



# Modeling of Chromium Removal from Tannery Wastewater using Bagasse

BY

## **Dina Diaa Mohammed El-Sawy**

A Thesis Submitted to the

Faculty of Engineering at Cairo University

In Partial Fulfillment of the

Requirements for the Degree of

MASTER OF SCIENCE in CHEMICAL ENGINEERING

FACULTY OF ENGINEERING CAIRO UNIVERSITY GIZA, EGYPT

# Modeling of Chromium Removal from Tannery Wastewater using Bagasse

BY

## **Dina Diaa Mohammed El-Sawy**

A Thesis Submitted to the Faculty of Engineering at Cairo University In Partial Fulfillment of the Requirements for the Degree of

### MASTER OF SCIENCE in CHEMICAL ENGINEERING

**Under the Supervision of** 

Prof. Dr. Shakinaz Taha El-Sheltawy

Chemical Engineering Dept., Faculty of Engineering, Cairo University Prof. Dr. Maha Mostafa El-Shafei

Sanitary and Environmental Engineering Institute, Housing and Building National Research Center

Dr.

**Khaled Zaher Abd Allah** 

Public works Engineering Dept., Faculty of Engineering, Cairo University

> FACULTY OF ENGINEERING CAIRO UNIVERSITY GIZA, EGYPT

> > 2017

# Modeling of Chromium Removal from Tannery Wastewater using Bagasse

BY

# **Dina Diaa Mohammed El-Sawy**

A Thesis Submitted to the Faculty of Engineering at Cairo University In Partial Fulfillment of the Requirements for the Degree of

## MASTER OF SCIENCE in CHEMICAL ENGINEERING

Approved by the Examining Committee

Prof. Dr. / Shakinaz Taha El-Sheltawy

Thesis Main Advisor

Prof. Dr. / Salwa Raafat Mostafa **Internal Examiner** 

Prof. Dr. / Mahmoud Mohamed Abd El-Azeim

**External Examiner** 

(Prof. Dr., Faculty of Engineering, Ain Shams University)

FACULTY OF ENGINEERING CAIRO UNIVERSITY GIZA, EGYPT **Engineer:** Dina Diaa Mohammed El-Sawy

**Date of Birth:** 25 / 8 / 1985 **Nationality:** Egyptian

**E-mail:** eng.dinadiaa@yahoo.com

**Phone:** 01273045510

**Address:** 18, Eltdamon street, Rod Elfarag, Shobra, Cairo

Registration Date: 1/10/2012
Awarding Date: //2017
Degree: Master of Science
Department: Chemical Engineering

**Supervisors:** Prof. Dr. / Shakinaz Taha El-Sheltawy

Prof. Dr. / Maha Mostafa El-Shafei

Dr. / Khaled Zaher Abdullah

**Examiners:** Prof. Dr. / Shakinaz Taha El-Sheltawy

Prof. Dr. / Salwa Raafat Mostafa

Prof. Dr. / Mahmoud Mohammed Abd El Aziem (Prof. Dr., Sanitary and Environmental Engineering, Faculty of Engineering, Ain Shams University).

#### **Title of Thesis:**

Modeling of Chromium Removal from Tannery Wastewater using Bagasse

#### **Key Words:**

Tannery waste, Chromium removal, Bagasse waste, Adsorption, Wastewater.

#### **Summary:**

The objective of this study is the removal of chromium ions from tannery wastewater using bagasse as adsorbent. The batch kinetic studies indicated that the use of bagasse as adsorbent is an effective tool to remove around 70% of chromium from tannery wastewater after 2 hours and that the best pH was 6. The equilibrium data based on correlation coefficients could be best explained by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm. The Langmuir isotherm was found to describe the best adsorption isotherm in comparison with other isotherm. The kinetic data obtained have been analyzed using pseudo-first-order and pseudo-second-order models. The best fitted kinetic model was found to be pseudo-second-order model.

The results revealed that waste bagasse may efficiently be used for the removal of chromium from tannery wastewater effluents with pH around 6, weight ratio 10 g/l, using agitation rate 250 rpm at 75°C.



### **ACKNOWLEDGEMENT**

First and above all, I praise God, the almighty for providing me this opportunity and granting me the capability to proceed successfully. This thesis appears in its current form due to the assistance and guidance of several people. I would therefore like to offer my sincere thanks to all of them.

**Prof. Dr. Shakinaz El-Sheltawy**, my academic advisor, my cordial thanks for accepting me as a MSc student, your warm encouragement, thoughtful guidance, critical comments, supporting my attendance at various conferences and correction of the thesis.

