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**Cr (VI) Removal from Tanning Effluents Using  
Functionalized-Pyroxene Nanoparticles Supported into  
Diatomite: Batch and Continuous Processes**

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## Thesis Approval

### Cr (VI) Removal from Tanning Effluents Using Functionalized-Pyroxene Nanoparticles Supported into Diatomite: Batch and Continuous Processes

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Jerusalem – Palestine

1440 – 2018

## **Dedication**

This thesis work is dedicated to my husband, Baha, who has been a constant source of support and encouragement during the challenges of graduate school and life. I am truly thankful for having you in my life. This work is also dedicated to my parents, who have always loved me unconditionally and whose good examples have taught me to work hard for the things that I aspire to achieve.

## **Declaration**

I certify that the thesis is submitted for the degree of master is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not be submitted for a higher degree to any other university or institution.

Signature: .....

Name: Wisal Mohammed Abed Al-Hadi Khderat

Date:22/12/2018

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## **Abstract**

Chromium is commonly found in huge quantities in tannery wastewaters. For this reason, the removal and recovery of the chromium content of tannery wastewaters is crucial for environmental protection and economic reasons. Removal and recovery of chromium were carried out by using low-cost potential adsorbents. As a novel solution, nanotechnology holds great potential in water and wastewater treatment to improve water quality efficiently. Here, we introduce an innovative technique using environmentally friendly, multifunctional, and effective poly (ethylenimine)-functionalized iron silicate nanoparticles and embedded into Diatomite (D4500) a commonly used filter aid, at < 6 wt% to remove chromium from tannery wastewater in a batch and continues fixed-bed column setup. SEM technique was carried out for the Diatomite embedded nanoparticles. The characterization results showed that the filter aid was mainly composed of pour diatomaceous earth; its adsorption surface area and capacity toward the chromium were improved significantly via embedding iron silicate nanoparticles. Chromium uptake over the Diatomite embedded with 6 wt% of PEI-iron silicate nanoparticles has been investigated in batch equilibrium adsorption study, with isotherms being fairly explained by the Sips model. After that, the adsorption performance of fixed-bed column was tested for D4500 before and after embedding it with virgin and PEI-functionalized nanoparticles of iron silicate to determine the breakthrough curves under different operational conditions (e.g., inlet concentration of C(VI), inlet flow rate and bed height). The results revealed that the hexavalent chromium is significantly adsorbed on PEI-functionalized nanoparticles as an efficient technique for removal of Cr (IV) and purification of tannery wastewaters.

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## List of Abbreviations and Units

<b>BTCs</b>	<b>Breakthrough curves</b>
<b>Cr(VI)</b>	<b>Hexavalent Chromium</b>
<b>D4500</b>	<b>Diatomite</b>
<b>HNO<sub>3</sub></b>	<b>Nitric Acid</b>
<b>NaOH</b>	<b>Sodium Hydroxide</b>
<b>NPS</b>	<b>Nanoparticles</b>
<b>SEM</b>	<b>Scanning Electron Microscopy</b>
<b>WHO</b>	<b>World Health Organization</b>

<b>Unit</b>	
<b>cm</b>	<b>Centimeter</b>
<b>L</b>	<b>Liter</b>
<b>m</b>	<b>Meter</b>
<b>mg</b>	<b>Milligram</b>
<b>mL</b>	<b>Milliliter</b>
<b>nm</b>	<b>Nano Meter</b>
<b>ppm</b>	<b>Part Per Million</b>

## Organization of Thesis

The present thesis comprises of six chapters.

**Chapter One** gives an introduction of the thesis along with objectives of the research work, and 'literature review' to describe the existing literature relevant to the research topic. This chapter provides an overview of tanning process, tannery wastewater composition, impacts of tannery wastewater on environment and health, chromium chemistry and toxicity, treatment methods usually adopted to treat the effluents.

**Chapter Two** presents the methodology for carrying out the present work. It includes collection of samples, experimental setup and procedures.

**Chapter Three** this chapter introduce theoretical background

**Chapter Four** provides a detail analysis of results of the laboratory tests and discusses the results.

**Chapter Five** analysis and characteristics of tannery wastewater

**Chapter Six** Presents the conclusion and recommendations of this study.

# Chapter One

---

## Introduction

### 1.1 Background

Day by day pollution increased and possible accumulation of waste discharged by chemical industries in water, air and soil. In these industries one is tannery industry from many type of waste discharged in water, air and soil. The tannery effluents are characterized by high contents of dissolved, suspended organic and inorganic solids and chromium metal ion. In all of these chromium is very toxic in nature that's why it is necessary to reduce the amount of chromium from tannery waste water (WW). There are two types of chromium present in the tannery WW one is Cr (III) and Cr (VI). There are two oxidation state of chromium +6 and +3. It is mutagenic in +6 and bio element in +3 states (Singh, 2014).

Cr(III) is convoluted in hydrolysis behavior and produced mononuclear species,  $\text{Cr}(\text{OH})_4^-$ ,  $\text{Cr}(\text{OH})_2^+$ , neutral compound  $\text{Cr}(\text{OH})_3$ , and poly nuclear compound  $\text{Cr}_2(\text{OH})_2$  (Maria,2017). The hexavalent form of chromium is more toxic than trivalent. After hydrolysis of Cr (III) whatever generated stabilized by electron donor species ( $\text{OH}^-$ ) while hydrolysis of Cr (VI) produced anions are hardly stabilized (Kanagaraj, 2006).

Cr (III) is a necessary element for human as well as for other living organism for metabolism. Blood glucose level reduced by Cr (III) and also helps transport of amino acid. Cr (III) also decreases the blood cholesterol and reduces the possibility of diabetes (Ozgunay, 2007).

Trivalent chromium ions are less toxic than hexavalent chromium due to their less mobility and less solubility in water. Due to high concentration of hexavalent chromium there are many disease causes like nausea, liver, respiratory system, and kidney damage, diarrhea (Maria, 2017).The solubility of trivalent chromium in water is very less and mobility is also very less. Chromate and dichromate ions of Cr (VI) are very toxic in nature. Through oxygen rich conditions Cr (VI) converted into Cr (III). Chromium effluent from tannery industry cannot discharge without removing it from tannery waste water. A minimal national standard (MINAS) is set by World Health Organization (WHO) for Cr (VI) as 0.1 mg/l in the industrial discharge in the surface water. In the tannery industry high

concentrated Cr (VI) 1500-2000 mg/l discharged into the sewage (Ozgunay, 2007).

Many widely used technologies have been adapted to provide high efficiency removal of organic and inorganic pollutants, these technologies including chemical and biological treatments. In early wastewater treatment technologies, chemical treatment has preceded biological treatment. Recently, the biological treatment precedes chemical treatment in the treatment process (Chen, 2013). Chemical treatment is now considered as a tertiary treatment that can be more broadly defined as treatment of wastewater by a process involving chemical treatment. The mostly implemented chemical treatment processes are chemical precipitation, neutralization, disinfection chlorine, ozone, ultraviolet light, and ion exchange.

However, these techniques have many disadvantages (Singh, 2011). These disadvantages include sludge generation, high cost, formation of byproducts, releasing of toxic molecules, requiring a lot of dissolved oxygen, limitation of activity for specific dyes and requiring of long time (Mahimairaja, 2014). However, these typical technological treatments have no robust effect in tannery wastewater treatment. Several factors hinder the efficiency of these processes, such as cost and process workability (Segneanu, 2013). Adsorption is a more effective alternative to these inefficient and costly technologies (Moosa, 2015; Hyder, 2015). Adsorption is a promising technology that is more capable of removing pollutants from textile wastewater, as it is superior in terms of flexibility and simplicity. Because it is flexible, it can be applied on its own or as an integrated technology; like the case of combining magnetic field and adsorption for treatment of the biologically treated palm mill effluent (Fahim, 2005). Conventional adsorbents like activated carbon (AC) showed a satisfactory result in the fixed bed column studies when followed by the biological treatment (Kundu, 2012; Onundi, 2010; Amuda, 2006). However, AC has recently been replaced with other adsorbent materials that have a higher adsorption affinity for various types of pollutants and are more environmentally friendly (Onundi, 2010; Marshall, 2003; Natale, 2014). In addition, AC has major shortcoming pertaining to its pore disordered structure that leads to slow adsorption kinetics and low adsorption capacity for large molecules. Alternatively, several researchers have been studying the use of nanoadsorbents either as powder nanoparticles or functionalized with some active species, in which the latter performed well in removing heavy metals and some organic substances from the wastewater (Marshall, 2003; Natale, 2014). For instance, iron silicate type nanoparticles when functionalized with different polymeric materials its removal efficacy for organic and trace pollutants has been improved outstandingly, especially in batch adsorption processes (Kundu, 2014; Amuda, 2006; Marshall, 2003). Nevertheless, the batch mode is limited when it comes to real wastewater treatment processes. Moreover, the data obtained in the batch studies cannot be applied to wastewater



treatment plants where the contact time is not sufficient for attaining equilibrium. Thus, from an industrial practice point of view, continuous flow fixed-bed column studies are needed (Amuda, 2006; Natale, 2014; Hethnawi, 2017; Karegar, 2015). This column is usually simple to operate by packing it through a stationary bed of a specified adsorbent. However, for the case of nanoparticles, using powder nanoparticle as filter medium in a packed bed column is challenging as it will result in low loading rate with high head loss (Natale, 2014).

