorized the chromium in the group A of contaminant and recommended a Maximum Contaminant Level (MCL) of 100 μg/L for total chromium in surface water. The California state has a specific MCL of 10 μg/L for Cr(VI) in drinking water [13]. According to Ethiopian standard guidelines the maximum permissible level of chromium in drinking water is 0.05 mg/L [14].

Numerous treatment techniques have been employed to separate hexavalent chromium from water/wastewater. These include ion exchange [15], membrane separation [16], Photoreduction [17], chemical precipitation [18], chemical coagulation and electrocoagulation [19], electrochemcal method [20], biological treatment [21], physical filtration process using nanofiltration and microfiltration [22], and adsorption [23]. Among these existing removal methods, adsorption might be a selection priority, because of its great advantages, such as a low operation cost, high regeneration capacity, and excellent efficiency of hexavalent and trivalent chromium removal from water media even at low concentrations [11, 24]. Thus, adsorption process involves several adsorbents so far to remove Cr(VI), including natural and modified pumice, chitosan, alumina, clay materials and so on. In this study, polyacrylamides (PAMs) modified diatomite was used for remove Cr(VI) from aqueous water solution.

1.1. Statement of the problem

Due to wide usage by different industries, huge quantity of chromium is being discharged into the environment. Most of the chromium is discharged into aqueous systems as Cr(III) and Cr(VI). Generally, hexavalent chromium being more toxic than trivalent chromium because of its high mobility and being more oxidizing agent [25]. Cr(VI) toxicity is related to its easy diffusion across the cell membrane in prokaryotic and eukaryotic organisms and subsequently Cr(VI) reduction in cells, which gives free radicals that, may directly cause DNA alterations as well as toxic effects [26]. Even in low concentrations, it has a toxic effect upon aquatic biota such as fish and disrupting the food chain [27]. Therefore, it is necessary to remove/reduce the concentration of Cr(VI) in industrial wastewaters to the permissible level prior to discharge into the environment.

Several treatment techniques have been used for the removal of Cr(VI) from wastewater including adsorption. In adsorption, adsorbent selection is among the most important parameter to be considered for the efficient removal of ions. Adsorption process can be performed in batch and continuous mode. Batch mode experiments are usually done to measure the capability and effectiveness of adsorption process using specific adsorbent and to determine the maximum adsorption capacity. For industrial purposes the continuous adsorption in fixed-bed column is often desired [28]. Adsorbents such as clay minerals, pumice-from porous rocks, biosorbents, and surfactant modified zeolites, etc have been tested for the removal Cr(VI). However, to the best of our knowledge polyacrylamides (PAMs) modified diatomite as adsorbent for removal of Cr(VI) has not been reported. In this study, synthesized polyacrylamide modified diatomite composite was used as adsorbent for removal of Cr(VI) from aqueous solution in batch mode.

1.2. Objectives of the study

1.3.1 General objective

To investigate the adsorptive removal of Cr(VI) from aqueous solution using polyacrylamide modified diatomite.

1.3.2 Specific objectives

- To evaluate the adsorptive capacity of polyacrylamide modified diatomite as adsorbent.
- To assess the effects of various parameters such as contact time, pH, adsorbent dosage, and initial Cr(VI) concentration on the adsorption efficiency of polyacrylamide modified diatomite.
- To describe the responsible adsorption isotherm models that represent the adsorption of Cr(VI) onto polyacrylamide modified diatomite.

1.3. Significance of the study

Generally, the importance of this research is the development of adsorption technology that can solve the problem of water pollution related with Cr(VI) ions. It helps to reduce the problem associated with wastewater management for industrial sectors. Furthermore, it would help other researchers to see at different perspectives for method development in wastewater management. It also provides information about the modified adsorbent and encourages any concerned bodies to conduct further study on topic and related areas.

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2. LITERATURE REVIEW

2.1. Chemistry of Chromium

Chromium was first discovered in 1797 by the French chemist Louis Vauquelin as a constituent of the mineral crocoite ($PbCrO_4$), which was widely used pigment because of its powerful coloring potential, from which the name ‘chromium’ is derived (Greek word ‘chroma’, means color) [29]. Elemental chromium (Cr) is a transition group metal belonging to group VIB of the periodic table. Chromium (atomic number 24) is a steely-grey, lustrous, hard and brittle metal occurring in the earth's crust crystalline solid [30]. Among the various oxidation states, the most common in the aquatic environment are the trivalent(III) and hexavalent(VI) states, which differ in physico-chemical properties and toxicity [31]. Cr(III) is an essential nutrient in trace amounts, nontoxic and poorly absorbed. Its deficiency results in glucose intolerance, inability to use glucose and other metabolic disorders. However, an excess quantity of chromium above the recommended value may be toxic to human health and results in severe acute effects and death may occur following cardiovascular shock. Whereas Cr(VI) is toxic and carcinogenic, producing liver and kidney damage, internal hemorrhage and respiratory disorders. Sub-chronic and chronic effects include dermatitis and skin ulceration [32].

Solubility of the compounds varies: Cr(III) compounds, like $Cr(OH)_3$ which precipitate at neutral pH, are generally insoluble in water; Cr(VI) is highly soluble in the full pH range [31]. The ratio between chromium hexavalent, Cr(VI), and trivalent, Cr(III), strongly depends on the solution pH, oxidative properties (redox potential) and kinetics. Depending on these conditions, chromium in water can hence change from one oxidation state to another [30]. At pH 1, the chromium ions exist in the form of H_2CrO_4, while in the pH range of 1–6 different forms of chromium ions such as $Cr_2O_7^{2-}$, $HCrO_4^{-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ coexist, of which $HCrO_4^{-}$ is the dominant species at pH 2. As pH increases this form shifts to CrO_4^{2-} and $Cr_2O_7^{2-}$ .Chromium exists in different oxidation states and the stability of these forms depends upon the pH of the system [33].

The principal chromium ore is ferric chromite, $FeCr_2O_4$, less common sources include crocoite, $PbCrO_4$, and chromeochre, Cr_2O_3 [11]. In rocks and soil, Cr (III) is a common trace mineral, found as amorphous Fe(III), Cr(III) hydroxides, eskolaite (CrO_3(s)), and chromite ($FeCr_2O_4$(s)), all Cr(III) forms. There are a wide natural variation in chromium concentrations in soils and rocks. River materials and soils with fine grain sizes have the highest concentrations, whereas granite carbonates, and large grained (sandy) sediments have the lowest concentrations [34].

2.2. Natural sources and industrial emissions of chromium

Both, natural processes and anthropogenic emissions contribute to the presence of chromium in aquatic systems. Weathering of rocks and soil erosion and leaching by rainwater are major natural processes favouring the input of chromium to rivers, lakes, estuaries, and ocean [35]. Recent research also indicate that Cr(VI) is most likely naturally occurring and ubiquitous in groundwater from the Piedmont region in the eastern United States, which could pose health risks to residents in the region who consume well water as a major drinking water source [13]. Chromium is among the most toxic trace elements released to surface waters and ground waters due to its widespread use in industrial applications [31]. Discharges of industries such as electroplating, leather tanning, stainless steel welding, and ferro-chrome and chrome pigment production contribute to chromium concentrations in aquatic environment above the regional baseline values [30]. Hexavalent chromium has a key role in metal finishing industry modifying the surface of a product to enhance its appearance and reflectivity, such as colour or brightness, corrosion resistance and good hardenability. It also used in many industrial applications like tanning agents, paint pigments, to produce alloys and catalysts to impregnation solution for wood or photography [36]. The release of trivalent chromium worldwide responsible for approximately 20% of chromium emissions is the leather tanning industry where putrescible hide or skin is converted into leather. The permanent stabilization of the skin matrix against biodegradation is possible using basic chromium sulphate [37].

2.3. Health Effects of Chromium

Cr(VI) exits widely in wastewater of electroplating, leather tanning, pigment, paint, metal, printing, dyeing, and printing industry, etc. It is very dangerous to organism with strong carcinogenic change, teratogenic, mutagenic effects, and strong oxidizing. Besides, it is accredited as one of the 17 kinds of chemicals which are most harmful to human health [38]. Cr(VI) is a group 1 carcinogen classified by the International Agency for Research on Cancer (IARC) and is pervasive throughout the environment [39].