I want to express my deep thanks to my supervisor **Prof. Dr. Maha El-Shafei**, for the trust, the insightful discussion, offering valuable advice, for your support during the whole period of the study.

I extend my sincere thanks and high appreciation to **Dr. Khaled Zaher**, for his great attention.

I thank profusely all the staffs of Chemical Engineering Laboratory in Chemical Engineering Department, Faculty of Engineering , Cairo University and in Tabbin Institute for Metallurgical Studies for their kind help and co-operation throughout my study period.

I am extremely thankful to my friend **Eng. Rabie Elagayza**, Department of Chemical Engineer, Cairo University for providing me necessary technical suggestions during my research pursuit.

Finally, working on this thesis was a very difficult experience; I would not be able to complete this thesis without the love and support of my husband **Eng. Mohamed Moharam**. Thanks a million to my Parents for their encouragement help and support.

## **Table of Contents**

ACKNOWLEDGMENT	1
TABLE OF CONTENTS	
LIST OF TABLES	VI
LIST OF FIGURES	VII
LIST OF SYMBOLS	IX
LIST OF ABBREVIATIONS	X
ABSTRACT	XI
CHAPTER ONE: INTRODUCTION	1
1.1. Background	1
1.2. Objectives	2
1.3. Outline of Thesis	2
CHAPTER TWO: RECENT TRENDS IN WASTEWATER PURIFICATION	3
2.1. Introduction	3
2.2. Industrial Wastewater (IWW)	3
2.2.1. Characteristics of industrial wastewater	4
2.2.2. Characterizations of wastewater produced by tannery plants	11
2.2.3. Limits standards of heavy metals contaminating IWW	12
2.2.4 Advanced industrial wastewater treatment techniques	12
2.2.5. Comparison of some methods for IWW treatment	16
2.3. Adsorption of Heavy Metals Using Various Adsorbents	16
2.3.1. Agricultural waste as heavy metal adsorbent.	16
2.3.2. Industrial by-product as heavy metal adsorbent.	21
2.3.3. Natural materials as heavy metal adsorbent.	22
2.3.4. Other adsorbent for heavy metals	25
2.4. Adsorption of Heavy Metals from IWW Overview	27
2.5. Leather Industry	27
2.5.1. Egyptian leather tanning sector.	27
2.5.2. Environmental Impact of Tanneries	29
CHAPTER THREE: THEORETICAL CONSIDERATIONS	32
3.1. Introduction	32
2.2 Kingtics models	22

	3.2.1. Pseudo-first order kinetic model	
	3.2.2. Pseudo second order kinetic model	
3.	3. Adsorption Isotherm34	
	3.3.1. Langmuir adsorption isotherm	
	3.3.2. Freundlich adsorption isotherm35	
	3.3.3. Temkin isotherm36	
	3.3.4. Dubinin-Radushkevich isotherm37	
3.	4. Error Analysis of Isotherm Data	
	3.4.1. Coefficient of determination ( $R^2$ )	
	3.4.2. Marquardt's percent standard deviation	
СНА	PTER FOUR: METHODS AND MATERIALS39	
4.	1. Introduction39	
4.	2. Materials39	
	4.2.1. Adsorbents (Bagasse)	
	4.2.2. Adsorbate (Tannery wastewater)41	
	4.2.3. Nitric acid (HNO <sub>3</sub> )42	
	4.2.4. Sodium hydroxide (NaOH)42	
4.	3. Equipment used42	
	4.3.1. pH meter42	
	4.3.2. Atomic absorption spectrometer (AAS)43	
	4.3.3. Jar test	
	4.3.4. Scanning electron microscopy (SEM)44	
4.	4. Methodology44	
4.	5. Effect of Different Operating Variables on Equilibrium Uptake of Chromium from Tannery Wastewater:	45
	4.5.1. Effect of initial pH on the removal of Cr ions using bagasse45	
	4.5.2. Effect of adsorbent dose of bagasse on the removal of Cr ions45	
	4.5.3. Effect of particle size of bagasse on the removal of Cr ions45	
	4.5.5. Effect of temperature on the removal of Cr ions using bagasse as adsorbent 45	
4.	6. Experimental steps46	
4.	7. Equilibrium studies48	
	4.7.1. Kinetic experiments	
	4.7.2. Effect of pH	
	4.7.3. Effect of bagasse dose	