In this project we need to use nanoparticles to treat wastewater which comes out from the tanneries process.

Nanoparticles are very effective as a separation medium for water purification as they contain a number of key physico-chemical properties. They are known for their high surface area to mass ratio which occurs as a result of decreasing the size of the adsorbent particle from bulk to nano-scale dimensions (Nassar, 2010). This property of nanoparticles leads to the availability of a high number of atoms or molecules on the surface of contaminants thereby enhancing the adsorption capacities. Moreover, this large surface area coupled with their size, electronic and catalytic properties provide unparalleled opportunities to develop more efficient water purification adsorbents catalysts and redox active media. Lastly, since more adsorbent atoms/molecules are present per unit mass of the adsorbent, less waste will be generated post treatment as these atoms will be actively utilized for adsorption (Hethnawi. et al., 2017). The value of their application to wastewater treatment has grown. Because of their multi-functionalities properties, iron-silicate nanoparticles are the most commonly used adsorbent and/or catalyst for wastewater remediation (Nassar, 2010). Furthermore, iron silicate is naturally occurring, inexpensive, and stable over a wide range of temperatures and acidity levels. There have been numerous studies on the use of iron-silicate nanoparticles as catalysts for degradation of contaminants, usually organic materials from wastewater, and as adsorbents for adsorptive removal of pollutants, mainly metal ions, from wastewater (Hethnawi. et al., 2017). Due to these unique properties, nanoparticles have potential applications for the treatment of wastewater and drinking water. Hence, their application in treatment of tannery effluent is promising.

## 1.2 Literature Review

According to a field assessment of health conditions in occupied Palestine (WHO, 2016), the water quality varies widely in West Bank. The state of Palestine has one of the scarcest water availability (per capita supply) in the world. The country's water scarcity is due to both natural and man-made constraints; it's resulting from the Israeli occupation. As a result of population growth, higher standards of living the time water shortage in Palestine will increase and become a greater problem as a result of population growth, higher standards of living,

expected climate change, and above all, Israeli practices and restrictions imposed on both the water resources and its sector's development.

WW with different sources were making a big problem in Palestine, and the main source of this waste was leather industry. Tanneries use large quantity of water for processing hides. During the manufacturing process, tanneries WW having large amount of solids and liquids waste as well as gaseous emissions and unpleasant odors (Andrioli et al., 2015).

A large amount of chemicals are added in leather processing. All of these operations increasing the pollutant loads, such as biological oxygen demand (BOD) chemical oxygen demand (COD), organic nitrogen, sulfide and chromium (Thorstensen, 1997). The chromium (Cr) used in the manufacture of leather from hides has well known adverse effects when inappropriately disposed in the environment. The removal and recovery of chromium from tanneries WW is an environmental friendly and economically alternative avoiding the disposal of large amount of Cr containing sludge in the land.

Many previous studies were carried out to treat WW from tannery industry. (Maher et al., 2012) were investigated an environmental method, these method was treated waste by waste. The method feasibility of Cr removal from wastewater in leather making by its treatment with solid waste from stone cutting industry is demonstrated experimentally, and found to be an efficient approach. Approximately full removal of chromium is achievement at optimum conditions using a specific amount of solid waste (limestone) and allowing contact time between the two wastes. The removal of Cr percentage decrease in concentration of Cr increase with increasing contact and with increasing solid content. This study also was investigated the adsorption of Cr on limestone particles with approximately 50% removal was achieved at pH less than 5, and nearly full removal occurred at large pH. The technic that was used in this study is accomplished by two mechanisms: Adsorption and precipitation, but in another side, using limestone as adsorbent has a lot of disadvantages such as, does not treat alkaline waste, limestone chips are easily coated rendering them useless and high loading of suspended solids and dissolved solids.

(Bianca et al., 2015) studied the removal of Cr from the tanning wastewater through chemical precipitation (CP) and electrocoagulation (EC) techniques and its reuse in tanning process. In the EC method, three electrode with different materials, Al, Cu, and Fe were used. The best removal efficiency of 97.76% was obtained with Al electrodes for 110 min. In the CP method, high removal of Cr from wastewater was achieved, with up to 99.74% removal efficiencies. Cr was recovered and used as a tanning agent in leather processing, by using sludge to

prepare a liquor to use it for tanned leather, and the pH and ash content values were measured. A good hydrothermal stability and Cr content by hides tanned with the Cr-containing liquor recovered by CP and by EC with Cu electrodes, which were 2.5% Cr<sub>2</sub>O<sub>3</sub>, the hides tanned with Cr-containing liquors recovered by chemical precipitation and by EC conducted with Fe and Cu electrodes showed contents of Cr according to technical specifications. However, the Cr samples obtained with the iron electrode showed a dark coloration due to oxidation of the iron. It can be concluded that the tanning process with Cr recovered by CP and by EC with Cu electrodes showed the best results. Currently these method comparatively mature, but there are still many problems, such as chemical precipitations need many stages for treatment and may require working with corrosive chemicals, increasing operator safety concerns. The addition of treatment chemicals, especially lime may increase the volume of waste sludge up to 50 percent. And also large amount of chemicals may need to be transported to the treatment location and its need more cost.

In addition, (Lkhagvadulam et al., 2017) investigates the removal of Cr by using maghemite nanoparticles (MNPs) from the tannery wastewater. The co-precipitation method was used to synthesis the MNPs with 122 nm size and characterized by nanometer particle size analysis, transmission electron microscopy (TEM) and X-ray diffraction (XRD). The operation conditions that was investigated were effect of MNPs dosage, pH effect and contact time. The result show the maximum removal efficiency of Cr was achieved 96.7% at an optimum condition.

In this study, the poly (ethylenimine) (PEI) was used to functionalize iron silicate nanoparticles. The functionalized nanoparticles were embedded into diatomite and used to remove chromium Cr (VI) from tannery wastewater in a batch and continuous process. The results showed a high removal efficiency and rapid kinetics of the adsorption process for PEI-iron silicate nanoparticles (donated for functionalized-pyroxene with PEI) compared with that of Diatomite (D4500) without nano and commercial activated carbon. Further, the column experimental results under different test conditions ( Bed hight(Z), initial concentration (Co), and inlet flow rate(Q) in D4500) were fitted with the convection-dispersion equation to describe the breakthrough curves. Batch adsorption experiments were also conducted to determine the adsorption capacity as well as kinetic parameters, which later used to estimate the breakthrough profiles for the adsorption column operation.

### 1.3 Research Motivation

The pure water progressively becomes a rare source because the high consumption of freshwater by many industries and increased the discharge wastewater amount. Day by day access to pure and clean water is being a big problem faced by many human all over the world. In addition, the industrial wastewater contains high toxicity ions of heavy metals and some types of organic pollutants (Danielsson, 2013; Pimentel, 2013).

Recently, treatment of Chromium (Cr) from industrial effluents has been recognized because many industries, including: tanning industries, which produce a high amount of Cr, colloidal suspended and dissolved organic pollutants. These pollutants need to be treated because it causes negative impacts for environment and human health.

The development of techniques for treatment of pollutants need to be efficient, costly effective, and environmentally friendly. Adsorption using various types of adsorbents like the activated carbon (AC) and iron silicate has been widely used to remove the dissolved organic pollutants. AC and iron silicate shown very satisfactory results in the dissolved organic removal especially when it was integrated with biological treatment as tertiary or advance treatment (Hethnawi. et al., 2017). AC had an outstanding performance in total dissolved solids when it followed coagulation/flocculation method. Nevertheless, it has a low efficiency due to its slow mass transfer kinetics in adsorbing the heavy molecules, which lengthens the adsorption equilibrium time (Mohan et al., 2006). Furthermore, production and regeneration of the AC are not environmentally safe nor cost-effective in industrial applications (Lakshmanan et al., 2014). Thus, many studies focus their efforts on developing an adsorbent with unique properties that can provide better performance than AC.

Nanoadsorbents were the alternative, because it has good sorption efficiency, large surface area, and easily accessible sorption sites with organic contaminants (Nassar, 2010). Hence, using nanoparticles may allow for better and more affordable wastewater treatment process development. Nanoparticles in a synergistic combination with other conventional techniques provide a greater possibility for large-scale applications of wastewater treatment. For multifunctionality and stability purposes, various types of nanoparticles have been anchored during or after the synthesis with a wide range of functionalizing agents like polymers, surfactants, and inorganic materials (Nassar, 2010). Nevertheless, nanoparticles need an initiator that primarily attaches to the surface of the nanoparticles under a well monitored and high specificity conditions (Zhao et al., 2014). This initiator binds the nanoparticle surface before the final functionalization, which can be considered as one significant drawback of using the functionalized nanoparticles in the wastewater treatment fields.

The motivation of this study is to explore a possible way for efficient, costly effective and environmentally friendly treatment of Chromium from a tannery wastewater.

