An-Najah National University Faculty of Graduate Studies

Synthesis and characterization of magnetic nano cellulose from olive waste (Jeft) for the effective removal of methylene blue from water

By

Abeer Mohammed Rasheed Melhem

Supervisor

Prof. Shehdeh Jodeh

Co- Supervisor

Dr. Othman Hamed

This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Chemistry, Faculty of Graduate Studies, An-Najah National University, Nablus - Palestine.

2017

Synthesis and characterization of magnetic nano cellulose from olive waste (Jeft) for the effective removal of methylene blue from water

By

Abeer Mohammed Rasheed Melhem

This Thesis was Defended Successfully on 10/8/2017, and approved by:

Defense Committee Members		<u>Signature</u>
1. Prof. Shehdeh Jodeh	/ Supervisor	
2. Dr. Othman Hamed	/ Co-supervisor	
3. Dr. Wadie Sultan	/ External Examiner	
4. Dr. Mohammed Al-nur	i /Internal Examiner	

ii

Dedication

Every challenging work needs self-efforts as well as encouragements of others especially those who were very close to our heart.

To my father, Brother Majdi and my dear family whose love and encouragement make me able to get success and honor. To my husband Muhsen .To my great mother (mercy to her) who has sacrificed for our sake.

To all of them I dedicate my modest efforts.

Acknowledgments

Praise be to Allah, the lord of the worlds and peace and blessings of Allah be upon the noblest of the Prophets and Messengers, our Prophet Mohammad.

Foremost, I would like to express my sincere gratitude to my advisor Prof. Shehdeh Jodeh and Dr. Othman Hamed for there professional advice, guidance, and continued support throughout this project.

Many thanks to whom our thanks go as well to them for their follow up the project.

I would like to thank all the technicians and staff of the chemistry department at An-Najah National University, especially Mr. Omair Al-Nabulsi and Mr. Nafiz Dweikat for their help.

I would like also to express my thanks to all friends in the master program for the great and lovely time that we spent together.

Last but not the least, I would like to thank my family: my parents Alham and Mohammed Melhem, for giving birth to me at the first place and supporting me spiritually and financially throughout my life.

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Synthesis and characterization of magnetic nano cellulose from olive waste (Jeft) for the effective removal of methylene blue from aquous solution

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يُقدم لنيل أية درجة أو لقب علمي أو بحثى لدى أى مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's Name: اسم الطالب: Signature: التوقيع: Date: التاريخ:

vi Table of contents

No.	Content	
	Dedication	iii
	Acknowledgement	iv
	Declaration	v
	List of tables	viii
	List of figures	Х
	List of abbreviations	xii
	Abstract	xiv
	Chapter One: Introduction	1
1.1	Overview	1
1.2	Adsorbents Cellulose (Cs), nanocellulose (NCs) and	2
1.2	magnetic nanocellulose (MNCs):	5
1.2.1	Nanotechnology	4
1.2.1.1	Nanocellulose	4
1.2.2	Magnetic nanocomposites	6
1.2.2.1	Magnetic nanocellulose	6
1.2.2.2	Magnetic chitosan	8
1.3	Water pollutants and adsorbents	8
1.3.1	Dyes	8
1.4	Methylene Blue Dye	10
1.4.1	Structure and properties	10
1.4.2	Toxicity of methylene blue	12
1.4.3	Uses of methylene blue	13
1.4.3.1	Medical uses of methylene blue	13
1.4.3.2	Industrial uses of methylene blue	14
1.5	Research Objectives	14
1.5.1	General Objectives	14
1.5.2	Specific Objectives	15
	Chapter Two	16
2.1	Adsorption	16
2.1.1	Adsorption Definition, Features and Types	16
2.2	Equilibrium Isotherm Models	17
2.2.1	Langmuir Adsorption Isotherm	18
2.2.2	Freundlich Adsorption Isotherm	20
2.3	Adsorption Kinetic Models	21
2.3.1	Pseudo First–Order Kinetics	22
2.3.2	Pseudo Second–Order Kinetics	22
2.3.3	Intra-Particle Diffusion Kinetic Model	23
2.4	Adsorption Thermodynamics	23