4.7.4. Effect of bagasse particle size	
4.7.5. Effect of temperature49	
4.7.6. Effect of agitation speed	
CHAPTER FIVE: RESULTS AND DISCUSSIONS	
5.1. Introduction:	
5.2. Charctreization of Bagasse as Adsorbent:51	
5.2.1. Chemical compostion of bagasse51	
5.2.2. Scanning electron microscopy of bagasse51	
5.3. Kinetics Study of Adsorption of Chromium from Tannery WW using bagasse52	
5.3.1. Effect of pH on adsorption of chromium from tannery WW52	
5.3.2. Effect of particle size on adsorption of chromium from tannery WW55	
5.3.3. Effect of adsorbent dose bagasse particles on adsorption of chromium from tannery WW 58	
5.3.4. Effect of mixing speed on adsorption of chromium from tannery WW60	
5.3.5. Effect of temperature on adsorption of chromium from tannery WW62	
5.4. Kinetics models64	
5.4.1. Pseudo-first order kinetic model64	
5.4.2. Pseudo-second order model69	
5.5. Equilibrium Isotherm Study73	
5.6. Adsorption Isotherm Study73	
5.6.1. Langmuir isotherm model study74	
5.6.2. Freundlich isotherm model study75	
5.6.3. Temkin isotherm model study	
5.6.4. Dubinin-Radushkevich (D-R) isotherm model study77	
5.7. Economic Aspects of Chromium Removal from Tannery Wastewater79	
5.7.1. Source of used chromium in tannery industry:79	
5.7.2. Source of tannery wastewater in tannery industry:82	
5.8. El Salam Tannery Plant Overview83	
5.8.1. Water consumption in El Salam tannery plant83	
5.8.2. Approximate design of an adsorption unit for tannery wastewater84	
5.8.3. Cost of chromium adsorption from tannery wastewater85	
CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS	
REFERENCES88	
Arabic Summary	

## **List of Tables**

Table (2.1): Physical, chemicals and biological characteristics of wastewater5	
Table (2.2): Sources of heavy metals8	
Table (2.3): Impacts of some heavy metals9	
Table (2.4): Typical wastewater resulting from different process in a tannery with chrome and bark tanning 11	
Table (2.5): The maximum contamination limit standards (MCLS) according to EPA, WHO and EEAA 12	
Table (2.6): Precipitating agents for some heavy metals	
Table (2.7): Flotation technique14	
Table (2.8): Ion exchange processes for heavy metals removal14	
Table (2.9): Electrochemical Treatment	
Table (2.10): Advantage and disadvantage of different methods for wastewater treatment.16	
Table (2.11): Adsorption of heavy metals using risk husks	
Table (2.12): Adsorption of heavy metals using tea waste	
Table (2.13): Adsorption of heavy metals using banana peels18	
Table (2.14): Adsorption of heavy metals using coconut husk and peanut hulls19	
Table (2.15): Adsorption of Cr using sawdust19	
Table (2.16): Adsorption of heavy metals using bagasse	
Table (2.17): Adsorption of heavy metals using industrial by-products22	
Table (2.18): Adsorption of heavy metals using zeolite	
Table (2.19): Adsorption of heavy metals using Bentonite	
Table (2.20): Adsorption of heavy metals using Kaolinite and Montmorillonite24	
Table (2.21): Different adsorbents for heavy metal25	
Table (2.22): Overview of the Egyptian tanning industry	
Table (2.23): Environmental effects caused by tannery polluting constitunts31	
Table (4.1): Sieve analysis of bagasse	
Table (4.2): Used wastewater characterization42	
Table (4.3): Experimental plan for studying kinetics of chromium ion adsorption onto bagasse at optimum conditions	50
Table (5.1): Chemical composition of bagasse51	
Table (5.2): Effect of pH on the % removal of Cr ions from tannery wastewater [Bagasse as adsorbent, m = 2g, $\varphi$ = 0.3 r 150 rpm, C <sub>o</sub> = 113 mg/L and T = 30°C]53	nm, v =
Table (5.3): Effect of particle size of bagasse on the % removal of Cr ions from tannery WW using bagasse as adsorbent 2g, $v = 150$ rpm, pH: 6, $C_0 = 113$ mg/L and $T = 30^{\circ}$ C]56	[m =

Table (5.4): Effect of dose of bagasse on the % removal of Cr ions from tannery WW [bagasse as adsorbent, $\phi$ = 0.3 mm, v = 150 rpm, pH: 6, C <sub>o</sub> = 113 mg/L and T = 30°C]59
Table (5.5): Effect of agitation speed on the % removal of Cr ions from tannery WW [bagasse as adsorbent, m = 2 g, $\varphi$ = 0.3 mm, pH: 6, C <sub>o</sub> = 113 mg/L and T = 30°C]61
Table (5.6): Effect of temperature on the % removal of Cr ions from tannery wastewater [bagasse as adsorbent, m = 2 g, $\varphi$ = 0.3 mm, v = 150 rpm, pH: 6 and C <sub>o</sub> = 113 mg/L]63
Table (5.7): Parameters of pseudo first order kinetic model at different operating variables for adsorption of Cr from tannery wastewater onto bagasse
Table (5.8): Parameters of pseudo second order kinetic model at different operating variables for adsorption of Cr onto bagasse
Table (5.9): Isotherm parameters for chromium ions removal using bagasse78
Table (5.10): Chemicals commonly used in leather tanning
Table (5.11): Water requirement (L/Kg hide) pattern in various operations in the leather processing 82