Chromium residues tend to be amplified along the food chain [32]. Chromium causes irritation and ulcers in the stomach and small intestine, damage on kidney and liver, sperm, and male reproductive system [30, 32]. Also, it can cause respiratory problems, including irritation of the lining of the nose, runny nose, and breathing problems such as asthma, cough, shortness of breath and wheezing. Chromium can lead to cancer in lung, stomach and intestinal tract. Regarding Chromium threshold for drinking water, although most EU countries apply a legal limit of 50 µg/L of chromium, limits are going to be reduced soon to 25 µg/L, according to a recent recast of the Directive 2001/83/EC, which occurred in 2018. A few years ago, in some Italian cities, chromium levels were already at the limits of the Directive 2001/83/EC on the quality of water intended for human consumption. This has led Italy to notify the European Commission of the need to change the parameters of hexavalent chromium in drinking water, as well as to introduce a limit of 10 µg/L for Cr(VI) in drinking water in the current Legislative Decree [40].

Contaminated wastewater primarily affects aquatic organisms including fishes and amphibians. Moreover, by using contaminated wastewater for irrigation, the quality of soil and crop products deteriorates as well as the microbial fauna of the soil [41]. In plants, Cr(VI) is connected with decrease in enhancement take-up and photosynthesis which thusly prompts plants moderate development rate. It impacts the receptive oxygen species in plant cells in a few different ways, for example, physiological, morphological and in biochemical way. Its toxic derivatives impede (hinder) growth in plants by causing damage to chlorophyll content and poor intake of nutrients [42], poor seed germination [43], and reduction in yield [44]. The harmfulness of Cr is referenced in plants for the sake of chlorosis and corruption [29].

2.4. Chromium removal technologies

2.4.1. Coagulation–precipitation–filtration

Chemical precipitation processes are the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers [46]. The coagulant encourages the colloidal material in the water to join together into small aggregates called "flocs". Suspended matter is then attracted to these flocs. Flocculation is a slow gentle mixing of the water to encourage the flocs to form and grow to a size which will easily settle out. In the conventional water treatment process, coagulation using alum and ferric (Fe(III)) coagulants has been used for Cr(III) removal, in which the removal is due to precipitation as $Cr(OH)_3$ and co-precipitation with $Al(OH)_3$ or $Fe(OH)_3$ [45].

However, the two above mentioned coagulants are ineffective for Cr(VI) removal. Alternatively, chemical reduction of Cr(VI) to Cr(III) using Fe(II) sulfate, zero valent iron, sulfur dioxide or sodium bisulfite followed by precipitation of $Cr(OH)_3$, has long been applied for Cr(VI) removal. It has been observed that, when Fe(II) sulfate is used, Cr(VI) removal is nearly 100%. The reason for this is that Cr(VI) reduction by the Fe(II) ion, with subsequent precipitation as $Cr(OH)_3$ [45]. The removal of chromium by coagulation–precipitation is pH-dependent. In general, the reduction of Cr(VI) to Cr(III) is done under acidic conditions and then precipitation of hydrated chromium oxide is achieved by raising the pH with the addition of NaOH or lime. Sometimes, when chromium is present as Cr(III) only, its removal is achieved simply by raising the pH with the addition of NaOH. Moreover, heavy metal removal by coagulation–precipitation has some practical limitations: (i) precipitation is often ineffective if metals are complexed or they are present as anions (e.g. CrO_4^{2-}), (ii) the lowest metal concentration achievable is limited by the solubility product and (iii) precipitated metals may form small particles that do not settle readily. As a result, a large settling basin may be required to collect metal precipitates, usually followed by a large filtration unit. Furthermore, this method produces a large amount of chromium rich sludge that must be disposed [32].

2.4.2. Ion exchange

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus an acquired an electrical charge) from solution is exchanged for similarly charged ion attached to an immobile solid particle. These solid ion exchanged particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. Ion exchange resins are classified as cation exchangers, whom it has positively charged mobile ions available for exchange, and anion exchanger. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers [46].

Ion exchange is one of the “best available technologies” for the removal of chromium. It is a proven technology for small systems for the removal of low concentrations of chromium. Cation exchangers are effective for Cr(III), while anion exchangers are appropriate for Cr(VI) removal. For removal of Cr(VI), strong-basic anion exchangers, with an exchangeable counter ion of Cl^-, are commonly used [47].

2.4.3. Membrane technology

Membrane filtration processes have high efficiencies for removing heavy metals and are easy to operate. The major drawback of these processes is the high power consumption due to the pumping pressures and fouling of the membranes [2]. Membrane processes that could be applied to remove heavy metals from water are ultra filtration, electrodialysis, reverse osmosis and nanofiltration.

2.4.3.1. Electrodialysis

Electro Dialysis (ED) is a membrane process, by which ions are transported through semi permeable membrane, under the influence of an electricpotential. The membranes are cation- or anion-selective, which basically means that either positive ions or negative ions will flow through. Cation-selective membranes are polyelectrolytes with negatively charged matter, which rejects negatively charged ions and allows positively charged ions to flow through [46].

2.4.3.2. Ultrafiltration

Ultrafiltration is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron. Ultrafiltration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. It is a pressure-driven purification process in which water and low molecular weight substances permeate a membrane while particles, colloids, and macromolecules are retained. The primary removal mechanism is size exclusion, although the electrical charge and surface chemistry of the particles or membrane may affect the purification efficiency [46].

2.4.4. Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It refers to an accumulation of adsorbates at a surface of an adsorbent or the interface between two phases [48]. The substance which is being adsorbed on the surface of another substance is called adsorbate and the substance, present in bulk, on the surface of which adsorption is taking place is called adsorbent. Adsorbates may attach on the adsorbent through electrostatic attraction, ion exchange, ionpair interactions, van der Waals forces, cation–π and hydrophobic hydration [49]. Adsorption could be described by physisorption and chemisorption processes. In physisorption, the bonding of adsorbates to the surface of adsorbent proceeds through weak reversible van der Waals forces while chemisorption takes place via chemical bonds that is mainly irreversible [40]. In physical sorption the possible attraction forces between adsorbate–adsorbent include dipole–dipole interactions, dispersion interactions and hydrogen bonding. Chemisorption sorption is irreversible in nature and occurred due to stronger forces such as covalent or electrostatic chemical bonds [50].

In the adsorption system, the contact between adsorbate and adsorbent can be occurred by batch, continuous moving bed, continuous fixed bed (upflow or downflow) and continuous fluidize bed techniques [51]. Batch operations are only limited to treatment of small quantity of water/ wastewater and are easy to apply on laboratory studies [52]. The adsorption performances obtained from batch equilibrium experiments are useful in providing fundamental information about the effectiveness of material in removing contaminants but are generally not applicable to most treatment systems such as column operations where contact time is not sufficiently long for the attainment of equilibrium [53]. Column or continuous adsorption system therefore has significant process engineering advantages such as treating large volumes of wastewater and easy to scale-up from laboratory scale processes to industrial scale [54].

2.5. Polyacrylamide (PAM)

Polyacylamides are high molecular weight water soluble or swellable polymers formed from monomer acrylamide or its derivatives. It is the collective term for acrylamide homopolymers and polymers obtained by co-polymerization with other monomers [55]. Polyacrylamides, in general, are colorless, odorless, and usually powdered, although they may be found in an oil emulsion form. Molecular weights range from 200,000 to 20,000,000. Polyacrylamide softens at 188 to 210 °C and may tend to decompose at temperatures greater than 200 to 300 ℃ [55].

Acrylamide is an organic compound with the chemical formula C_3H_5NO. It is a compound widely used in the industry to generate polyacrylamide, polymer. Single unit of acrylamide are harmful to the central nervous system and exhibits a high degree of neurotoxicity, has been shown to be carcinogenic to laboratory animals, and are suspected to be carcinogens in humans. It is readily absorbed through intact skin; and it can be easily inhaled. It is generally believed that the main toxicological concern with polyacrylamide is its acrylamide monomer content [55, 56]. PAM can be manufactured as a cationic, anionic, and nonionic polymer for various uses. Polymerisation (copolymerization and homopolymerisation) occurs through a free-radical mechanism in aqueous solution. Anionic polyacrylamides have a negative charge, and are controlled by their charge density, which is the percentage of OH^- groups substituted for NH_2 groups on the polymer (hydrolysis) [57]. Cationic polyacrylamides are presently is not used in erosion control as it may have adverse effects on aquatic life [58].

Polyacrylamide is recovered by precipitation, for example in methanol or acetone, possibly in the presence of an electrolyte such as alkali hydroxide, hydrochloride, nitric acid or their salts .The residual monomer after polymerization is minimized by forcing the process to completion by using more than one initiator, e.g. the addition of an azo catalyst after polymerization is completed by a redox one [59]. Presently, the main methods of synthesizing PAM include polymerization using an aqueous solution, inverse emulsion, inverse micro-emulsion, suspension, or precipitation [60]. Acrylamide may be polymerized via free radical initiation or by an anionic mechanism. The most important free radical initiators employed commercially are persulfates, peroxides, redox systems involving a reducing component along with the latter two types of catalysts, azo compounds, UV light, and ionizing radiation [61].