## 1.4 Research Objectives

### 1.4.1 Main Objectives

Employing functionalized iron silicate nanoparticles and embedding of silicone dioxide (Diatomite) with iron silicate nanoparticle for treating real tannery effluent for the first time in Palestine

### 1.4.2 Specific Objectives

The following items are considered as the specific objectives of this research:

1. Conduct a survey on the tannery effluent industry in Palestine. And the application of nanoparticles in wastewater treatment.
2. Synthesis of nanoparticle from locally sourced materials following the procedure developed by Nassar group at university of Calgary (Nassar, 2010)
3. Employ functionalized nanoparticle in the treatment of tannery effluent for the first time.
4. Establish a new method and employ it for the treatment of tannery effluent in Palestine using nanoadsorbents.
5. Study and evaluate the effect of the following variables on the treatment process efficiency:
  - a. Contact time (kinetics).
  - b. Initial concentration of Cr (VI) in tannery effluent.
  - c. Solution pH.
  - d. Coexisting contaminants.
6. Construct models that capture the effect of the above variables on the adsorption removal efficiency.
7. Incorporate nanoparticle technology with bed filtration for cleaning tannery effluent following the procedure employed by Dr. Nassar group on the olive mill and textile wastewater treatment (Nassar et al., 2014).

## Chapter Two

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### Materials and Methods

#### 2.1 Adsorption Studies

##### 2.1.1 Materials

The following chemicals were purchased from Sigma Aldrich, Ramallah, Palestine: Nitric acid ( $\text{HNO}_3$ ) (97%), sodium hydroxide NaOH (99%) and potassium chromate ( $(\text{K}_2\text{CrO}_4)^{-2}$ ) (99%). The nano particles (nps) were prepared in the University of Calgary by Dr. Nassar group as shown in preparation and characterization of iron silicate nanoparticle section.

##### 2.1.2 Adsorbent

Iron silicate was used in this study for adsorption of chromium Cr (VI) from the tannery waste water. This adsorbate has many properties to make it a good choice for this work, such as it's an environmentally friendly, inexpensive and less toxic.

Three types of adsorbents were tested to select the best one, activated carbon, Diatomite with nano, and embedded with Diatomite (PNP-D). After the removal was tested for each type the result showed the percentage of removal was low, the naps used in this study was prepared by mixing two types of particles to improve the removal percentage. This particle was a Diatomite and polyethylene mine (PEI). The PEI was adding to the Diatomite, suspend the resulting mixture into water at 20% wt under stirring for 15 min the filter and dry the mixture to remove the water.

#### 2.2. Preparation and Characterization of Iron Silicate Nanoparticle.

This part of work was done in collaboration with Dr. Nassar group at the University of Calgary. And the preparation steps were explained in details below.

Iron silicate NPs with controlled size and shape are technologically important due to strong correlation between these parameters, and for comparative purposes. Comprehensively, iron

silicate nanoparticles were prepared from a hydrothermally treated gel. Two solutions prepared separately, the first one was acidic which prepared by adding 18.067 g of sulfuric acid in 90 g of deionized water; then, 20.793 g of iron tri-chloride was gradually added to the solution, which was continuously stirred (300 rpm). The second solution was basic solution, which formed by adding 21.413 g of sodium hydroxide to 60.0 g deionized water; 30.707 g of sodium silicate was then added while the solution was stirred (Hethnawi. et al., 2017). Two solutions were mixed under stirring condition for 15 min. The magnetic stirring was done to provide a homogenous orange-yellowish gel. The gel was loaded into a hydrothermal reactor vessel (A2230HCEB, Parr Instrument Company, Moline, IL, USA) of 300 ml capacity to make it crystalize hydrothermally. The reactor has a gauge pressure and mechanical stirrer with a speed controller. This reactor contains a heating mantle, which is connected to a temperature controller. For the successful ways of growing crystals for iron silicate NPs the reactor was heated to 433 K at 300 rpm for 72 h. After that, the reactor was cooled down for 4 h and the resulting gel was removed from the reactor vessel. After that, the reactor was cooled down for 4 h and the resulting gel was removed from the reactor vessel. Naturally cooled to room temperature and the precipitates were washed with distilled. The final product was dried (Hethnawi. et al., 2017).

## 2.3. Characterization of Embedded Nanoparticles in Diatomite

### 2.3.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. An electron microscope can resolve objects as small as 0.001  $\mu\text{m}$  ( $=10 \text{ \AA}$ ), as compared to 0.2  $\mu\text{m}$  by a light microscope. The resolving power of an electron microscope is 200 times greater than that of a light microscope. It can produce magnification up to 400,000 times. In this study a field emission Quanta FEG 450 scanning electron microscopy (SEM), which was manufactured by FEI, was used to confirm the successful embedding of silicone dioxide (Diatomite) with iron silicate nanoparticle. The sample for the analysis was prepared by coating very small quantity of each powder with gold (Bhishma, 2016).

## 2.4 Batch Adsorption Experiments

Batch experiments were carried out to determine the adsorption isotherms of iron silicate onto the adsorbents in 100 mL glass tube. The study was performed at room temperature (298 K) to be representative of environmentally relevant condition. All experiments were carried out in duplicate and the average value was used for further calculation. In part of identified the factors that affected on the adsorption, the effect of pH was studied which measured with a HACH-pH meter and by using solution pHs of 2–12 with iron silicate dosage of 0.05 g/10 mL solution. The pH of the solution was varied by using either about 1 M HNO<sub>3</sub> or 1 M NaOH and the initial Cr (VI) concentration was kept at 100 mg/L to investigate optimum pH. The best value of pH that was given a higher percentage of removal was 9. The initial Cr (VI) concentrations of 10, 20, 50–

300mg/L were evaluated with 0.05g of optimum iron silicate dosage in 10mL solution and with optimum pH to determine the Sips properly (Singh. et al., 2012). The tubes were plugged and kept closed to avoid the fluctuation of pH during the experiment. Potassium chromate (99%) was used as the source of chromium in the synthetic wastewater. The optimum parameters were then used to analyses adsorption capacity, adsorption reaction kinetics, and equilibrium isotherm. About 2.83 g of potassium chromate ( $(K_2CrO_4)^{-2}$ ) salt was dissolved in deionized water to prepare the stock solution of 1000 mg/L of Cr (VI), this solution was subsequently diluted using deionized water to the required working concentration prior to use in the batch tests. The tubes that contains the Cr (VI) and iron silicate nanoparticle mixture was placed on a platform shaker (New Brunswick Scientific, model: Innova 2300) at 200 rpm, allowing sufficient time for adsorption equilibrium. It was assumed that the applied shaking speed allows all the surface area to come in contact with contaminates over the course of the experiments. The samples were then filtered through 0.45mm syringe filter (Sterlitech, Kent, WA, USA), then analyzed to measure the Cr (VI) concentrations by using a spectrophotometer model SL -218 (ELICO) at a wavelength of 470 nm, and chromium concentration of tested samples was determined by a calibration curve prepared using standard solutions of concentrations of Cr (VI) between 50 and 300 mg/l. The amount of Cr (VI) adsorbed was determined by mass balances according to the following equation:

$$Q = \frac{C_0 - C_e}{m} * V$$

Where  $C_0$  is the initial concentration of Cr (VI) in the solution (mg/L),  $C_e$  is the equilibrium concentration of Cr (VI) in the solution (mg/L),  $V$  is the solution volume (L), and  $m$  is the mass of adsorbent (g) (Antonio et al.,2006)

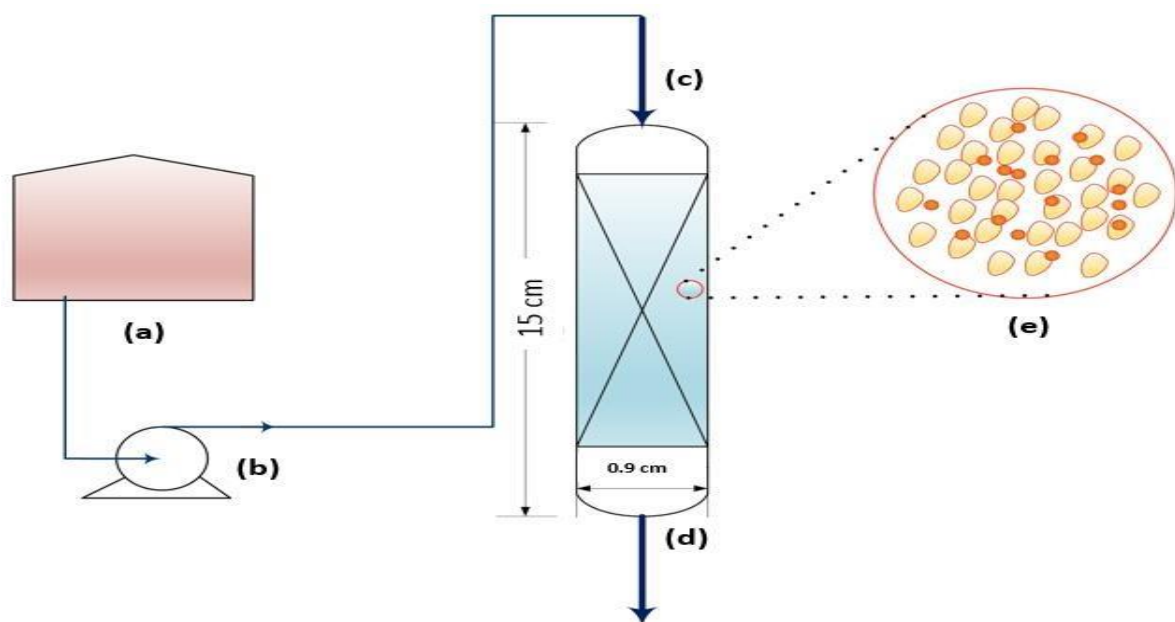
## 2.5. Column Adsorption Study

The adsorption experiments were carried out in columns that were equipped with a stopper for controlling the column flow rate. Column experiments were carried out using a glass column a glass tube of 0.9 cm diameter and 15 cm height. A schematic of the experimental setup used for column study is shown in Fig 2.1. All experiments were carried out under room temperature (298 K). The nps was packed in the column with a layer of cotton at the bottom. Bed height of (2.5) cm, (3.5) cm and (7.5) cm was used. The tank containing the chromium solution was placed at higher elevation so that the chromium solution could be introduced into the column by gravitational flow. The tank was equipped with a pipe to help maintain a constant solution level in the tank in order to avoid fluctuation of the flow rate of the solution being delivered to the column (Busto. et al., 2016). The valves help to regulate the flow rate. Four individual experiments with different type of adsorbents were conducted. These adsorbents were AC, Diatomite, PNP-D and Diatomite (SEF 3%). Then, the best one from the previously mentioned adsorbents was selected. The screening was performed based on long period time of breakthrough. Afterward, the kinetic parameters. The effect of NPs mass study was performed by running 3 experiments with different mass of 2, 1.5,