2.5	Adsorption as an effective method for removing dyes		
2.3	2.5 from wastewater		
	Chapter Three: Experimental Work	26	
3.1	Chemicals and Materials	26	
3.2	Instrumentations	26	
3.3	Preparation of adsorbents (Cs, NCs and MNCs)	27	
3.3.1	Cellulose nanocrystalline	27	
3.3.2	Magnetic cellulose nanocomposite	27	
3.3.3	Characterization of adsorbents (Cs, NCs and MNCs)	28	
3.4	Statistical Analysis	28	
3.5	Preparation of methylene blue solutions	28	
3.6	Calibration Curve	29	
3.7	Adsorption Experiments	30	
3.7.1	Optimization of contact time and initial concentration of MB dye	32	
3.7.2	Effect of pH	32	
3.7.3	Effect of adsorbent dose	33	
3.7.4	Effect of temperature	33	
3.8	Thermodynamics and Kinetics of Adsorption	33	
	Chapter Four: Results and Discussion		
4.1	Cs, NCs and MNCs Characterization	35	
4.1.1	SEM Analysis of the	35	
4.1.2	FT-IR Characterization	37	
412	Analysis cellulose substrates by TEM and Variable		
4.1.3	Scanning Magnetometry (VSM).	30	
4.1.4	TGA Analysis and Thermal Stability	39	
4.2	Investigation of adsorption parameters	40	
4.2.1	Effect of contact time and MB dye concentration	40	
4.2.2	Effect of pH on MB dye adsorption	42	
4.2.3	Effect of amount of adsorbent	43	
4.2.4	Effect of temperature on MB dye adsorption	44	
4.3	Adsorption isotherm of MB dye	45	
4.3.1	Langmuir Adsorption Isotherm	46	
4.3.2	Freundlich model Isotherm	48	
4.4	Adsorption kinetics of MB dye	52	
4.5	Adsorption Thermodynamics	60	
4.6	Recovery of MB dye and reusability of the adsorbent	62	
	Conclusions	65	
	References	67	
	الملخص	ب	

List of Tables

No.	Table	Page
1.1	Physical and chemical properties of MB dye	11
1.2A	Dose-related toxicity of MB dye	13
1.2B	Dose-related toxicity of MB dye	13
4.1 (a)	Langmuir isotherm model parameters and correlation coefficient for adsorption of MB dye on Cs at 15, 30, 45 and 55 °C.	48
4.1(b)	Langmuir isotherm model parameters and correlation coefficient for adsorption of MB dye on NCs at 15, 30, 45 and 55 °C.	48
4.1 (c)	Langmuir isotherm model parameters and correlation coefficient for adsorption of MB dye on MNCs at 15, 30, 45 and 55 $^{\circ}$.	48
4.2(a)	Freundlich isotherm model parameters and correlation coefficient for adsorption of MB dye on Cs at 15, 30, 45 and 55 °C.	50
4.2(b)	Freundlich isotherm model parameters and correlation coefficient for adsorption of MB dye on NCs at 15, 30, 45 and 55 °C.	50
4.2 (c)	Freundlich isotherm model parameters and correlation coefficient for adsorption of MB dye on MNCs at 15, 30, 45 and 55 °C.	50
4.3 (a)	Parameters and correlation coefficient of Langmuir, Freundlich and for adsorption of MB dye on Cs at 15, 30, 45 and 55 °C.	50
4.3 (b)	Parameters and correlation coefficient of Langmuir, Freundlich and for adsorption of MB dye on NCs at 15, 30, 45 and 55 °C.	51
4.3 (c)	Parameters and correlation coefficient of Langmuir, Freundlich and for adsorption of MB dye on MNCs at 15, 30, 45 and 55 °C.	51
4.4 (a)	Pseudo first order and pseudo second order kinetic model parameters for MB dye adsorption on Cs at 25°C.	56
4.4 (b)	Pseudo first order and pseudo second order kinetic model parameters for MB dye adsorption NCs at 25°C.	56