Polyacrylamide is a water-soluble polymer which undergoes reactions typical of the amide group. The structural unit of PAM comprises amide groups, which facilitate the formation of hydrogen bonds, endowing PAM with good water solubility and very high chemical activity. Many modified products with branched or networked structures can be easily obtained through grafting or cross linking. The usage of PAM is largely determined by the relative molecular mass of the polymer [62]. Organic macromolecular materials are widely used to adsorb metal ions because their numbers of active groups which can adsorb various ions. Most of the Organic macro-molecular materials are folcculant. It will accelerate settlement of suspended particles by bridge and adsorption effects [38]. Li et al., [63] reported that the group of $-NH_3^+$ played an important role in the Cr(VI) adsorption[63]. Moreover, Deng and Ting [64] presented that the $-NH_2$ group could be protonated at a certain pH. Then, -NH_3^+ could adsorb anionic hexavalent chromium via electrostatic attraction through: $NH_3^+ + HCrO_4^- \rightarrow NH_3^+ \text{ --- } HCrO_4^-$.

a) Acrylamide monomer b) Polyacrylamide (PAM)

Figure 1: Structural formula of acrylamide (a) and Polyacrylamide (b)

2.5.1. Applications of Polyacrylamide

PAM is used for treatment of drinking water, by simultaneous improvement of its physicochemical properties. Polyacrylamide finds a wide application in production of paper, flotation of minerals and enhanced oil recovery, as a fertilizer inhibiting soil erosion and soil conditioning, municipal water treatment, sewage treatment and reverse osmosis membranes [59, [64]. It has also found numerous applications in wastewater treatment, cosmetic and textile industries and in the laboratory as a solid support for the separation of proteins by electrophoresis [65]. PAM is used as binders and retention aids of the fibers and to maintain the pigment of paper fibers in the pulp and paper industry, a thickening agent in pesticides, increase surfactants capabilities and to reduce spray drift in herbicides, as a binder of bone cement and as a medium for hydroponically grown crops [66]. It is also used in small quantities for molecular biology applications, permanent press fabrics, adhesive manufacture, electrophoresis, cosmetic additives, food processing and photographic emulsions [67].

2.5.2. Modified PAM

Modified PAM exhibited more properties of an efficient adsorbent than PAM and creates more strength [68]. Pure PAM is not effective as an adsorbent. Thus, the material should be modified either by chemical or physical method. Physical modification involves the mixing of PAM with other substances without chemical reaction [69] but by the internal forces hydrogen bonds and van der Waals forces. By contrast, chemical technique, which is commonly used to modify PAM, involves grafting [70, 71], co-polymerization [71], and cross-linking. Modified PAM in aqueous solution possesses great adsorption capacity for dyes and heavy metal ions [72].

2.6. Diatomite

Diatomite (Diatomaceous Earth or DE) (SiO_2nH_2O) is a sedimentary rock primarily composed of the fossilized remains of unicellular fresh water plants known as Diatoms. Diatomite is a chalk-like, soft, friable, earthy, very fine-grained, siliceous lightweight sedimentary rock, particle size ranging typically from 10 to 200 micrometers, usually white powder and created by the deposition of cell walls (frustules) of dead microscopic single-cell algae (diatoms) on the ocean and fresh water floors. It is very finely porous, very low in density, and essentially chemically inert in most liquids and gases [74, 75]. 80–90% of its composition is Silica, alumina (2-4%), iron oxide (0.5-2%) and other impurities like metals and organic components. It is industrially useful in a variety of ways because of its unique properties which include: low density, high porosity, large surface area, high absorptive capacity, low thermal conductivity and chemical inertness, good hydrophilicity, and high chemical stability. The major uses of diatomite include filtration media for various inorganic and organic chemicals, catalyst carrier, cement additives, fillers and absorbents [75]. Diatomite used as a support for nanoparticle coating, or used to adsorb contaminants from aqueous solution [74].

3. MATERIALS AND METHODS

3.1 Materials and Chemicals

3.1.1 Chemicals

The chemicals used for study were: potassium dichromate, $K_2Cr_2O_7$ (99.5%, FINKEM, England), Acrylamide, $CH_2CHCONH_2$, (99.5%, UNI-CHEM), Hydrogen peroxide, H_2O_2, (30%, Blulux, UK), Methanol, CH_3OH, (99.8%, Turkey), 1,5 diphenylcarbazide (DPC), (98%, Analar, England), Diatomaceous earth, (99.5%, PSPARK, UK), sulphuric acid, H_2SO_4 (98%, UNI - CHEM, Germany), Hydrochloric acid, HCl (37%, Riedel-deHaën, Germany), Sodium hydroxide, NaOH (90%, BDH, England). All chemicals were analytical reagent grade and used without further purification.

3.1.2 Instruments

Double beam UV-Vis Spectrophotometer (Model SPECORD 200/PLUS, analytikjena, Germany), FTIR spectrophotometer (Shimadzu 8201 PC) spectrophotometer using KBr, pH meter (HANNA instruments, pH 211), Digital balance (Model AFP-110L, ADAM, China) and Thermostatic water bath shaker (Model Grant GLS 400, England).

3.2 Methods

3.2.1 Preparation of stock solution

A stock solution of Cr(VI) with a concentration of 1000 mg/L was prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$, 99.5%) in 1000 mL distilled water. Then standard solution containing 100 mg/L of Cr(VI) was prepared in 500 mL volumetric flask by dissolving 50 mL of stock solution with distilled water and filled up to the marked. The working solution was prepared by diluting 10 mL from 100 mg/L standard solution with distilled water in 1000 mL volumetric flask to give the appropriate working solution containing 1 mg/L of Cr(VI). The pH of the test solution was adjusted by 0.1M hydrochloric acid or 0.1M sodium hydroxide and measured using a pH meter. During residual Cr(VI) determination, the color chelating agent was prepared by dissolving 0.25 g 1,5-diphenylcarbazide with 50 mL of acetone in volumetric flask, then stored in brown bottle in refrigerator [76].

3.2.2 Construction of Standard Calibration Curve

Cr (VI) ions of different concentrations 0.05, 0.1, 0.2, 0.4, 0.8 and 1.6 mg/L were prepared in 100 mL volumetric flask by serial dilution of the standard solution. 25 mL from each of these solutions were acidified by adding 2 mL of 3M H_2SO_4. Then, 1 mL of the diphenylcarbazide solution was added and the mixture was allowed to stand for 10-15 minutes to obtain full color development [76]. Then, the solution was introduced to UV-Visible spectrophotometer accompanied with each session of each parametric test. The calibration curve (graph) construction and quantification of Cr(VI) ions concentration were done by double beam UV-Visible spectrophotometer [77].

3.2.3 Preparation of Polyacrylamide

The polyacrylamide was prepared from its monomer acrylamide. Polymerization experiment was carried out under photoactivation with visible light [78]. To a 250 mL beaker containing 50 mL of distilled water, 8 g of acrylamide was dissolved. Next, 0.08 g of Mohr's salt was added by stirring. Then, 5 mL of H_2O_2 was added to the solution while stirring. The beaker containing the solution was let rest after stirred for a few seconds. After 30 minutes the reaction mixture was poured drop wise to 250 mL beaker containing 100 mL of water/methanol (30/70 V/V) to terminate the polymerization process and precipitate the product. Finally, the polymer was displayed after decanted and rinsed with distilled water.

3.2.4 Preparation of Polyacrylamide Modified Diatomite

To the beaker containing synthesized PAM, distilled water was added up to less than 200 mL. The polymer was dissolved by stirring up to it disappeared in the solution. Following that, 25 g of diatomite was blended to the solution by stirring. Then, water was added up to 200 mL and stirred till it was homogenized. Finally, it was lets to dry at room temperature.

3.2.5 Characterization of Adsorbent

The modified PAM was characterized using Fourier transform infrared (FTIR) spectroscopy before and after adsorption process to investigate the functional group incorporated during modification and adsorption.

3.3 Batch Adsorption Study

Depending on the parameters under study the effect of contact time, pH, adsorbent dose and initial Cr(VI) ions concentration were varied to study the adsorption efficiency of the adsorbent. The batch adsorption studies were carried out using 25 mL of 1 mg/L Cr(VI) solution in plastic bottles under different period of time, adsorbent dosage and a desired pH values in thermo stated water bath shaker at 25 ℃. The pH of the solution was adjusted using 0.1M HCl or 0.1M NaOH. The bottles were agitated at a speed of 200 rmp in thermostatic water bath shaker for predetermined time. When adsorption time was completed the aqueous phase was filtered through Whatman filter paper, Cat No 1001 090 (90 mm), and the residual Cr(VI) ions left in the filtrate was introduced to double beam UV-Visible spectrometer for determination of adsorption efficiency. The Cr(VI) removal efficiency (% removal), amount of Cr(VI) adsorbed per mass unit of adsorbent at equilibrium, q_e (mg/g) and at time t (min), q_t (mg/g) were determined using the following equations:

$$\text{Adsorption}(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\% \text{ ----------------------- } 1$$

$$q_e = (C_0 - C_e)\frac{V}{m} \text{ ------------------------------ } 2$$

$$q_t = (C_0 - C_t)\frac{V}{m} \text{ ------------------------------ } 3$$

Where, C_0, C_e and C_t (mg/L) are the initial Cr(VI) concentration, equilibrium concentration and the concentration at time t (min), respectively, V is volume of solution (L) and m (g) is the mass of adsorbent [79].