and 0.8 g. Three flow rates (1, 1.5 and 2ml/min) were used while initial Cr (VI) concentrations of 200, 80 and 40mg/l were used. The effluent samples were collected at specified intervals and using double beam spectrophotometer at 470nm.

The design of a fixed bed adsorption system depends on the effects of various operational parameters, such as type of adsorbent, initial Cr (VI) concentration, bed depth and flow rate. Due to its priority influence on the general position of the breakthrough curves (BTC) (Singh. et al., 2012). The time to reach the breakthrough point and shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic responses of an adsorption column. Breakthrough happens when an adsorption column is saturated. A breakthrough curve was measured of the changes after the column over time. When this curve no longer changes, the column was saturated (Fahim. et al., 2005).



**Figure.2.1:** Schematic representation of the fixed-bed experimental set up. (a) Cr (VI) Feed tank, (b) syringe pump, (c) inlet flow rate, (d) outlet flow rate, and (e) nanoparticle embedded on Diatomite (Hethnawi. et al., 2017)

## Chapter Three

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### Theoretical Background

#### 3.1 Analysis of Chromium Ions

The concentration of chromium ions left in the liquid phase was determined by using a spectrophotometer model SL -218 (ELICO). The amount of Cr (VI) adsorbed was determined by mass balances according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad [1]$$

where  $q_e$  adsorption capacity,  $C_0$  is the initial Cr (VI) concentration in mg/L,  $C_e$  is the equilibrium Cr (VI) concentration in mg/L,  $V$  is the volume of the solution in liter (L), and  $m$  is the dry mass of iron silicate nano particle in gram (g) (Hyder. et al., 2014).

#### 3.2. Batch Equilibrium Adsorption

Sips equations have been used to model the kinetics adsorption of chromium A non-linear regression was used for these models. It must be noted that all analyses were repeated in triplicate. The Sips equation was generally expressed as

$$q_e = \frac{q_{ms} * K_s * C_e^{ns}}{1 + K_s * C_e^{ns}} \quad [2]$$

where  $q_e$  is the adsorption capacity (mg/g) at equilibrium,  $q_{ms}$  is the Sips maximum adsorption capacity (mg/g),  $K_s$  is the Sips equilibrium constant  $(L \text{ mg}^{-1})^{ns}$ , and  $ns$  represents the surface heterogeneity lying between 0 and 1. If the value of  $ns$  is equal to 1 then this equation will become a Langmuir equation. Alternatively, as either  $C_e$  or  $K_s$  approaches 0, this isotherm reduces to the Freundlich isotherm (Nethaji. et al., 2013).

### 3.3. Breakthrough Curve (BTC)

In fixed bed adsorption, the concentrations in the fluid phase and the solid phase change with time. At first, most of the mass transfer takes place near the inlet of the bed, where the fluid contacts the adsorbent. After a few minutes, the solid near the inlet was nearly saturated. Most of the mass transfer takes place farther from the inlet. The concentration gradient becomes S-shaped. The region where most of the change in concentration occurs was called the mass-transfer zone (MTZ), and the limits are often taken as  $C/C_0$  values of 0.95 to 0.05. Using the breakthrough curve data from an adsorption breakthrough run. The time required for a bed to become totally saturated was obtained by integrating as time goes to infinity:

$$t_t = \int_{t=0}^{t=\infty} \left(1 - \frac{C_t}{C_0}\right) dt \quad [3]$$

where  $t_t$  the time equivalent to the total or stoichiometric capacity  $C_t$  is the concentration of Cr (VI) at time  $t$ , and  $C_0$  is the feed concentration of Cr (VI) (Hethnawi. et al., 2017).

In operation, needs to stop the process before solute breakthrough, so integration to the breakpoint time gives the "usable" capacity:

$$t_u = \int_{t=0}^{t=t_b} \left(1 - \frac{C_t}{C_0}\right) dt \quad [4]$$

Most of the time the breakthrough time is very close to the time elapsed at usable capacity

The capacity times are directly related to bed length:

$$H_{UNB} = \left(1 - \frac{t_u}{t_t}\right) H_T = \left(1 - \frac{t_b}{t_t}\right) H_T \quad [5]$$

where  $H_T$  is the total bed height (cm). Used bed length  $H_B$  up to the break point can determine by:

$$H_B = \left(\frac{t_b}{t_t}\right) H_T \quad [6]$$

## Chapter Four

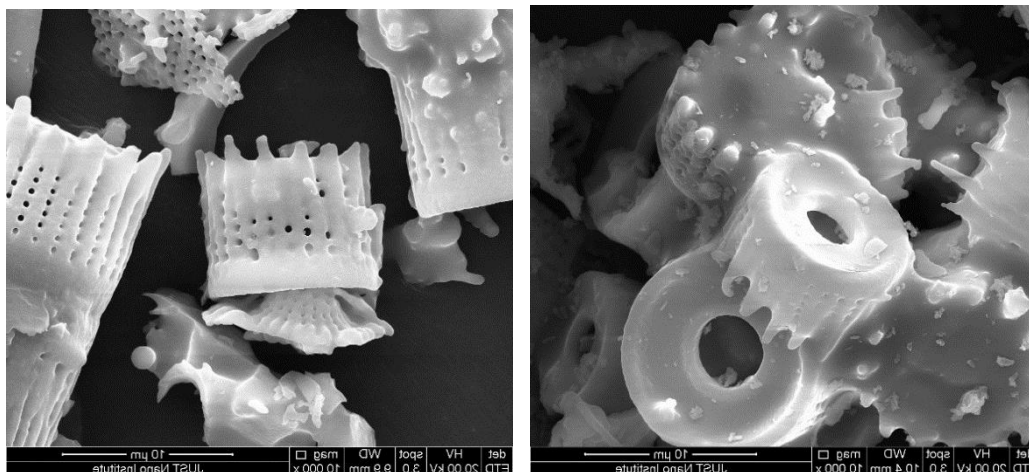
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### Results and Discussion

#### 4.1 Characterization of Embedded Nanoparticles in Diatomite

##### 4.1.1 Scanning Electron Microscope

To observe the surface textures of Diatomite the scanning electron microscope (SEM) was used. Figures 4.1a, 4.1b illustrate the SEM micrographs of the Diatomite, before and after embedding with nps, respectively. Before analyzing the Diatomite by SEM, it was treated, by using a strong acid (sulfuric acid) or by heat or by embedded with nanoparticles (Wen et al., 2005). At the first method the pores on the surface of Diatomite were preserved and slightly opened, but some changes were perceived in the Diatomite structure after calcination at high temperature (Bhishma, 2016). As showed in fig4.1a only the presence of Diatomite, many solid shapes and voids. In the other side the fig4.1b was showed the good distribution of iron silicate nanoparticles on the Diatomite structure without changing it. In addition, the presence of small amount of nanoparticle increase the ability of Diatomite to trap the chromium from the wastewater.

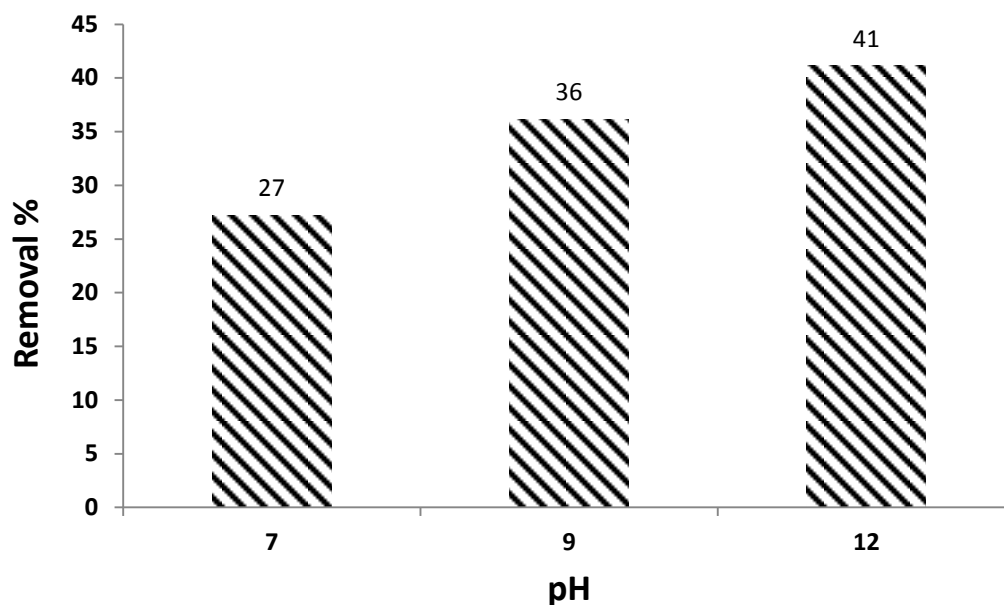


**Figure 4.1:** a) SEM images for silicon dioxide (left), b) silicon dioxide embedded with iron silicate (right). Line mark in the images corresponds to  $10\mu\text{m}$ .