r		
4.4(c)	Pseudo first order and pseudo second order kinetic model parameters for MB dye adsorption MNCs at 25°C.	57
4.5 (a)	Intraparticle diffusion for adsorption of different initial concentrations of MB by Cs	59
4.5 (b)	Intraparticle diffusion for adsorption of different initial concentrations of MB by NCs	59
4.5 (c)	Intraparticle diffusion for adsorption of different initial concentrations of MB by MNCs	59
4.6 (a)	Thermodynamic parameters for the adsorption of MB onto Cs ($C_{\circ} = 10$ ppm, pH = 10 ,adsorbent dose = 100 mg , t = 50 min	62
4.6 (b)	Thermodynamic parameters for the adsorption of MB onto NCs ($C_{\circ} = 10$ ppm, pH = 10 ,adsorbent dose = 100 mg , time = 50 min	62
4.6 (c)	Thermodynamic parameters for the adsorption of MB onto MNCs ($C_{\circ} = 10$ ppm, pH = 10 ,adsorbent dose = 100 mg , time = 50 min.	62
4.7	Percentage of MB dye removal by the regenerated adsorbent compared with a fresh one at (Temperature= 25°C, pH= 10, solution Volume= 50 mL, adsorbent dose= 0.1 g, contact time= 50 min)	63

List of Figures

No.	Figure	Page
1.1	Molecular structure scheme of the methylene blue	10
1.2	A reversible oxidation-reduction system of methylene blue and leucomethylene blue.	11
3.1 (a)	Linear calibration curve between absorbance and concentration for MB concentrations in the range 0.5-50 mg/L	29
3.1 (b)	Linear calibration curve between absorbance and concentration for MB concentrations in the range 50-200mg/L	30
4.1	SEM Image of OISW at a) 250x. b) 500 x. c) 1000 x.	36
4.2	X-Ray Spectra of OISW	37
4.3	FT-IR of Cellulose Extracted from OISW	38
4.4	TEM and (b) Variable Scanning Magnetometry (VSM)	39
4.5	Thermogravimetric curves of (a) cs. (b) NCs. (C) MNCs.	40
4.6	Effect of contact time and MB dye concentration to determine the time of maximum adsorption of MB dye. (Temperature= 25oC, pH= 10, concentration Of MB dye= (a) 5 mg/L, (b)10 mg/L, (c) 20 mg/L respectively sontituel Volume= 50 mL, adsorbent dose= 0.1 g)	41
4.7	Effect of pH on MB dye adsorption. (Co= 10 ppm, T=25OC, time= 50 min., adsorbent dose= 0.1 g, solution Volume= 50 mL)	43
4.8	Effect of amount of adsorbent on the removal of MB dye. (Temperature= 25° C, time= 50 min., pH= 10, concentration Of MB dye= 10 mg/L, solution Volume= 50 mL)	44
4.9	Effect of temperature on MB dye adsorption. ($C_0=10$ ppm, time= 50 min., adsorbent dose= 0.1 g, solution Volume= 50 mL)	45
4.10	Langmuir plot for MB dye adsorption on (Cs,NCs and MNCs). Temperature= (a)15oC, (b) 30 $^{\circ}$ C,(c) 45 $^{\circ}$ C, (d) 55 $^{\circ}$ C, pH= 10, time= 50 min., solution Volume= 50 mL, adsorbent dose= 0.1 g.	47