3.3.1 Effect of contact time

The adsorption of the Cr(VI) by PAM modified diatomite was studied at various interval of time (15, 30, 60, 90, 120, 180, 240, 300 and 360 min). This was done by weighing 0.1 g of the adsorbent in to plastic bottles containing 25 mL of 1 mg/L Cr(VI) at pH 2. The plastic bottles were shaken in thermostatic water bath shaker with 200 rpm at 25 ℃ for various period of time. The solutions in the plastic bottles were filtrated at different time intervals by whatman filter paper, Cat

No 1001 090 (90 mm). Then, 2 mL of 3M H_2SO_4 and 1 mL of the diphenylcarbazide solutions were added to each sample and allowed to stand for 10-15 min until red violet full color was developed. The residual Cr(VI ions left in the filtrate was analyzed using double beam UV-Visible spectrophotometer at a wavelength of 548 nm. The equilibrium time was determined at a time with the highest adsorption efficiency of Cr(VI).

3.3.2 Effect of pH

The effect of pH on adsorption of Cr(VI) was studied between pH 2-6, by contacting 0.1 g of PAM modified diatomite adsorbent in 25 mL of 1 mg/L Cr(VI) working solution in plastic bottles. The pH of each solution was adjusted to the desired values by drop wise addition of 0.1M HCl or 0.1M NaOH before addition of the adsorbent to the working solution. The bottles containing the mixture were left in to a thermostatic water bath shaker and shaken by 200 rpm at 25 ℃ for equilibrium time. When equilibrium time for adsorption was completed, the bottles were removed from the thermostatic water bath shaker and filtered by whatman filter paper, Cat No 1001 090 (90 mm). The The residual Cr(VI) ions left in the filtrate was analyzed by double beam UV-Visble spectophotometer at 548 nm using 1,5 diphenylcarbazide reagent. The optimum pH was determined by pH with the highest adsorption efficiency of Cr(VI).

3.3.3 Effect of Adsorbent Dose

The adsorption of Cr(VI) onto PAM modified diatomite was investigated using the following adsorbent doses: 0.07, 0.1, 0.13, 0.16, 0.19, 0.22, 0.25, 0.375, and 0.5 g in 25 mL of 1 mg/L Cr(VI) by keeping other variables constant (pH 2, shaking speed 200 rpm, contact time of 120 min and temperature of 25 ℃). After adsorption time was completed the adsorbents were removed from the solution by filtration and the concentrations of residual Cr(VI) ions left in each solution was determined by double beam UV–Vis spectrophotometer using DCP method.

3.3.4 Effect of Initial Chromium (VI) Concentration

The effect of initial Cr(VI) concentrations on the adsorption efficiency were studied in 25 mL of Cr(VI) having a various initial chromium concentrations of 1, 5, 10, 20 30, 40, 80 and 100 mg/L at the optimum conditions: contact time 120 min, pH 2, adsorbent dose (0.25 g), shaking speed 200 rpm, and temperature of 25 °C. After adsorption equilibrium time was completed the adsorbent was removed from each solution and the concentration of residual Cr(VI) ions left in each solution was determined by beam UV-Visible spectrophotometer using DCP method. Proper dilution and dilution factor were made in determination of the concentrations of 10, 20, 30, 40, 80 and 100 mg/L.

3.4 Adsorption Isotherm Study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species between the solid and liquid phases when the adsorption process reaches an equilibrium state and can give an indication of the adsorption mechanism of the adsorbate on the adsorbent surface [80]. The adsorption capacity and the performance of the adsorbent are usually predicted from equilibrium sorption isotherm [81]. Several models have been used to describe experimental data for adsorption isotherm. The most commonly used isotherms are the Langmuir and Freundlich isotherms [82].

The Langmuir isotherm model is based on the assumption that there are a finite number of homogeneous active sites distributed over the surface of the adsorbent and forms a monolayer, once a molecule occupies a site no further adsorption takes place. These active sites have the same affinity for the adsorption of a mono molecular layer and there is no interaction between adsorbed molecules [83]. The linear form of the Langmuir isotherm equation can be given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad ----------------------------4$$

Where, q_e is the adsorption capacity at equilibrium time (mg/g), C_e is equilibrium concentration of the adsorbate in solution (mg/L) (i.e., the concentration of Cr(VI) left after adsorption), q_m is maximum adsorption capacity (mg/g), and K_L is the Langmuir adsorption equilibrium constant (mg/L) [85, 86].

When the adsorption obeys the Langmuir isotherm, a plot of C_e/q_e versus C_e should be a straight line with a slope of $1/q_m$ and intercept $1/K_L\, q_m$. This is important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L, known as the separation factor, is given as:

$$R_L = \frac{1}{1 + K_L C_0} \text{ -------------------------------- } 5$$

Where, C_0 is the highest initial Cr(VI) concentration (mg/L).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) [86].

The Freudlich isotherm model describes the 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. The activation of adsorption sites takes place, leading to increased adsorption probably through the surface exchange mechanism [87]. The Freundlich adsorption equation is given as:

$$q_e = K_F C_e^{1/n} \text{ -------------------------------- } 6$$

The linear form of the Freundlich isotherm equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \text{ ---------------------------- } 7$$

Where, q_e is the amount of Cr(VI) adsorbed at equilibrium (mg/g), K_F is the Freundlich constant, 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 1/n ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface. The isotherm constants of Langmuir and Freundlich are calculated from the slope and intercept of the plots of C_e/q_e versus C_e and $\log q_e$ versus $\log C_e$ respectively [88].

4. RESULTS AND DISCUSSION

In this batch adsorption studies, different parameters such as effect of contact time, pH, adsorbent doses and initial concentration were studied in order to determine the efficiency of the adsorbent towards the removal of Cr(VI) from aqueous solution. The data collected from these studies were used to describe the effect of various parameters and the responsible adsorption isotherm models hexavalent chromium onto PAM modified diatomite.

4.1. Characterization of the adsorbent

The FT-IR spectroscopy is a known method for detection of functional groups and in some extent quantitative analysis of samples. In this case, the changes in the spectrum before and after adsorption of Cr(VI) observed to extract the functional groups involved and the mechanism of adsorption are considered. FT-IR of polyacrylamide modified diatomite before and after adsorption process has been studied is shown in Figure 2 (a and b). The spectra were recorded in the region 450-4000 cm^{-1} using a pressed KBr pellet technique.

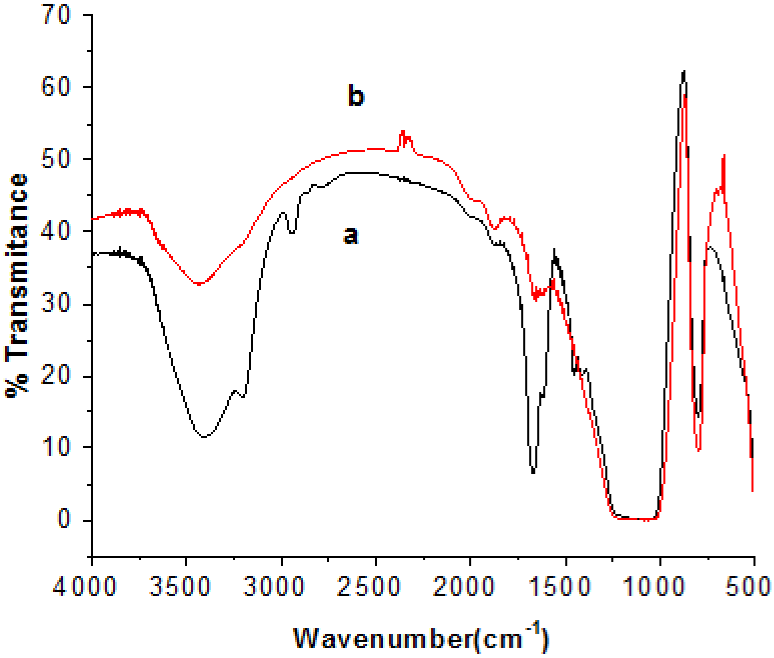

Figure 2: FTIR spectra of PAM modified diatomite (a) before Cr(VI) adsorption, (b) after Cr(VI) adsorption

The spectrum of PAM modified diatomite before adsorption (Figure 2a), absorption peak at 3423 cm^{-1} indicates the presence of –NH groups on the surface of adsorbent, the band that was observed at 2950 cm^{-1} indicates the -CH stretching vibration in -CH and -CH_2 from PAM , the peak at 1667 cm^{-1} was assigned to C=O group of amide, 1454 cm^{-1} for -CN starching vibration, 1130 cm^{-1} for C-C stretching vibration and 750 cm^{-1} indicates -C-C-H_2 rocking vibration (the presence of long-chain band) [90, 91]. FTIR bands at near 800 cm^{-1} was assigned to Si–O–Si symmetric stretching vibration [92]. The FTIR spectrum of PAM modified diatomite after Cr(VI) adsorption (Figure 2b), adsorption of the two peaks of NH and C=O groups of amide were shifted to higher wave numbers show the main role of NH group in the adsorption of Cr(VI) [91].