## 4.2 Batch Adsorption

### 4.2.1 Effect of pH

pH is an important parameter that affects the adsorption of metal ions, and its important parameter which controls the adsorption process. It influences the ionization of the adsorptive molecule and hence the surfaces charge of the adsorbent. A set of experiments was conducted to determine the optimum pH for Cr (VI) removal. In this study, the pH was varied from 2-12 to determine the optimum value for Cr (VI) adsorption on nps. The results are shown in Fig 4.2. It was found that when the pH values was increased from 2 to 7 the adsorption of Cr (VI) was decreases because many positive charges, and at pH higher than 7 the adsorption of Cr (VI) on the solid surface took place (Danielsson, 2013). Therefore, for anionic chemical species, adsorption decreased when alkaline media is increased. So, it would be expected that the maximum adsorption of chromium ions could occur at higher pH values, because, at initial acid media the chromium ions form negatively charged hydrolyzed species ( $(K_2CrO_4)^{-2}$ ) the adsorption of Cr (VI) takes place and therefore the removal is higher than the other points (Ruihua. et al., 2013). The adsorption of the studied metal increased as pH increases and recorded its minimum values at acidic pH. The value of pH was 9 which was selected as an optimum value, however, the high pH values were ignored to prevent the happened of corrosion in real applications.



**Figure4.2:** Removal efficiencies of Cr (VI) onto iron silicate with different pHs at initial Cr concentration of 200 mg/l and 0.5g of iron silicate.

#### 4.2.2 Kinetics of Adsorption

On the purpose of investigating the mechanisms of adsorption and its potential rate-controlling steps that include mass transport and chemical reaction process, kinetic models have been exploited to test the experimental data. In practice, kinetic studies were carried out in batch reactions using various initial adsorbate concentrations, adsorbent doses, and pH values. Then, nonlinear regression was used to determine the best-fitting kinetic rate equation. Generally, adsorption of metal ions increased with time until the equilibrium was achieved between the amounts of adsorbate adsorbed on the adsorbent, and the amounts of adsorbate remained in solution. Generally, adsorption reactions took place rapidly at initial stages and gradually slowed down until reaching its equilibrium state. The time to reach equilibrium varied with the adsorbents, initial concentration and the condition of the solution (Pandey et al.,2010). In general, many kinetic models were applied to fit the adsorption process, which include pseudo-first and pseudo-second-order rate model, mass transfer model (Pandey, 2010; Rengaraj, 2004).

The variation in the amount of adsorption with time at different initial concentrations was analyzed for evaluating the role of diffusion in the adsorption process. Adsorption was considered to be a three steps process. The first step involves transport of the adsorbate molecules from the aqueous phase to the film surrounding the adsorbent (external mass transfer). This step can be neglected due to mixing and no pores on the surface of nanoparticle due to coating. In the second step diffusion of the solute molecules from the film to the adsorbent surface takes place (film diffusion). Finally, in

the third step the adsorbate molecules diffuse into the pore interiors (surface diffusion) also this step can be ignored because the adsorption was very fast (Rengaraj et al., 2004; Vijayakumar et al., 2012).

### 4.2.3 Adsorption Isotherm

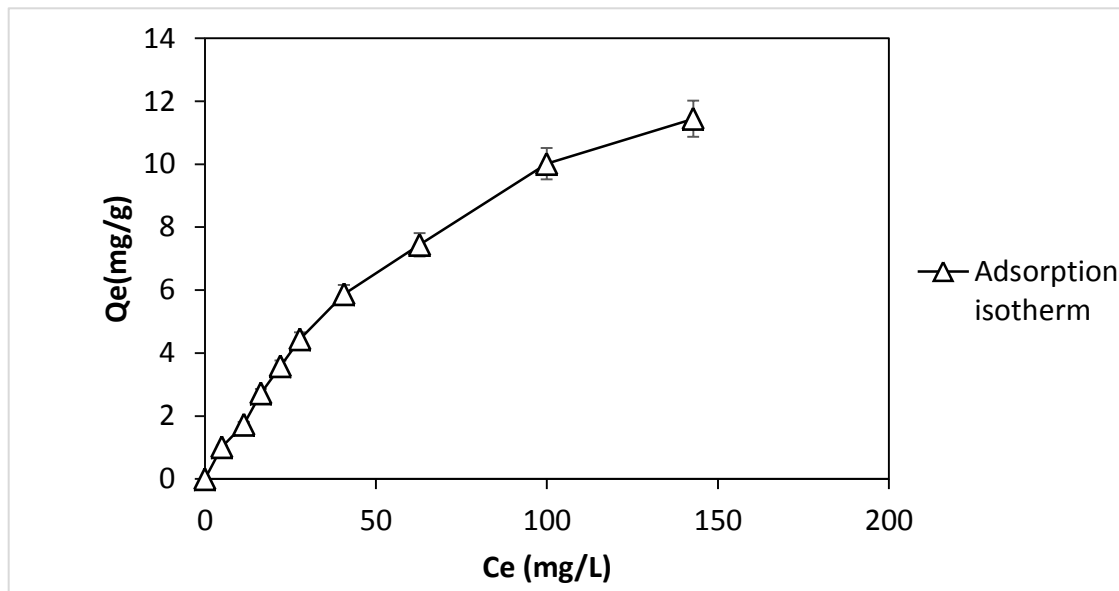
In general, the isotherm studies for solid – liquid systems were carried out by changing Cr (VI) concentration and keeping other conditions, such as: volume of solution, adsorbent type, temperature, and solution pH as constant. The performance of adsorbent is usually gauged by its uptake. Adsorbents can be compared based on their respective maximum uptake value, which can be calculated by fitting different isotherm models to the actual experiment data if it fits. Adsorption isotherm gives the explanation on how adsorbent and adsorbate interact with each other and therefor in optimizing the use of adsorbents. Various adsorption isotherm models available to describe the equilibrium of adsorption, including Langmuir, Freundlich, and Sips (Nethaji. et al., 2013). According to the majority of reviewed papers, Langmuir, Freundlich and Sips isotherm models are best fitted models for Cr (VI)adsorption onto iron silicate nano adsorbents (Danielsson, 2013; Tahir, 2006; Talokar, 2011). Langmuir described the presence binding sites and the uniformity of surface, while Freundlich ignore the presence interaction between adsorbed molecules and doesn't work at high concentration (Nethaji. et al., 2013). In general, both Langmuir and Freundlich describe the homogeneity of the surface. In this study the heterogeneity of surface and the interaction between adsorbed molecules were considered, and Langmuir and Freundlich can't use, for these Sips isotherm was regards which can be used to describes the equilibrium model between the amount of solute adsorbed per unit mass of adsorbent and the solute remaining in the solution on heterogeneous surfaces. Sips proposed three-parameter equation, which is a combined two-parameter equation of Langmuir and Freundlich model (Nethaji. et al., 2013). The isotherm reduces to the Freundlich isotherm and to the monolayer Langmuir isotherm when the corresponding adsorbate concentrations are low and high. The nonlinear Sips model is expressed as Eq.8

$$q_e = \frac{q_{ms} * K_s * C_e^{ns}}{1 + K_s * C_e^{ns}} \quad [7]$$

Where  $q_e$  is the adsorption capacity (mg/g) at equilibrium,  $q_{ms}$  is the Sips maximum adsorption capacity (mg/g),  $K_s$  is the Sips equilibrium constant ( $L \text{ mg}^{-1}$ )<sup>ns</sup>, and ns represents the surface heterogeneity lying between 0 and 1. If the value of ns is equal to 1 then this equation will become a Langmuir equation. Alternatively, as either  $C_e$  or  $K_s$  approaches 0, this isotherm reduces to the Freundlich isotherm (Nethaji. et al., 2013).

In this study, the efficiency of the functionalized nanoparticles as a new adsorbent in removal of Cr (VI) was examined. The results from the study of Cr (VI) removal by means of nps have shown that these adsorbents are effective for the removal of heavy metals especially Cr (VI) as shown in fig 4.3 the removal percentage increased after Cr (VI) concentration increase from 10 to 200 mg/l.

To cite the cause, those adsorbents have a limited number of active areas; so active areas become saturated quickly by pollutant and the efficiency of removal process goes down in high concentrations.



