

**DETERMINATION OF SOME CHEMICAL RESIDUES IN THE EFFLUENT OF
PHARMACEUTICAL INDUSTRY
AND ATTEMPT FOR TREATMENT**

Submitted By

Eslam Mohamed Tawfik Mohamed

B.Sc. of Science, (Zoology/Chemistry), Faculty of Science, Ain Shams University, 2010

A thesis submitted in Partial Fulfillment
Of
The Requirement for the Master Degree
In
Environmental Sciences

Department of Environmental Basic Sciences
Institute of Environmental Studies and Research
Ain Shams University

2017

APPROVAL SHEET
**DETERMINATION OF SOME CHEMICAL RESIDUES IN THE EFFLUENT OF
PHARMACEUTICAL INDUSTRY
AND ATTEMPT FOR TREATMENT**

Submitted By

Eslam Mohamed Tawfik Mohamed

B.Sc. of Science, (Zoology/Chemistry), Faculty of Science, Ain Shams University, 2010

A thesis submitted in Partial Fulfillment

Of

The Requirement for the Master Degree

In

Environmental Sciences

Department of Environmental Basic Sciences

This thesis Towards a Master Degree in Environmental Sciences

Has been Approved by:

Name

Signature

1-Prof. Dr. Mahmoud Mohamed Abd El Hamid Mashaly

Prof. of Inorganic Chemistry

Faculty of Education

Ain Sham University

2-Prof. Dr. Abd El-Aziz Youssef El-Sayed Youssef

Prof. of Inorganic Chemistry

Faculty of Science

Al-Azhar University (Assuit)

3-Prof. Dr. Mostafa Mohamed Hassan Khalil

Prof. of Inorganic and Analytical Chemistry

Faculty of Science

Ain Shams University

4-Prof. Dr. Taha Abd El Azeem Mohamed Abd El Razek

Prof. of Environmental Chemistry

Head of Department of Environmental Basic Sciences

Institute of Environmental Studies and Research

Ain Shams University

**DETERMINATION OF SOME CHEMICAL RESIDUES IN THE EFFLUENT OF
PHARMACEUTICAL INDUSTRY
AND ATTEMPT FOR TREATMENT**

Submitted By

Eslam Mohamed Tawfik Mohamed

B.Sc. of Science, (Zoology/Chemistry), Faculty of Science, Ain Shams University, 2010

A thesis submitted in Partial Fulfillment
Of
The Requirement for the Master Degree
In
Environmental Sciences
Department of Environmental Basic Sciences

Under The Supervision of:

1-Prof. Dr. Mostafa Mohamed Hassan Khalil

Prof. of Inorganic and Analytical Chemistry
Faculty of Science
Ain Sham University

2-Dr. Taha Abd El Azeem Mohamed Abd El Razek

Prof. in Department of Environmental Basic Sciences
Institute of Environmental Studies and Research
Ain Shams University

2017

ACKNOWLEDGEMENTS

First and foremost I am extremely grateful and thankful to **Allah** Who gave me the ability and the power to finish this work.

I would like to express my sincere appreciation to Prof. Dr. Mostafa Mohamed Hassan Khalil, for

providing his best efforts in supporting and guiding me through this work, as well as
Promoting it in many ways.

I would also like to thank Prof. Dr.Taha Abd El-Azim M. A.Razek for his valuable and expert advice, constructive criticism, cooperation and suggestions, which enhanced the quality of this work.

I would like to show my appreciation to all my friends and colleagues
for their invaluable help and for debugging both my work and this thesis.

I would like to acknowledge the support I received from Ain Shams University and
Institute of environmental studies and research, administratively.

Finally, I would like to express my deep gratitude to my Family specially my parents ,my Wife and my son for their continuous encouragement and for their Unconditional love and support by any possible means, without which this work would not be possible.