4.2. Effect of contact time on adsorption

One of the most important parameter that the amount of Cr(VI) adsorbed depends on is the contact time taken to establish the adsorption equilibrium. The time dependent adsorption of Cr(VI) onto PAM modified diatomite was investigated by varying the contact time in the range of 15-360 min while the effect of other parameters: pH 2, adsorbent dose 0.1 g and initial Cr(VI) concentration (1 mg/L) were kept constant. The effect of contact time on Cr(VI) adsorption efficiency is shown in Figure 3.

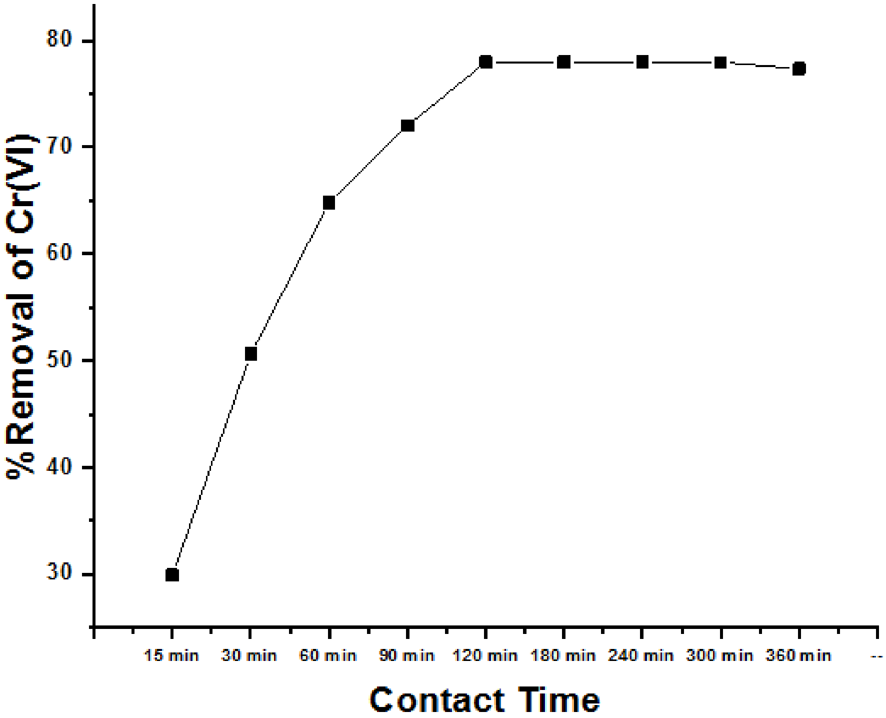

Figure 3: Effect of contact time on the Cr(VI) removal by PAM modified diatomite (conditions: Cr(VI) of 1 mg/L, pH 2, adsorbents dose 0.1 g, shaking speed 200 rpm and temperature 25 °C).

As indicated in Figure 3, the adsorption removal efficiency of Cr(VI) onto PAM modified diatomite was increased with increased in contact time. Maximum percentage of adsorption occurred at 120 minutes and then it becomes almost remained constant. At initial stage rapid rate of adsorption may be due to the availability of the vacant surfaces of the adsorbent for anionic Cr(VI) species present in the solution and the concentration gradient of Cr(VI) between the solution and the surface of the adsorbent was larger, which accelerates the diffusion of Cr(VI) from the solution to the surface of adsorbent and promote the rate of Cr(VI) adsorption [93]. Afterwards, the chromium uptake rate by adsorbent decreased, due to the surface adsorption sites of the adsorbent reduced, the concentration gradient of Cr(VI) between the solution and the surface of adsorbent decreased and electrostatic repulsion hindrance caused by already adsorbed adsorbent species [93, 94]. From the results obtained the optimum contact time for adsorption process onto adsorbent was chosen to be 120 min as the efficiency of removal became constant after this contact time.

4.3. Effect of pH on adsorption

Solution pH is another most important parameter that affects adsorption of Cr(VI) by influencing the surface properties of the adsorbent and ionic forms of the chromium ions in the solution [95]. The pH of Cr(VI) solutions were adjusted before adding adsorbent and its optimization was carried out by studying the extent of removal efficiency of Cr(VI) using a fixed mass (0.1 g) of the adsorbent in 25 mL of 1 mg/L Cr(VI) solution in the pH range from 2-6 for 120 min at 25 ℃. The reason why pH 1 was excluded is that at pH 1 the chromium ions exist in the form of H_2CrO_4 and at pH 2 the dominant species is $HCrO_4^-$ [33, 96]. The effect of pH on Cr(VI) adsorption efficiency is shown in Figure 4.

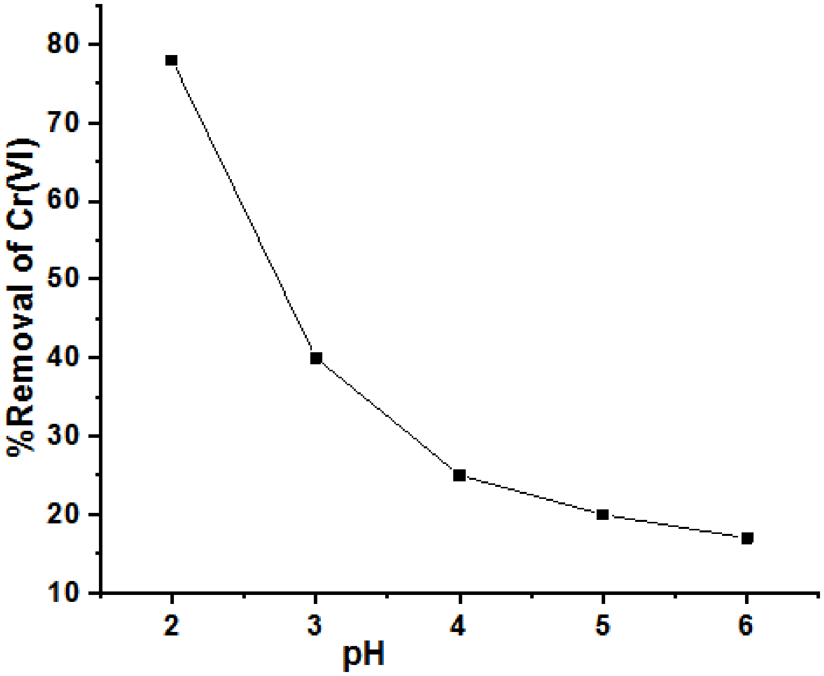

Figure 4: Effect of pH on the Cr(VI) removal by PAM modified diatomite (conditions: Cr(VI) of 1 mg/L, contact time 120 min, adsorbents dose 0.1 g, shaking speed 200 rpm and temperature of 25 ℃).

As shown in Figure 4, the percentage removal of Cr(VI) decreased with increased in pH values and maximum adsorption was achieved (78%) at pH 2. The chromium removal was higher at lower pH values and diminished with increment in pH values. According to Kong et al., [97] high Cr(VI) uptake is between pH 2–6. Similar trends were also reported by other by researchers [96]. The reason for this decrease can be explained by the fact that the dominant species of Cr(VI) in the acid medium is the $HCrO_4^-$ and increase in pH shifts concentration of $HCrO_4^-$ to other forms (CrO_4^- and $Cr_2O_7^{2-}$) chromates [96]. On the other hand at lower pH the surface of PAM modified diatomite was surrounded by adequate H^+ and the amide groups of the PAM were easily protonated and positively charged [99, 100, 101]. Therefore, the increase in Cr(VI) adsorption at acidic pH could be attributed to strong electrostatic attraction between positively charged amide group of adsorbent and negatively charged $HCrO_4^-$ ions and the decrease in removal of in Cr(VI) due to an increase in pH may be as a result of decrease of electrostatic attraction and competitiveness between Cr(VI) anionic species (CrO_4^-, $Cr_2O_7^{\ 2-}$) and the OH^- ions in the solution for adsorption on active sites of the adsorbent [33, 64, 102]. Thus it was found that removal of Cr(VI) from solution was strongly dependent up on pH values and in view of these observations, the value of pH 2 was taken as the optimum pH for further experimental studies.