**Figure 4.3:** Adsorption isotherm of Cr (VI) onto adsorbent of nps. Adsorbent dose: 0.5g/L; shaking rate: 200 rpm; T: 298 K.

The removal percentage increased with increasing the concentration of. To cite the cause, those adsorbents have a limited number of active areas, so active areas become saturated quickly by pollutant and the efficiency of removal process goes down in high concentrations.

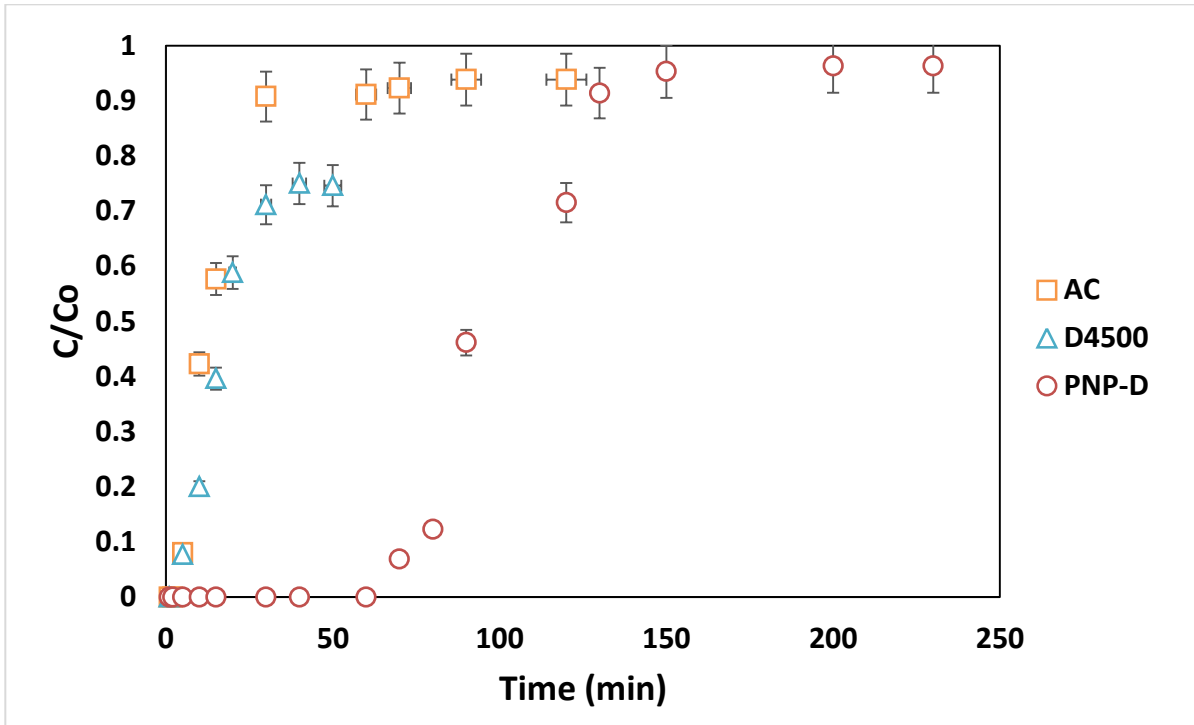


## 4.3 Column Adsorption Study

### 4.3.1 Effect of Adsorbent Type

Some parameters were estimated from the experimental BTC. All parameters were defined in theoretical background section. The calculation of  $t_b$ ,  $t_u$ , HUNB, HB,  $q_{total}$ ,  $W_{total}$  and %Removal was very important to design a successful column, all of these parameters were explained in theoretical background chapter.

The experimental breakthrough curves at different type of adsorbents were presented in fig 4.4. The figure shows the BTC for three types of adsorbent; activated carbon, Diatomite and Diatomite embedded with nanoparticles. For more details, the column that filled with AC and Diatomite becomes saturated faster more than Diatomite that embedded with nanoparticles (Onundi, 2010). AC has some drawbacks that make it poor choice such as it has a low adsorption capacity for large molecules and slow adsorption kinetics (Kundu,2014), where Diatomite with nano had a higher breakthrough time ( $t_b=75\text{min}$ ) and the greatest removal efficacy (34.3%) compared with other type of adsorbents as shown in table 4.1. This behavior may be explained by the fact that the binding sites became saturated more quickly in the system at AC and Diatomite. It would take a longer time for adsorbent material to be completely saturated with the adsorbate, and it can use the adsorbent for longer time before it needs to be replaced or regenerated (Moosa. et al., 2015), which mean that the adsorption capacity of the Cr (VI) in fixed-bed by using Dolomite that was embedded by low mass percentages (< 6 wt%) of functionalized PEI nanoparticles was improved. It is because this nanoparticle type had very high adsorption capacity toward Cr (VI), which led to improve the sorption surface area and subsequently the adsorption capacity of the Diatomite (Hethnawi. et al., 2017).



**Figure 4.4:** Breakthrough curve (BTC) of fixed-bed column for different adsorbents (AC, Diatomite and Diatomite embedded with nanoparticle 6 wt%).

**Table 4.1:** Fixed bed adsorption parameters for Cr (VI) adsorption by using

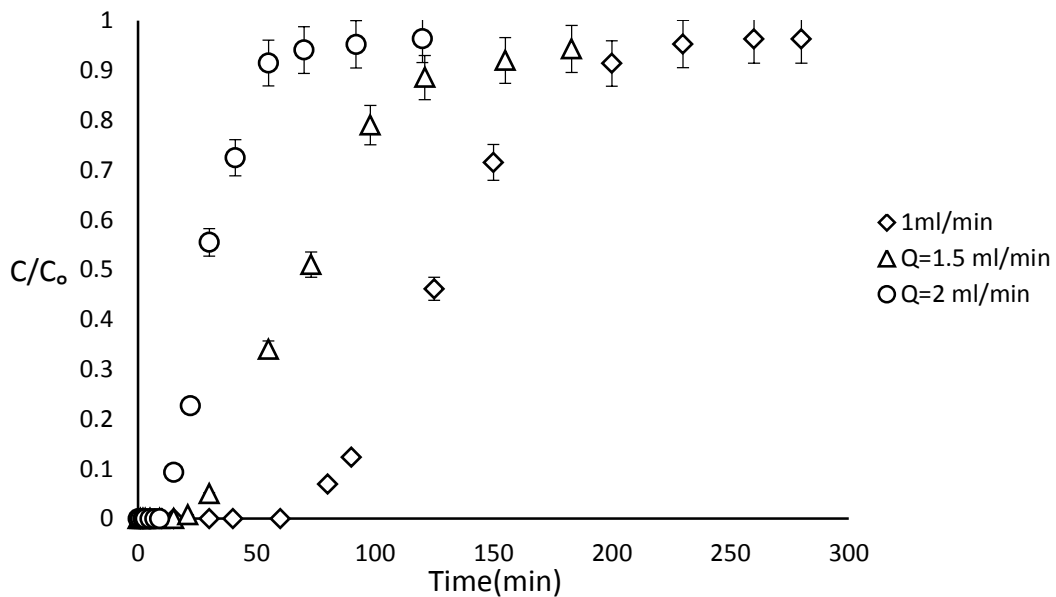
<b>Adsorbent type</b>	<b>Q (ml/min)</b>	<b>Z (cm)</b>	<b>Co (mg/l)</b>	<b><math>t_b</math> (min)</b>	<b><math>t_t</math> (min)</b>	<b>Removal %</b>	<b><math>H_{UNB}</math></b>	<b><math>q_t</math> (mg)</b>	<b><math>W_t</math> (mg)</b>
<b>D4500</b>	1	12	200	4	12.75	25.5	8.2	2.55	10
<b>AC</b>	1	10.5	200	4	15.3	12.75	7.7	3.06	24
<b>PNP-D</b>	1	12.4	200	75	154.4	34.3	6.4	30.9	90

\* Q: Influent flow rate,  $Co$ : inlet Cr (VI) concentration, Z: bed height,  $t_b$ : breakthrough time,  $t_t$ : The time required for a bed to become totally saturated,  $H_{UNB}$ : The capacity times are directly related to bed length,  $q_t$ : the adsorbed quantity of Cr (VI) and  $W_t$ : the total amount of Cr (VI) sent to the column.