		0
4.11	Freundlich plot for MB dye adsorption on (Cs,NCs and MNCs). Temperature= (a)15°C, (b) 30 °C,(c) 45 °C, (d) 55 °C, pH= 10, time= 50 min., solution Volume= 50 mL, adsorbent dose= 0.1 g.	49
4.12	Pseudo first order sorption kinetics of MB dye on (Cs,NCs and MNCs). (Temperature= 25°C, pH= 10, solution Volume= 50 mL, adsorbent dose= 0.2 g)	54
4.13	Pseudo second order adsorption kinetics of MB dye on (a) Cs, (b) NCs and (c) MNCs). (Temperature= 25°C, pH= 10, solution Volume= 50 mL, adsorbent dose= 0.1 g)	55
4.14	The intraparticle diffusion of MB dye on (a) Cs, (b) NCs and (c) MNCs). (Temperature= 25°C, pH= 10, solution Volume= 50 mL, adsorbent dose= 0.1 g)	58
4.15	Plot of lnK_d versus 1/T for MB dye adsorption on (Cs, NCs and MNCs). (Temperature= 15° C, pH= 10, time= 50 min., solution Volume= 20 mL, adsorbent dose = 0.1 g)	61
4.16	A representative structure showing the interaction between MNCs and MB	64

xii List of Abbreviations

Symbol	Abbreviation		
MB	Methylene Blue		
MAC	Minimum alveolar concentration		
SVR	Systematic Vascular Resistance		
MAOI	Monoamine oxidase inhibitors		
LD50	Lethal Dose which cause the death of 50% (one half) a		
	group of test.		
C _e	The equilibrium concentration of the adsorbate (mg/L).		
Co	The initial concentration of the adsorbate (mg/L).		
q _e	The amount of adsorbate per unit mass of adsorbent		
-	(mg/g).		
K _L	Langmuir isotherm constant (L/mg).		
Q _o	maximum monolayer coverage capacity at equilibrium		
	(mg/g).		
V	The volume of the solution (L).		
М	The mass of the adsorbent (g).		
R _L	Dimensionless constant separation factor		
K _F	The Freundlich constant related to adsorption capacity		
	(mg/g).		
Ν	The heterogeneity coefficient that gives an indication of		
	how favorable the adsorption process (g/L).		
q_t	The mass of adsorbate per unit mass of adsorbent at		
	time t (mg/g).		
\mathbf{K}_1	The rate constant of pseudo first-order adsorption model		
	$(mg.g^{-1}.min^{-1}).$		
K_2	The equilibrium rate constant of pseudo second-order		
	adsorption model (g.mg ⁻¹ .min ⁻¹).		
K _{id}	The Intra-Particle diffusion rate constant (mg/g.min ^{1/2}).		
Z	Constant that gives an information about the thickness		
	of the boundary layer (mg/g).		
ΔG°	Standard Gibbs free energy change (J).		
ΔH°	Standard Enthalpy change (J).		
ΔS°	Standard Entropy change (J/K).		
T	The absolute temperature (K).		
K K	The universal gas constant (8.314 J.mol ⁻ .K ⁻).		
K _d	The thermodynamic equilibrium constant (L/g) .		
Cs NGC	Cellulose		
NCS	Nanocellulose		
MNCs	Magnatic nanocellulose		

	xiii
CNF	Cellulose nanofibrils
CNC	Cellulose nanocrystals
CNFs	Cellulose nanofibers
WHS	wheat shells
TAB	treated animal bone
MBD	methylene blue dye
SEM	Scanning Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
CI	crystallinity indexes
NMR	Nuclear Magnetic Resonance
XRD	X-Ray Diffraction
FTIR	Fourier Transform Infrared
MCNTs	Magnetic carbon nanotubes MCNTs
NPC	Nanoporous carbon
Al-PCP	Al-based porous coordination polymers
CNCs	Cellulose nanocrystals
MFC	Microfibrillated cellulose
FeNP	Iron nanoparticles
SCISR	Submerged Circulation Impinging Stream Reactor
AC	Activated Carbon
MCB	Magnetic Cellulose Beads
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
AAS	Atomic Absorption Spectroscopy
TGA	Thermal Gravimetric Analysis
UV	Ultra-Violet

xiv Synthesis and characterization of magnetic nanocellulose from olive wastefor the effective removal of methylene blue from aqueous solution By Abeer Mohammed RasheedMelhem Supervisor Prof. ShehdehJodeh Co- Supervisor Dr. Othman Hamed Abstract

The water pollution is a big problems faced by the countries of the world, without exception. This will lead to different health problems to both human beings and animals. The major problem here is to detect the concentration of one of the pollutants like methylene blue and try to remove it by adsorption.