# **List of Figures**

Figure (2.1): Schematic flow diagram for leather tanning and finishing process29	
Figure (4.1): Bagasse pretreatment phases (dried and ginding) a. bagasse dried in sun before grinding, b. bagasse after grindin as adsorbebnt, c. bagasse at particle size 1mm, d. bagasse at particle size 0.3 mm, e.bagasse at particle size 0.15 mm	g
Figure (4.2): Tanneries location in Cairo, Egypt41	
Figure (4.3): Tanneries in Sour Magra El-Oyoon, Misr El-Kadima, Cairo41	
Figure (4.4): pH meter (ProLine)43	
Figure (4.5): Atomic absorption spectrometer (Perkin Elmer)43	
Figure (4.6): Jar test44	
Figure (4.7): Scanning Electron Microscope (JSM 5900 LV SEM)44	
Figure (4.8): Experimental steps for determination of optimum pH of adsorption46	
Figure (4.9): Experimental steps for determination of optimum particle size of adsorption46	
Figure (4.10): Experimental steps for determination of optimum adsorbent dose of adsorption 47	
Figure (4.11): Experimental steps for determination of optimum temperature of adsorption47	
Figure (4.12): Experimental steps for determination of optimum agitation rate of adsorption48	
Figure (5.1): SEM pictures of bagasse52	
Figure (5.2): Effect of pH value on chromium uptake from tannery wastewater [bagasse as adsorbent, m = 2g, $\phi$ = 0.3 mm, v = 150 rpm, C° = 113 mg/L and T = 30°C]54	
Figure (5.3): Effect of pH on chromium uptake from tannery wastewater using bagasse adsorbent at equilibrium [m = 2g, $\phi$ = 0.3 mm, v = 150 rpm, C° = 113 mg/L, T = 30°C and t = 120 min]54	
Figure (5.4): Effect of particle size of bagasse on the % removal of Cr ions from tannery wastewater [bagasse as adsorbent, m 2 g, $v = 150$ rpm, pH: 6, $C^{\circ} = 113$ mg/L and $T = 30^{\circ}$ C]56	=
Figure (5.5): Effect of particle size on treatment cost	
Figure (5.6): Effect of bagasse dose on the % removal of Cr ions using bagasse as adsorbent [ $\phi$ = 0.3 mm, v = 150 rpm, pH: 6, C = 113 mg/L and T = 30°C].	<b>`</b> 0
Figure (5.7): Effect of agitation speed on the % removal of Cr ions from tannery WW [bagasse as adsorbent, m = 2 g, $\varphi$ = 0.3 mm, pH: 6, C <sub>o</sub> = 113 mg/L and T = 30°C]62	
Figure (5.8): Effect of temperature on the % removal of Cr ions from tannery WW [bagasse as adsorbent, m = 2 g, $\phi$ = 0.3 mm v = 150 rpm, pH: 6 and C <sub>o</sub> = 113 mg/L]64	,
Figure (5.9): Pseudo first order kinetics of Cr uptake from tannery wastewater by bagasse at different dose. 65	
Figure (5.10): Pseudo first order kinetics of Cr uptake from tannery wastewater by bagasse using different particle size. 65	
Figure (5.11): Pseudo first order kinetics of Cr ion uptake from tannery wastewater by bagasse at different pH. 66	