4.4. Effect of adsorbent dosage on adsorption

Variation of adsorbent dose is one of the significant part of the study as it determines the capacity of adsorbent for a given initial concentration of Cr(VI) at the operating conditions. The effect of adsorbent dose on the adsorption of Cr(VI) was investigated by varying the dosage in the range of 0.07-0.5 g in 25 mL of 1 mg/L Cr(VI) ions concentration, pH 2, at temperature of 25 °C for contact time of 120 minutes. The results obtained are shown as percentage removal of Cr(VI) versus adsorbent dosage in the Figure 5.

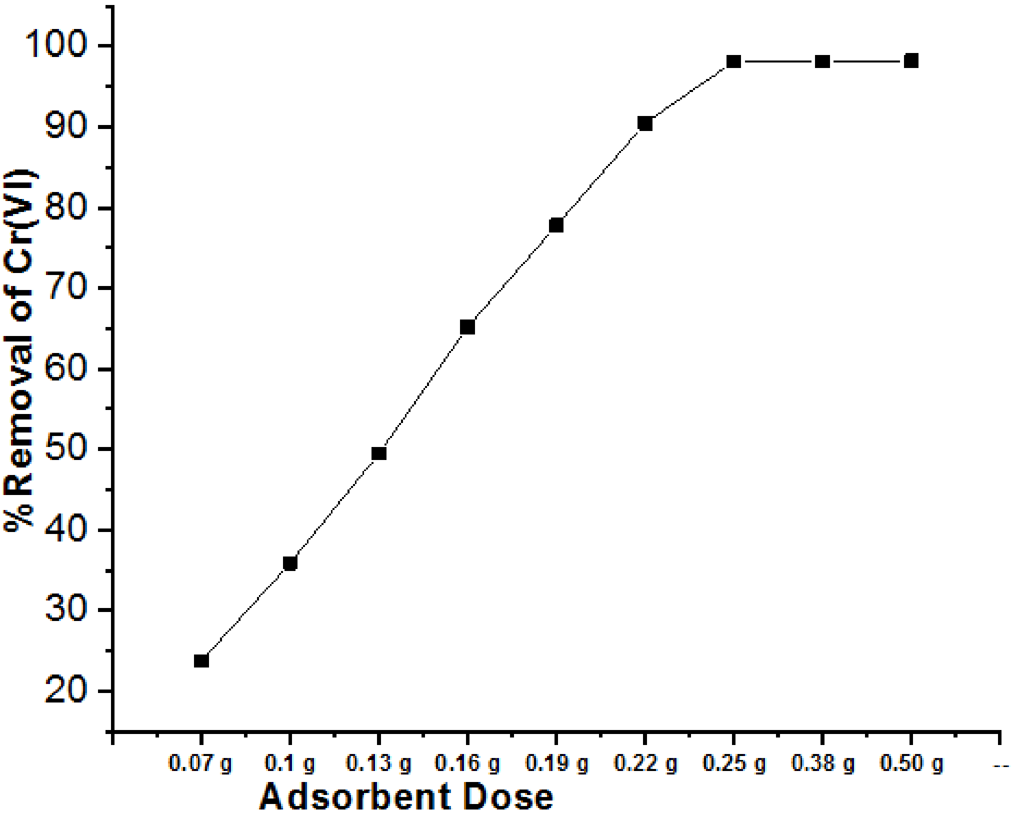

Figure 5: Effect of dose on the removal efficiency of PAM modified diatomite (conditions: Cr(VI) of 1 mg/L, contact time 120 min, pH 2, shaking speed 200 rpm and temperature 25 ℃).

As the results in the Figure 5 revealed that, the removal efficiency of Cr(VI) increased significantly from 25.5% to 89.8% and reach a saturation level (maximum) of 98.1% with increased adsorbent dosage from 0.07 g to 0.25 g. This was attributed probably due to the increased availability of surface functional groups at higher adsorbent dosage for Cr(VI) ions [98]. At lower dosage of adsorbent, there are insufficient active sites while at higher dosage there are sufficient active sites available for the adsorbate to occupy [96]. For adsorbent dose greater than 0.25g there was no significant change in percentage removal because of the resistance to mass transfer of Cr(VI) from solution to surface of adsorbent [103]. When removal efficiency reached 98.1%, the adsorption capacity decreased slowly with the increase in dosage [78]. Hence, 0.25 g of PAM modified diatomite was taken as optimum dosage for the next studies of Cr(VI) removal.

4.5. Effect of Initial Chromium (VI) Concentration

The effect of initial Cr(VI) concentration on adsorption by PAM modified diatomite was studied using Cr(VI) ions concentration of 1, 5, 10, 20, 30, 40, 80 and 100 mg/L at contact time of 120 min, pH 2, adsorbent dosage of 0.25 g and temperature of 25 °C. The obtained results are shown in Figure 6.

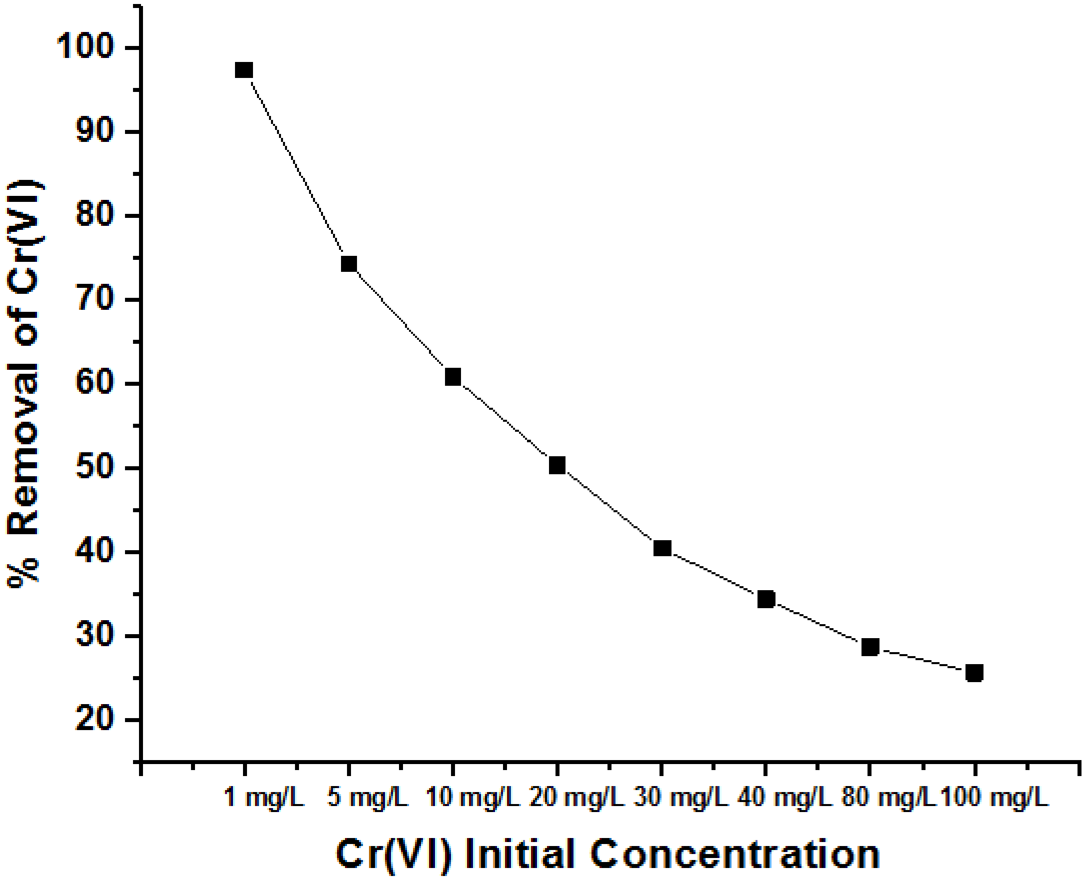

Figure 6: Effect of initial [Cr(VI)] ions on the removal of Cr(VI) by PAM modified diatomite (Conditions: Contact time 120 min, pH 2, adsorbents dose 0.25 g, shaking speed 200 rpm and temperature 25 °C).