Cellulose used in this study was extracted from Olive Industry Solid Waste

(OISW) by a multistep process, the extracted cellulose was then converted to cellulose nanocrystaline (CNC) by acid hydrolysis. Produced CNC was then converted to magnetic cellulose nanocrystalline (MCNC) by treating it with solution of FeCl₃.6H₂O and FeSO₄.7H₂O, and that was the first goal of this work.

A second objective was removing methylene blue dye from water, using these new prepared materials as an adsorbent for the solid-phase extraction of MB.

Produced magnetic CNC was characterized by several spectroscopic and analytical techniques SEM, TEM, XRD, FTIR VSM and TGA. SEM images of the cellulose surface showed rough and porous nature, indicating that the materials present good characteristics to be employed as an adsorbent.

The tendency of the prepared MNC for extracting methylene blue (MB) from was water evaluated and compared to the base polymers cellulose and CNC.

The base polymer cellulose and CNC showed acceptable tendency for methylene blue. However, CMNC showed excellent extraction efficiency toward MB. Three variable were monitored and evaluated during the extraction process: time, dosage, and concentrations.

The adsorption thermodynamics of the three materials cellulose, CNC and CMNC were evaluated, all of them followed Langmuir isotherm model and pseudo –second- order.

The negative ΔG° values for the three materials indicate that the adsorption

is favorable and spontaneous at these temperatures. The positive value of ΔH° reflects an endothermic adsorption and indicates that the adsorption is favored at high temperature.

Chapter One Introduction

1.1 Overview

The olive oil industry is one of the most economically important agro-food sectors in the Mediterranean and Middle Eastern regions including Palestine [1]. Oil produced at olive mills from crushed olive which is pressed and centrifuged to separate water from oil also produces environmental wastes causing a serious disposal problem of this waste in two aspects: the first is liquid waste (OILW) 56% of olive industry waste and is known in Palestine as "Zubarr"; the second is solid waste (OISW = pomace, also locally known as Jeft) 44% of olive industry waste[2].

Jeft components are similar to wood components, consisting of cellulose, lignin, Extractives (4-10%), and hemicelluloses [3]. The challenge is to utilize and convert these waste materials into useful and low-cost value added materials. In this work, the jeft component cellulose will be modified and used in purifying polluted materials.

Pollution is the process of making land, water, air or other parts of the environment dirty, unsafe and unsuitable for use. This can be done through the introduction of a contaminant into a natural environment. Toxic pollution affects more than 200 million people worldwide, according to Pure Earth organization (a non-profit environmental organization). In some of the world's worst polluted places, babies are born with birth defects, children have lost 30 to 40 IQ points, and life expectancy may be as low as 45 years because of cancers and other diseases [4].

One of the major cause of water pollution is textile was tewaters which contain high quantity of dye effluent [5]. Dyes are chemicals that give colors to the materials. Dyes should be ionic, aromatic organic compounds with structures including aryl rings which delocalized electron systems. The color of a dye is provided by the presence of chromospheres. Most dyes are non-biodegradable in nature for this reason they affect the photosynthetic activity in aquatic systems by reducing light penetration [6].

The release of dyes into wastewaters from textile, cosmetic, paper, and coloring industries poses serious environmental problems. The coloration of the water by the causes inhibitory effect on photosynthesis which then cause severe damage to the aquatic ecosystems [7].

The was tewater discharged from dying processes exhibit high biological oxygen demand (BOD), high chemical oxygen demand (COD), highly colored, alkaline and contain high amounts of dissolved solids [8]. The disposal of colored wastes such as dyes and pigments into receiving waters damages the environment, as they are carcinogenic and toxic to humans and aquatic life [9].

