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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**

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## 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

| | |
|---|---|
| **BTCs** | **Breakthrough curves** |
| **Cr(VI)** | **Hexavalent Chromium** |
| **D4500** | **Diatomite** |
| **HNO3** | **Nitric Acid** |
| **NaOH** | **Sodium Hydroxide** |
| **NPS** | **Nanoparticles** |
| **SEM** | **Scanning Electron Microscopy** |
| **WHO** | **World Health Organization** |

| Unit | |
|---|---|
| **cm** | **Centimeter** |
| **L** | **Liter** |
| **m** | **Meter** |
| **mg** | **Milligram** |
| **mL** | **Milliliter** |
| **nm** | **Nano Meter** |
| **ppm** | **Part Per Million** |

## 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 thaaery 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, $Cr(OH)_4^-$, $Cr(OH)_2^+$, neutral compound $Cr(OH)_3$, and poly nuclear compound $Cr_2(OH)_2$ (Maria,2017). The hexavalent form of chromium is more toxic than trivalent. After hydrolysis of Cr (III) whatever generated stabilized by electron donor species ($OH^-$) 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

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

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**المشرف: د. عامر كنعان**

## الملخص

إزالة (V) Cr 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 الممتزات 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 والفعّالة، والمدمجة في دياتوميت (D4500) بنسبة لم تتجاوز 6%. تم تنفيذ تقنية SEM من أجل اثبات أن الجسيمات النانوية متناهية الصغر جزءا لا يتجزأ من الدياتومايت. أظهرت نتائج الفحص جزيئات النانو قد كانت جيدة الانتشار على سطح الدياتومايت بدون أية تغيير في شكله وتركيبتهو 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 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 وتنقية مياه المدابغ.