As indicated in the Figure 6, percentage removal of Cr(VI) from the solution was decreased with an increased in initial Cr(VI) concentration from 1-100 mg/L. This is because at lower concentration there were sufficient active sites that the adsorbates can easily occupy. However, at higher concentrations, active sorption sites were not sufficiently available for the sorbate to occupy. These might due to limited adsorption sites of PAM modified diatomite for Cr(VI) ions adsorption. Hence, Cr(VI) ions were not completely adsorbed from solutions due to the saturation of binding sites [81, 98 , 104]. Moreover, the electrostatic repulsion between negative charges of adsorbate ions results in the decrease of the adsorption percentages, which is consistent with others work [80].

4.6. Adsorption Isotherm Study

In this study Langmuir isotherm model and Freundlich isotherm model were used to describe the adsorption of Cr(VI) ions on to PAM modified diatomite adsorbent using different initial Cr(VI) ions concentrations of 5, 10, 20, 30, 40, 80 and 100 mg/L by keeping the other variables constant (volume Cr(VI) solution 25mL, adsorbent dose 0.25 g, pH 2, contact time 120 min, and temperature 25 °C). The linear forms of these models are given in equation (4) and (7) respectively. The isotherm constants of Langmuir and Freundlich are calculated from the slope and intercept of the plots of C_e/q_e versus C_e and $\log q_e$versus $\log C_e$ respectively [88] .The isotherm models and the calculated constants from the experimental data are presented in Figure 7 and 8 and Table 1.

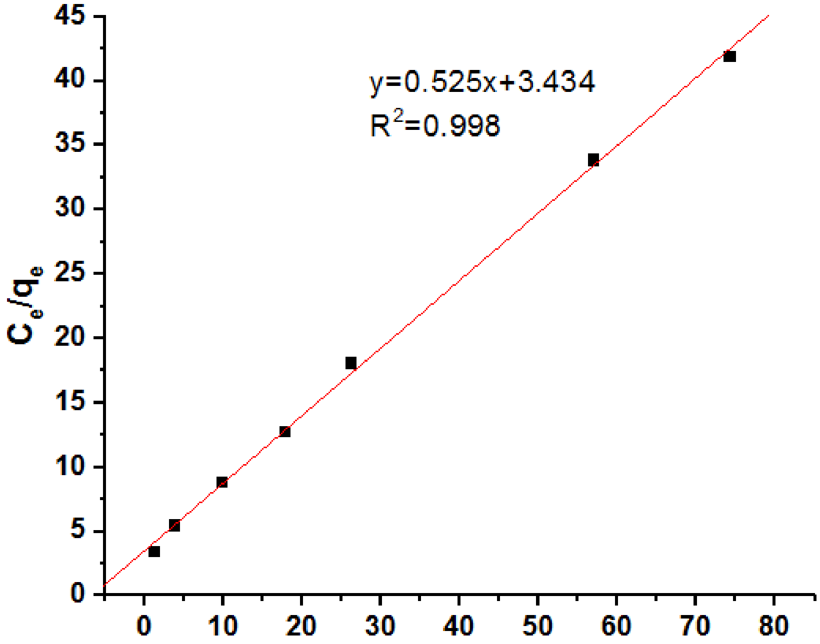

Figure 7: Langmuir isotherm model for the adsorption of Cr(VI) onto PAM modified diatomite

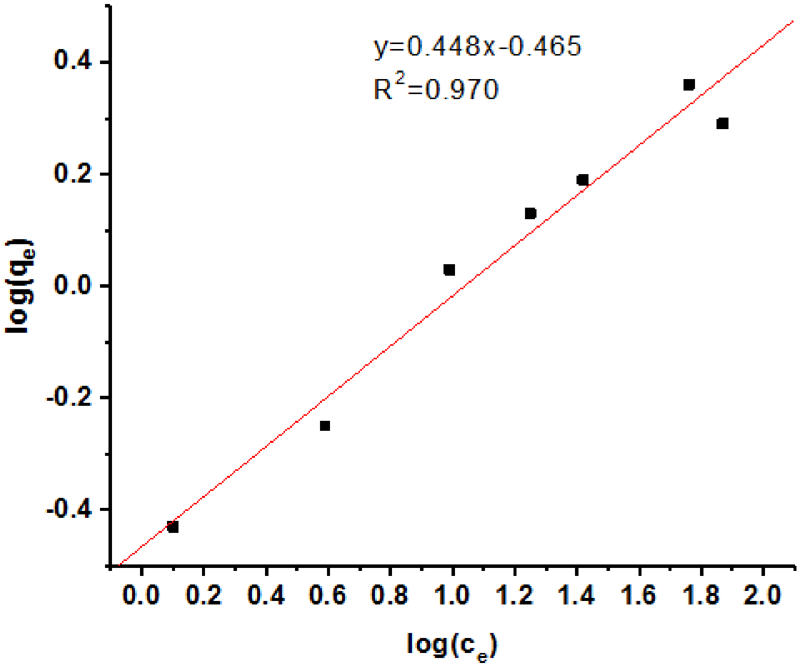

Figure 8: Freundlich isotherm model for the adsorption of Cr(VI) onto PAM modified diatomite

Table 1: Langmuir and Freundlich isotherm parameters for Cr(VI) adsorption onto PAM modified diatomite

Temperature (°C)	Langmuir model					Freundlich model		
	q_m(mg/g)	k_L (L)/mg	R^2	R_L		k_F	$^1/_n$	R^2
25	2.0	0.15	0.998	0.06		0.34	0.448	0.970

The results of the experimental data revealed that the adsorption equilibrium on PAM modified diatomite fitted to the Langmuir and Freundlich isotherm models. However, Langmuir isotherm model better fitted to the equilibrium isotherm data compared to the Freundlich model as it shows higher correlation coefficient (R^2= 0.998) values. This indicate that the Langmuir adsorption isotherm model represent the adsorption process than the Freundlich isotherm model, suggesting monolayer adsorption of Cr(VI) ions onto the adsorbent surface. The values of separation factor R_L from Langmuir model and 1/n from Frundlich model lies between 0 and 1 indicate that the favorable condition for the adsorption processes [105].

4.7. Comparison of adsorption capacities of Cr(VI) with other adsorbents

The adsorption capacity of the adsorbent for adsorption of Cr(VI) has been compared with others reported in the literature and the values of adsorption capacity and the pH presented in Table 2. Results indicate that the adsorbent has comparably adsorption capability with other adsorbents.

Table 2: Comparison of Cr(VI) adsorption of PAM modified diatomite with other adsorbents

Adsorbent	Capacity q_m(mg/ g)	pH	References
Polyacrylamide modified magnetic nanoparticles	35.186	3	[38]
Divinylbenzene copolymer resin	99.91	2	[90]
Sodium alginate-polyaniline nanofiber	73.34 mg g−1.	4.2	[105]
MgO_2	0.83	5.9	[106]
Sawdust	0.229	2	[107]
Raw race brain	0.07	2	[108]
Modified oak sawdust	1.7	3	[109]
PAM modified diatomite	2.0	2	This study

5. CONCLUSION

In this study, adsorption efficiency of PAM modified diatomite towards the removal of Cr(VI) ions in aqueous solution was investigated. The obtained results revealed that the adsorbent has Cr(V) removal efficiency of 98.1% within120 minutes at initial Cr(VI) ions concentration of 1 mg/L, pH 2, adsorbent dose 0.25 g, shaking speed of 200 rpm and temperature of 25 ℃. The adsorption was found to be dependent on contact time, pH of the solution, adsorbent dose and initial concentration of Cr(VI). The adsorption equilibrium data for the adsorption processes were well fitted to Langmuir and Freundlich adsorption isotherm models with good correlations. The maximum adsorption capacity (q_m) obtained using the Langmuir adsorption isotherm model prediction was 2.0 mg/g. The developed adsorbent could be promising in the treatment of chromium from wastewater and other sources of effluents before discharging into the aquatic environment.

6. RECOMMENDATIONS

Further evaluation of the adsorbent (PAM modified diatomite) in column and pilot scale are required in order to be applicable for removal of Cr(VI) from real wastewater sample and in treatment of wastewater in practical applications. Moreover, the effect of interference ions in real water samples as well as regeneration study for removal of chromium using the adsorbent should be investigated.