Figure (5.12): Pseudo first order kinetics of Cr uptake from tannery wastewater by bagasse at different temperature.	66
Figure (5.13): Pseudo first order kinetics of Cr uptake from tannery wastewater by bagasse at different agitation rate.	674
Figure (5.14): Pseudo second order kinetics of Cr uptake from tannery wastewater by bagasse at different dose of baga	sse.
Figure (5.15): Pseudo second order kinetics of Cr uptake from tannery wastewater by bagasse from tannery wastewater different particle size of bagasse	r at
Figure (5.16): Pseudo second order kinetics of Cr uptake from tannery wastewater by bagasse at different pH of wastewat	vater.
Figure (5.17): Pseudo second order kinetics of Cr uptake from tannery wastewater by bagasse at different temperature	. 71
Figure (5.18): Pseudo second order kinetics of Cr uptake from tannery wastewater by bagasse at different agitation rate	e. <b>71</b>
Figure (5.19): Adsorption Isotherm of Cr ions present in tannery wastewater against Cr in bagasse as adsorbent at 30°C	73
Figure (5.20): Langmuir isotherm plot for adsorption of chromium ions onto bagasse74	
Figure (5.21): Freundlich isotherm plot for adsorption of chromium onto bagasse76	
Figure (5.22): Temkin isotherm plot for adsorption of chromium from tannery wastewater onto bagasse 77	
Figure (5.23): (D-R) isotherm plot for adsorption of chromium from tannery wastewater onto bagasse 78	
Figure (5.24): Material flow sheet for beam house operation80	
Figure (5.25): Material flow sheet for tanning, past tanning and finishing operations81	
Figure (5.26): Quantity of water used and discharged in different operation in El Salam Tannery 83	
Figure (5.27): Approximate design for adsorption unit84	

### **List of Symbols**

Empirical constants for Langmuir isotherm  $\mathbf{a}_{\mathrm{L}}$ Initial concentration of the metal ions  $\begin{array}{c} C_o \\ C_i \\ C_e \\ D \end{array}$ Final concentration of the metal ions equilibrium concentration of adsorbate in solution after adsorption Dubinin-Radushkevich isotherm constant 3 Dubinin-Radushkevich isotherm constant.  $K_{\rm f}$ Freundlich capacity factor Empirical constants for Langmuir isotherm  $K_{L}$ Temkin isotherm equilibrium binding constant  $K_T$ rate constant of pseudo first order sorption  $\mathbf{k}_1$  $\mathbf{k}_2$ rate constant of pseudo-second order sorption Mass of adsorbent used m mass of adsorbate adsorbed per unit mass of adsorbent  $q_e$ Constant related to heat of sorption  $q_{\text{m}}$ sorption capacity at equilibrium and at time t  $q_t$ R gas constant Temperature, °C T

Volume of the solution

Particle size

#### **List of Abbreviation**

AAS Atomic Absorption Spectrometer
BOD Biochemical Oxygen Demand
COD Chemical oxygen demand

EEAA Egyptian Environmental Affairs Agency

EC Electro Coagulation

EPA Environmental Protection Agency FCE FeCl<sub>3</sub> induced crude extract

FS Filterable solids IWW Industrial Wastewater

MCLS Maximum Contamination Limit Standards
MPSD Marquardt's percent standard deviation

NTU Nephelometric Turbidity Units

PVC Poly Vinyl Chloride RO Reverse Osmosis

SEM Scanning electron microscopy

SS Suspended solids
TDS Total Dissolved solids
TKN Total Kjeidahi Nitogen
TOC Total Organic Carbon
TON Threshold Odor Number

TS Total solids UV Ultra Violet

WHO World Health Organization

WW Wastewater

#### **ABSTRACT**

The presence of heavy metals in the wastewater is wide spreading all over the world. In Egypt, industrial wastewater is considered the main source of pollution that leads to serious environmental problems which have reached 50000-70000 m<sup>3</sup>/year and from which tannery waste represents the most toxic streams with its chromium content. Agriculture wastes are being used also to eliminate heavy metals from wastewater through adsorption processes.

The present study evaluate the effect of different engineering parameters to develop a dual solution for environmental pollution by the uptake of chromium from chromium contaminated tannery wastewater using waste bagasse produced from sugarcane industry as adsorbent.

Removal of chromium ions from tannery wastewater was studied on both acidic and alkaline ranges of pH (2, 4, 6 and 8) with contact time (5, 15, 40, 80 and 120 min), bagasse to wastewater ratio (1, 2, 4, 8 and 10 g/l), using an agitation rate of (50, 150 and 250 rpm) at temperature, T, (30, 50 and 75°C) as main operation conditions.

The batch kinetic studies indicated that the use of bagasse as adsorbent is an effective tool to remove around 70% of chromium after 2 hours and that the best pH was 6. The equilibrium data based on correlation coefficients could be best explained by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm. The Langmuir isotherm was found to describe the best adsorption isotherm in comparison with other isotherm. The kinetic data obtained have been analyzed using pseudo-first-order and pseudo-second-order models. The best fitted kinetic model was found to be pseudo-second-order model.

The results revealed that waste bagasse may efficiently be used for the removal of chromium from tannery wastewater effluents with pH around 6, weight ratio 10 g/l, using agitation rate 250 rpm at 75°C.

#### **Key Words:**

Tannery waste, Chromium removal, Bagasse waste, Adsorption, Wastewater.