### 4.3.2. Effect of Flow Rate

**Figure 4.5** shows the effect of varying the feed flow rate (1.00, 1.5, 2 mg/L) with a constant bed-depth of 7.5 cm and inlet Cr (VI) concentration of 200 mg/L on the adsorption of Cr (VI). This effort was performed to achieve maximum removal of Cr (VI) and to investigate flow rate effect as an important parameter on the pilot or an industrial scale. The trend of the obtained BTCs as presented in **Figure 4.5**, the BTCs showed that the adsorption was rapid at the beginning, which refers to presence of sorption sites able to capture Cr (VI) molecules. Then was occupancy of these sorption sites by Cr (VI) molecules, which reduces the uptake. Finally, was progressive accumulation of Cr (VI) even after occurring the breakthrough on the obtained BTCs (Hethnawi et al., 2017). As seen in the figure, with the increased flow rate the BTC became steeper, that mean when the flow rate increase the removal percentage will decrease with which the breakpoint time and the adsorbed Cr(VI) concentration decreased. The reason behind this is that when the residence time of Cr (VI) in the column is not enough for adsorption equilibrium to be reached at that flow rate, the adsorption zone quickly saturates the top of the column, then; Cr (VI) left the fixed-bed column before the equilibrium. Therefore, the contact time of Cr (VI) is very short at a high flow rate. That subsequently reduced the Cr (VI) removal efficiency. On the other hand, when the

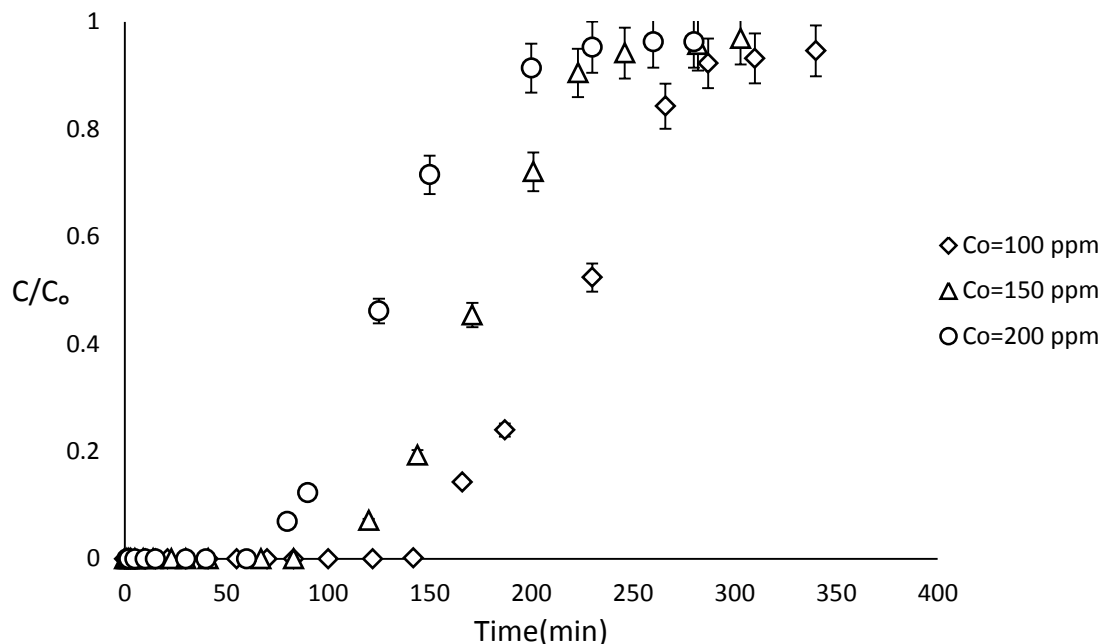
influent flow rate is low, the Cr (VI) had more time to contact the sorption sites of adsorbent that led to achieving a higher removal of Cr (VI) molecules in the column (Alhamed, 2009).



**Figure 4.5:** Breakthrough curves (BTCs) for adsorption of Cr (VI) at different flow rate. Experimental operational conditions: initial Cr (VI) concentration =200mg/L, bed height =7.5 cm, temperature=298 K, pH=8.5.

#### 4.3.3. Effect of Cr (VI) Initial Concentration

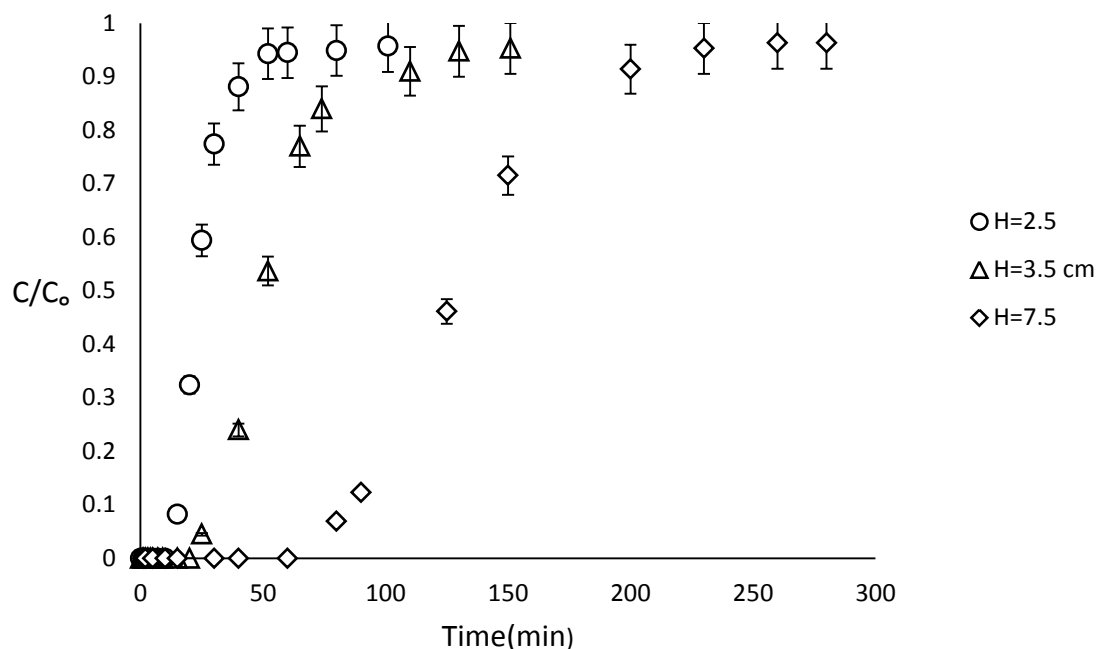
**Figure 4.6** illustrates the sorption BTCs obtained for different inlet Cr (VI) concentrations of 100, 150, and 200 mg/L at bed height of 7.5 cm and flow rate of 1.00 ml/min. This series of experiments aimed to study the effect of varying the inlet concentration on the performance of BTC in the column experiment. In the figure, it is observed that as inlet Cr (VI) concentration increased from 100 to 200 mg/L, the breakthrough was steeper because of lower mass transfer-flux from the bulk to the adsorbent surface. This is due to the weaker driving force in mass transfer process (Mantovaneli.et al., 2004; Fahim et al., 2005). In addition, more Cr (VI) molecules can be available at higher concentration, which led to higher uptake, then it followed more quickly saturation in the column, leading to earlier breakthrough time (Runping et al., 2009).



**Figure 4.6:** Breakthrough curves (BTCs) for adsorption of Cr (VI) at different initial Cr (VI) concentration. Experimental operational conditions: Cr (VI) flow rate=1.00 ml/min, bed height=7.5 cm, temperature=298 K, pH=8.

#### 4.3.4. Effect of Bed Heights

In order to carry out this investigation the performance of breakthrough curves at different bed heights (cm) at influent Cr (VI) concentration ( $C_0 = 200\text{mg/L}$ ) and Flow rate ( $q = 1\text{mL/min}$ ) for Cr (VI) was studied as shown in figure 4.7. With increase in the column bed height from 2.5 to 7.5, there was an increase in removal % of Cr (VI) was observed for the employed the adsorbent. When the bed height increased, Cr (VI) had more surface area or sorption sites to contact with the adsorbent, resulting in high uptake and improvement removal efficiency of Cr (VI). (Nwabanne, et al., 2012).



**Figure 4.7:** Breakthrough curves (BTCs) for adsorption of Cr (VI) at different bed heights, Experimental operating conditions: initial Cr (VI) concentration=200 mg/L, Cr (VI) flow rate=1.00 ml/min, temperature=298 K, pH=8.

In previous study, (Bianca et al., 2015) achieved a high percentage removal of Cr from tannery WW by using chemical perception and electrocoagulation, and the efficiency more than 90%. But these techniques need high cost to apply and high amount of sludge as a byproduct was produces from this techniques.

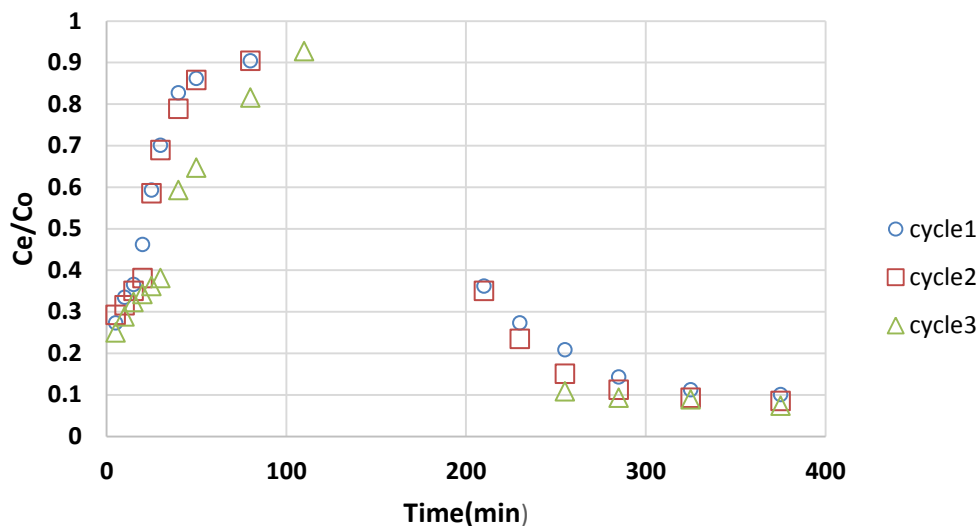
Additionally, (Maher et al., 2012) using limestone as adsorbent and the removal efficiency was achieved more than 95% but this method has a lot of disadvantages such as, does not treat alkaline waste, limestone chips are easily coated rendering them useless and high loading of suspended solids and dissolved solids. Cr (VI) was reduced from 200ppm to 0.2 ppm after using PNP-D , that mean the value less than the limit according to WHO the permissible limit of Cr (VI) which was 2 ppm as shown in table 4.2.