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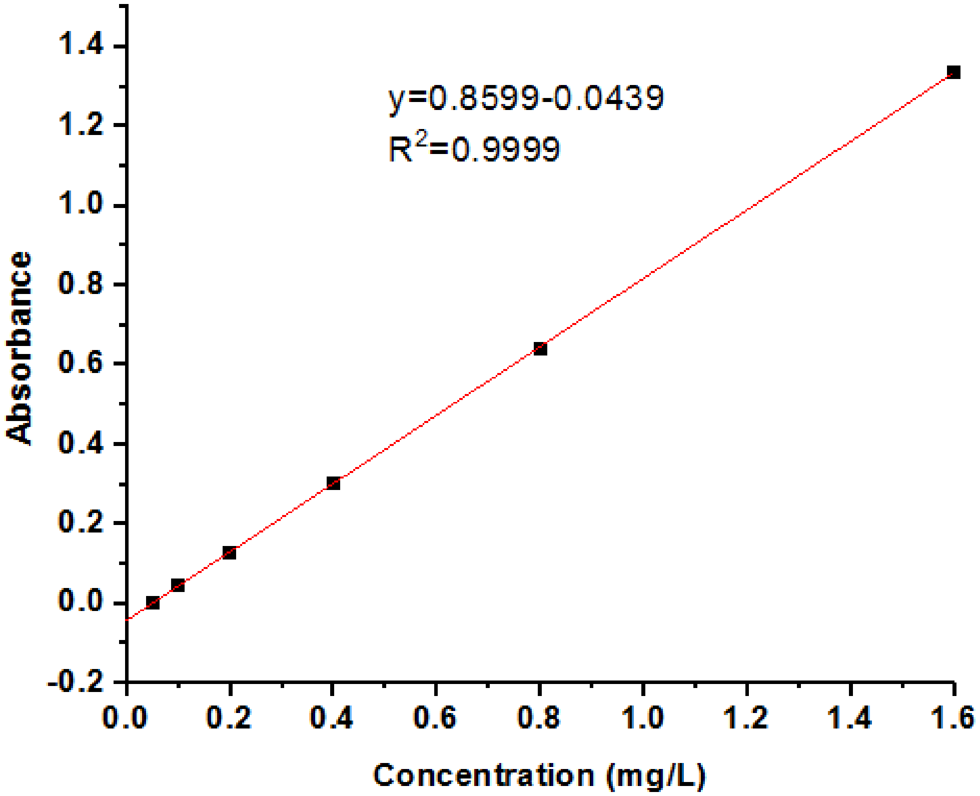
Annex

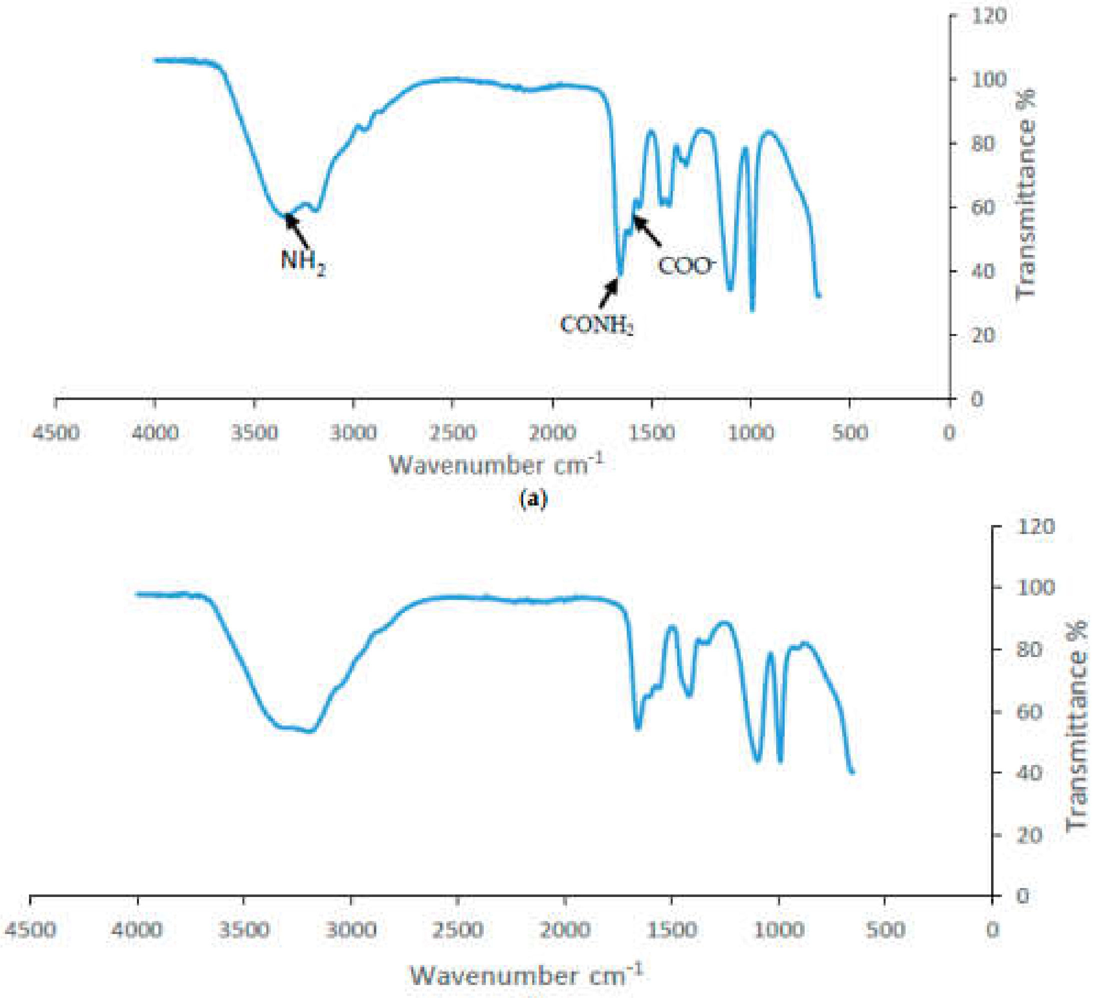
Calibration standards data for Cr (VI) quantifications

S.No.	Concentration (mg/L)	Absorbance
1	blank	0.0000
2	0.05	-0.0001
3	0.1	0.0433
4	0.2	0.1276
5	0.4	0.3020
6	0.8	0.6384
7	1.6	1.3346



The Standard Calibration Curve for Cr (VI)

Fourier Transform Infrared (FTIR) spectra of PAM



(a)

(b)

Figure 2. Fourier transform infrared (FTIR) spectra of PAM in pure water (**a**) and brine (**b**).

Fourier Transform Infrared (FTIR) spectra of Raw diatomite (Blue Color)

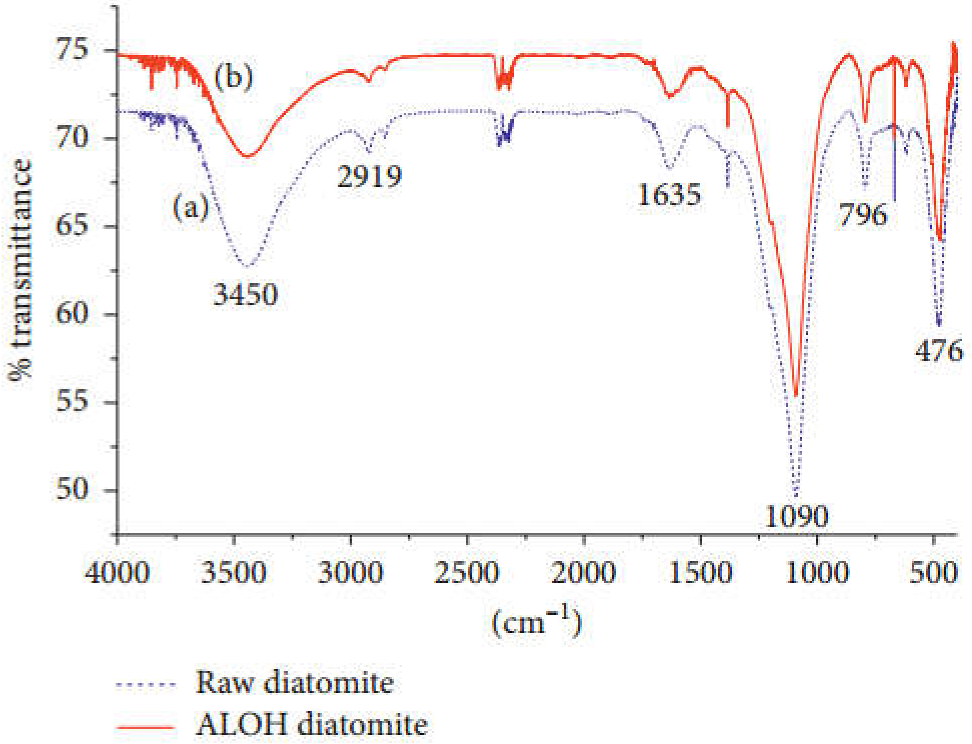


FIGURE 1: Fourier-transform infrared spectrum of raw diatomite (a) and aluminum hydroxide-treated diatomite after adsorption (b).