Adsorption has been found to be an efficient and economically cheap process to remove pollutants such as colors, dyes and metal impurities from waste water [10].

1.2 Adsorbents Cellulose (Cs), nanocellulose (NCs) and magnetic nanocellulose (MNCs).

To the best of our knowledge, cellulose from olive waste based magnetic oxides nanocomposites as an adsorbent toward removal of methylene blue (MB) have not been investigated. In this study, cellulose (Cs) was extracted from OISW and used for making nanocellulose (NCs) and magnetic nanocellulose (MNCs). The three materials were used for the removal of methylene blue (MB) from wastewater. Fe_3O_4 nanocrystals anchored on nanocellulose was synthesized by metal etching approach as an adsorbent to enhance MB molecules diffusion onto the cellulose surface to efficiently trap the dyes for removal.

Cellulose is an organic polymer, the repeating unit of the cellulose polymer is anhydroglucose with the formula $(C_6H_{10}O_5)_n$ [5] where n is the average value that can be more than 1000 or 10000 (depending on source) [11].

Cellulose present in a powder or fiber from, a water insoluble polymer, chiral, rigid, and biodegradable, odorless and has no taste. The density of powered cellulose ranges from 0.2-0.5 g/cm³, and the melting point is about 260-270 °C [12].

Cellulose is nearly inexhaustible polymeric raw material from renewable sources. Natural cellulose-based materials, such as wood and natural fibers, have been used as engineering materials for many years, and their use presently continues, as showed by the huge number of forest product-based worldwide industries [13,14].

1.2.1 Nanotechnology

The cellulose fibrils that contain crystalline and amorphous regions can be commonly separated from the given cellulose source into amorphous and/or crystalline components by mechanical, chemical or a combination of mechanical chemical and enzymatic processes , yielding cellulose nanofibrils (CNF) or cellulose nanocrystals (NCs). Both, CNF and NCs have been used recently to engineer new materials [15].

Nanotechnology is the understanding and controlling matter at dimensions about 1-100 nm can used in many novel applications. Nanomaterials from cellulose and lignocelluloses are very important in the nanotechnology field. The development of cellulose nanofibers (CNFs) has received a lot of interest in the last few decades because of unique characteristics they have such as high youngs modulus, high tensile strength and low coefficient of thermal expansion and high surface area to volume ratio[12].

1.2.1.1 Nanocellulose

Nanocellulose is a relatively inexpensive, highly versatile bio-based renewable material with advantageous properties, including biodegradability and nontoxicity. Nanocellulose has a numerous potential applications, such as its use in the preparation of high-performance

4

composites, has attracted much attention from industry. Owing to the low energy consumption and the addition of significant value, nanocellulose extraction from agricultural waste is one of the best alternatives for waste treatment. Different techniques for the isolation and purification of nanocellulose have been reported, and combining these techniques influences the morphology of the resultant fibers. In one study, nanocellulose was extracted from citrus waste. The morphology of nanocellulose was determined by Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FESEM), while cellulose crystallinity indexes (CI) from lyophilized samples were determined using solid-state Nuclear Magnetic Resonance (NMR) and X-Ray Diffraction (XRD) measurements [16].

Nanocellulose was characterized after extracted from cotton (Gossypiumhirsutum) linters. The nanocellulose was subjected to electronic microscopy, thermal analysis, X-ray diffractometry, light scattering, and contact angle [17].

Pomelo (Citrus grandis) peel is one of the waste materials that have potential in the production of functional ingredients, due to its high fiber content. One of recent studies was conducted to isolate and characterize cellulose and nanocellulose from pomelo albedo. Cellulose was prepared via alkali treatment followed by bleaching process, while nanocellulose was produced via hydrolysis using sulfuric acid [18]. Corn husk is one of the agricultural residues which are abundant, inexpensive, and readily available source of renewable lignocellulosic biomass. Cellulose nanocrystals (CNCs) were extracted from corn husk by alkali and bleaching treatments followed by sulfuric acid hydrolysis treatment [19].