Table 4.2 Permissible Limit of Cr (VI) According World Organizations

Organization	Permissible Limit (mg/l)
WHO	2
EU	5
EPA	2

#### 4.5 Desorption and Regeneration Study

Regeneration of adsorbent for repeated reuse is highly desirable and this not only makes the treatment process economically viable but also offers a prospective solution for the management of contaminant loaded adsorbent (Samadder. et al., 2015). In this work, in order to determine the effectiveness of 0.1 M of HNO<sub>3</sub> solution toward desorption and pH 4, this value was obtained from the batch adsorption study, was selected to provide the opportunity to recovery or regenerate the adsorbent. Also, an efficient desorption only occurs in an acidic medium that provides protons, which efficiently compete with the pollutant ions on the amino sites of PEI (Bessbousse. et al., 2008). The study was conducted in fixed bed column using 200mg/l of Cr solution and 0.05g of adsorption material. As shown in figure 4.8 HNO<sub>3</sub> (0.1M) have a good ability for the desorption of chromium anions from nanoparticles that was achieved by three back- wash cycles within 15 min, which indicates that the desorption occurred rapidly and it was approximately same through all cycles, that mean the type of nanoparticles that was used in this work had a high efficiency to adsorbed the chromium from the wastewater at low pH values (Zhang. et al., 2015).

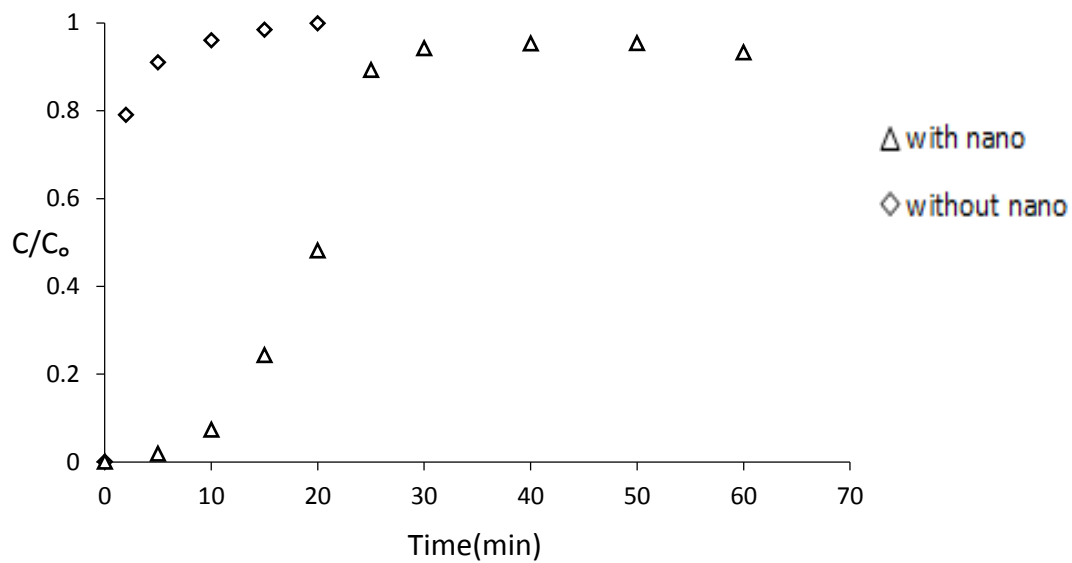


**Figure 4.8:** Desorption and regeneration Cycles of PNP-D with 0.1M of HNO<sub>3</sub> at pH of 4 and temperature of 298 K.

## 5. Analysis and the Characteristics of Tannery Wastewater

The characteristics of tannery wastewater vary considerably from tannery to tannery depending upon the size of the tannery, chemicals used for a specific process, amount of water used and type of final product produced by a tannery. The samples were collected from the tanneries located in Alfahies area in Hebron; have high chromium concentration exceeding the tolerable limit. The effluents from tanneries are directly disposed of into land without any treatment or ineffective method is used for treatment. The concentration of chromium was found to be 200 ppm. The pH of samples was found to be mostly alkaline (7.0-8.9) except after the using PNP-D nanoparticles to removal Cr(VI) from wastewater. Fixed bed column was used with nanoparticles dose, initial concentration and flow rate of 2 g, 150 mg/L, and 1 ml/min, respectively. Figure 5.1 shown the BTC for real sample.





**Figure 5.1:** Breakthrough curves (BTCs) for adsorption of Cr (VI) from tannery real sample, Experimental operating conditions: initial *Cr(VI)* concentration=200 mg/L, *Cr(VI)* flow rate=1.00 ml/min, temperature=298 K, pH=8

## Chapter Six

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### Conclusion and Recommendation

#### 6.1 Concluding remarks

In this study, effective poly (ethylenimine)-functionalized iron silicate nanoparticles (PNP) and embedded into Diatomite (D4500) was used to adsorb Cr (VI) from the tannery waste water. The optimum value of pH, adsorbent, and initial Cr (VI) concentration were found to be 9, 2 g/L, and 200 mg/L, respectively for the highest adsorption level of Cr (VI). The maximum adsorption capacity of 17.7 mg/g was obtained after 2 h of adsorption at initial Cr (VI) concentration of 200 mg/L. The Sips model showed a good fit for Cr (VI) adsorption onto the PET-IS with a regression coefficient ( $R^2$ ) of 0.9981. The results obtained in this study suggest that PNP-D has the potential to be an economical and efficient adsorbent for Cr (VI) removal from wastewater resources. Therefore, a filtration unit incorporating PET-IS as adsorbent can be operated based on the optimum conditions, adsorption isotherm and kinetic model obtained in this study in a full-scale wastewater treatment plant for the removal of Cr (VI) from the contaminated waters.

#### 6.2 Recommendations

The following recommendations are suggested for future studies in the field based on the obtained results:

- All the adsorption experiments were conducted for an in-house prepared pyroxene nanoparticles that have the same particles size under the same conditions. Considering different nanosizes is worth investigating as nanosize effect plays role in adsorption. Furthermore, pyroxene, as reported, has a superficial ion exchange properties. It is expected that functionalizing the pyroxene on acidic medium increases the loaded amount of the polyethyleneimine, which subsequently can increase the multi-functionality and the adsorption capacity for the functionalized nanoparticles.

- Polyethyleneimine, as reported, has a high adsorption capacity for the heavy metals like Pb (II), Cd (II), and Cu (II). Therefore, our innovative adsorption technology can be applied for heavy metal removal too.

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## إزالة (Cr (V) من دباغة النفايات السائلة باستخدام الجسيمات النانوية الوظيفية -البيروكسين المدعومة في الدياتومايت: الدفعات والعمليات المستمرة

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### الملخص

إزالة (Cr (V) من دباغة النفايات السائلة باستخدام الجسيمات النانوية الوظيفية -البيروكسين المدعومة في الدياتومايت: الدفعات والعمليات المستمرة

يوجد الكروم عادة بكميات كبيرة في مياه المخلفات. ولهذا السبب ، فإن إزالة واستعادة محتوى الكروم من مياه المخلفات من المولدات أمر بالغ الأهمية لحماية البيئة ولأسباب اقتصادية. تم إزالة واستعادة الكروم من خلال استخدام المميزات المحتملة منخفضة التكلفة. كحل جديد، تمتلك تقنية النانو إمكانات كبيرة في معالجة المياه ومعالجة مياه الصرف الصحي لتحسين جودة المياه بكفاءة. هنا، نحن نقدم تقنية مبتكرة باستخدام البولي السيليكات النانوية السليكونية المتفاعلة الصديقة للبيئة والمتعددة الوظائف والفعالة، والمدمجة في دياتومايت (D4500) بنسبة لم تتجاوز 6%. تم تنفيذ تقنية SEM من أجل اثبات أن الجسيمات النانوية متناهية الصغر جزء لا يتجزأ من الدياتومايت. أظهرت نتائج الفحص جزيئات النانو قد كانت جيدة الانتشار على سطح الدياتومايت بدون أية تغيير في شكله وتركيبته حيث أنه تم تحسين منطقة سطح الامتزاز لديه والقدرة لامتصاص الكروم بشكل ملحوظ عن طريق تضمين الحديد السيليكات النانوية. تم دراسة امتصاص الكروم على الدياتومايت المضمن بـ 6% بالوزن من جسيمات السيليكات النانوية من الحديد في عمود الامتصاص المستمر وتفسيره باستخدام نموذج Sips، لتحديد منحنيات الاختراق تحت ظروف تشغيلية مختلفة (على سبيل المثال، تركيز مدخل (VI) C، معدل تدفق مدخل وارتفاع السرير). أوضحت النتائج أن الكروم السداسي التكافؤ ممتزج بشكل كبير على الجسيمات النانوية المتوافقة مع PEI كأسلوب فعال لإزالة (IV) Cr وتثقية مياه المدابغ.