Eslam Mohamed

2017

ABSTRACT

Widespread occurrence of pharmaceuticals has started to attract attention as aquatic micropollutants that might have been affecting the ecological system in trace amounts. The risks associated with their introduction into wildlife habitats is becoming an important issue for both regulators and the pharmaceutical industry, because of incomplete elimination of pharmaceuticals wastewater and their metabolites. In this work monitoring of some pharmaceutical residues in industrial wastewater such as (caffeine, paracetamol, dexamethasone and naproxen) was carried out. The identification and quantification of chemical and pharmaceutical residues was investigated using GC/MS spectrometer and liquid chromatography-based tandem mass spectrometry LC/MS/MS spectrometer with electrospray ionization (ESI). The study recorded the presence of different types of pharmaceutical residues with different concentration levels in wastewater. The concentration level of dexamethasone in wastewater were detected at 254 ng/mL, for paracetamol at 7325 ng/mL, for caffeine at 9356 ng/mL and for naproxen at 2000 ng/mL. These concentrations representing about 500 fold higher than international safety margin of treated wastewater. Naproxen was selected (nonsteroidal anti-inflammatory drug) in the study due to when Naproxen exposed to sunlight it's converted into two related compounds these photodegradants are predicted to be more toxic than naproxen because they have lower polarity and some trials for treatment were carried out to degrade or remove naproxen using granulated activated carbon (GAC) and Sawdust (SD) with different activation types to show its effect and the study showed that there is an effect on the treatment of naproxen for GAC by 97.4% of removal after 2 hours contact time and the kinetic calculations in this study showed that all removal reactions were first order reaction and the suitable adsorption isotherm equation for naproxen was langmuir equation and for SD by 56% of removal after 2 hours contact time and the kinetic calculations in this study showed that all removal reactions were second order reaction and the suitable adsorption isotherm equation for naproxen was langumir equation.

Contents

List of tables	III
List of figures	V
List of abbreviations	X
Background and stating of the problem	2
1-Literature Review	6
Aim of work	40
2) Materials and Methods.....	42
2.1 Materials:	42
2.2 Methods	44
3) Results and discussion	59
3.1) Monitoring and Determination of some Chemical and Pharmaceutical residues.....	59
3.2) Treatment & Removal of naproxen by activated saw dust (SD) and granular activated carbon (GAC) :.....	70
3.2.1) Treatment & Removal of naproxen by activated sawdust (SD)	70
3.2.2) Treatment & Removal of naproxen by (GAC) :	86
Adsorption Equilibria.....	100
Freundlich Model	100

Contents

Langmuir Model	101
Conclusion and Recommendation	103
Summary	108
Reference	111
الملخص	
المستخلص	

List of Tables

Table No.	Title	Page
Table (1.1)	Amount of acetaminophen detected in inlet and outlet waters of Waste Water Treatment Plants .	12
Table (1.2)	Merits and demerits of different treatment technologies for the biosorption of heavy metals and organic pollutants from aqueous systems.	33
Table (2.1)	MRM method parameters selected in positive and negative ion modes.	47
Table (2.2)	Instrument Parameters	49
Table (3.1)	Compounds found in qualitative analysis of four samples	64,65
Table (3.2)	Concentration in (ng/mL) of 4 analytes in wastewater of a pharmaceutical and chemical industries facility	69
Table (3.3)	Naproxen removal by various amount of activated SD H ₂ SO ₄ Naproxen concentration at zero time was 2000 ng/mL	73
Table (3.4)	Effect of pH on naproxen removal	79
Table (3.5)	Effect of temperature on removal of naproxen	80
Table (3.6)	Naproxen removal by various amount of saw dust activated with H ₂ SO ₄ (SD) Naproxen concentration at zero time was	82

Table No.	Title	Page
	7000 ng/mL	
Table (3.7)	Naproxen removal by various amount of (GAC) $C_0=2000$ ng/mL	86
Table (3.8)	Effect of pH on Naproxen removal after Treatment by 0.2gm of GAC	92
Table (3.9)	Effect of temperature on removal of naproxen	95
Table (3.10)	Naproxen removal by various amount of GAC $C_0=7000$ ng/mL	96
Table (3.11)	Isotherm models and their linear plot	101
Table (3.12)	Parameters of Freundlich and Langmuir Isotherm models	102

List of Figures

Figure No.	Title	Page
Figure (1.1)	Sources of pharmaceuticals in the natural aquatic environment	9
Figure (1.2)	An illustration of analytical methods applied to detect pharmaceuticals in water and wastewater	14
Figure (1.3)	An illustration of Liquid Liquid extraction (LLE)	16
Figure (1.4)	Common SPE steps	17
Figure (1.5)	GC-MS schematic.	19
Figure (1.6)	The principle of The Multi Plereaction Monitoring (MRM) in triple quadruple mass spectrometer	21
Figure (1.7)	Therapeutic classes detected in the environment & expressed in relative percentage.	26
Figure (2.1)	Schematic Diagram of The System Used for The Preparation of Activated Carbons from Sawdust.	45
Figure (2.2)	Sample collection	46
Figure (2.3)	GC(Varian 3800) & mass detector(varian 320-MS)	46
Figure (2.4)	Abundance vs. acqui. time (min)	48