1.2.2 Magnetic nanocomposites

Magnetic ferrite nanocomposites which are composed of two or more types of metal nanoparticles are considered an important materials for many research due to their unique functions in many diverse areas, particularly in nanobiotechnology [14].

Over the past many decades, diverse ferrite nanostructures with specific particle sizes or compositions have been synthesized. Advanced synthetic techniques have promoted mixed-metal ferrites such as manganese ferrite (MnFe₂O₄) and cobalt ferrite (CoFe₂O₄). New ferrites with various cations that substitute the original metals have been synthesized by controlling their compositions during synthesis. Among these magnetic ferrites, Cu⁺²-merged nanoparticles (Cu_{1-x}Co_xFe₂O₄) have shown unique properties, large anisotropy energy, and high saturation [15].

1.2.2.1 Magnetic nanocellulose

A novel magnetic cellulose nanocrystal material decorated with Cu–Co ferrite was synthesized in situ by controlled hydrothermal chemistry in the presence of $NH_3.H_2O$. The ferrite nanoparticles immobilized on cellulose were found to be in their oxide forms as identified by FTIR and Raman spectra. They demonstrate very good dispersibility with smaller crystal size after being formed in situ on the surface of a nanocellulose crystal template by the application of ammonia. The crystalline structure of cellulose can only be maintained at relatively low contents of ferrite surface decoration (11.0 %) versus high contents (e.g., 75.6 %). Moreover, the magnetic properties of the resultant materials was controlled by changing the ratio of the molecular components in the ferrites. At the low ferrite contents, the composition was $Cu_{0.5}Co_{0.5}Fe_2O_4$ at a small crystal size of 13.5 nm that provided a maximum saturation magnetization of 10.95 emu/g. Finally, the thermostability of the nanocomposite was improved after immobilizing the magnetic nanoparticles [15].

In other study a novel adsorbent, magnetic iron nanoparticles modified microfibrillated cellulose (FeNP/MFC), was used for arsenate (As(V)) removal from aqueous solutions, Iron nanoparticle modified MFC was found to be an exceptional adsorbent material due to its magnetic properties, high surface area and a good adsorption capacity[20].

The adsorption and desorption of the organic dyes on MCB-AC were investigated to evaluate the removal of dyes (methyl orange and methylene blue) with different charges from aqueous solution [21].

1.2.2.2 Magnetic chitosan

Chitin is one of the most abundant natural polymers in world and it is used for the production of chitosan by deacetylation. Chitosan is antibacterial in nature, non-toxic, and biodegradable thus it can be used for the production of biodegradable film which is a green alternative to commercially available synthetic counterparts. However, their poor mechanical and thermal properties restricted its wide spread applications. Chitosan is highly compatible with other biopolymers thus it's blending with cellulose and/or incorporation of cellulose nanofiber and cellulose nanowhiskers are generally useful. Cellulosic fibers in nano scale are attractive reinforcement in chitosan to produce environmental friendly composite films with improved physical properties. Thus chitosan based composites have wide applicability and potential in the field of biomedical, packaging and water treatment [22].

1.3 Water pollutants and adsorbents

1.3.1 Dyes

Dyes in wastewater are an important class of pollutants, which can be identified by human's eye. The release of some dyes in water streams has serious environmental impacts[23]. Nano-cellulose hybrids containing polyhedral oligomeric silsesquioxane with multi-N-methylol (R-POSS) is one of the novel biosorbents for dyes. The removal capacities of nanocellulose hybrid materials for reactive dyes from aqueous solution were significantly higher than that of control cellulose [23]. Nano-cellulose hybrids have potential application as biosorbents in the low concentration dyeing wastewater [23].

Synthetic dyes are extensively used in textile, paper, leather tanning, plastics and food industries [24]. Dyeing and finishing of textile fabrics are generally performed in water based media. This process has environmental problems including water pollution due to discharge of various chemical additives, Reactive dyes are mainly dyes for cellulose fabrics[23].

Unfortunately, these dyes often contaminate surface and ground water resulting in a serious environmental problems. It is important that, the dye is removed from was tewater before its discharged to environment [25]. Methylene Blue (MB), a typical cationic dye which is a very toxic and potentially carcinogenic to human health, can be a model compound for adsorption studies of organic contaminants in aqueous solutions due to its stability to the heat, oxidizing agents as well as biodegradation [26].

Many adsorbents were used to remove methylene blue dye from aqueous solution.For example, wheat shells (WHS) was used for the removal of methylene blue from aqueous solutions at different contact times, temperatures, pH, adsorbent doses and initial dye concentration was investigated [27]. On the other hand, the adsorption behaviors of treated animal bone (TAB) with methylene blue dye (MB) were studied to remove MB from was tewater [28]. In other study, coconut fibres were grounded

9

and sieved into the size of 150 μ m granular form and filament form of uniform size 2.0 cm for absorption test of methylene blue dye [29].

1.4 Methylene Blue Dye

1.4.1 Structure and properties

Methylene Blue is a heterocyclic aromatic compound that has molecular formula of $C_{16}H_{18}CIN_3S$, its structure is shown in figure 1.1, its IUPAC name is *3,7_bis(Dimethylamino)_phenothiazin_5_ium chloride*. Methylene blue (MB) is a cationic thiazine dye which has deep blue color in its oxidized state while it is colorless in the reduced form leucomethylene blue [30].



Figure 1.1: Molecular structure of the methylene blue

MB and leucomethylene blue exist as a redox couple in equilibrium and together give a reversible oxidation-reduction system or electron donor-acceptor couple because they are in equilibrium as a redox couple as shown in Figure 1.2 [31].



Figure 1.2: A reversible oxidation-reduction system of methylene blue and leucomethylene blue.

Some physical and chemical properties of Methylene Blue are listed in **Table 1.1**[32].

 Table 1.1: Physical and chemical properties of MB dye

Physical and chemical properties	Values
Melting temperature	180°C
Boiling temperature	No data (Decomposes)
Solubility in water	35.5 g/L
pH value	3(10g/L H ₂ O)
Molecular weight	319.09 g/mol
Color	Dark blue-green in oxidized
	form, colorless in reduced
	form (leucomethylene blue
Chemical formula	$C_{16}H_{18}N_3ClS$

1.4.2 Toxicity of methylene blue

Methylene blue is a potent monoamine oxidase inhibitor (MAOI) in vitro, and also many deaths in humans were noticed due to serotonin toxicity because MB causes fatal serotonin toxicity. MB also has acetylcholinesterase antagonist activity and therefore help in memory and neuronal degeneration [33].

Large doses of methylene blue may cause chest pain, restlessness, tremors, dyspnea,

apprehension, urinary tract irritation, and a sense of oppression. It also produce mild hemolysis with moderate hyperbilirubinemia, slight anemia, and reticulosis [34].

Methylene blue is a biologically active substance, and if administered inappropriately, it can cause many of health complications, such as dysuria and gastrointestinal disturbances [35].

Methylene blue toxicity is almost associated with its administration to patients treated with psychotropic medications, especially those affecting central nervous system serotonin levels. Methylene blue should be administered with care to these patients. No safe dosage ardor has been established. No recommendations can actually be made regarding the safety of methylene blue administration if or when antidepressant medications are stopped. Methylene blue toxicity has existed at a wide range of doses [36]. Doses related toxicity of MB is listed in Table 1.2A and B [34].

Animal	Toxic doses	Manifestation
studies	(mg/Kg)	
Rat	5-50	Reduced MAC isoflurane, neuronal
		apoptosis, reduced MAC isoflurane
	1250 (LD50)	
Mouse	3500	
Sheep	40	
Dog	10-20	Pulmonary hypertension, renal blood
		flow,decreased SVR

 Table 1.2A: Dose-related toxicity of MB dye

Table 1.2D: Dose-related toxicity of MIB dy	Table	1.2B:	Dose-related	toxicity	of MB	dve
---	-------	--------------	---------------------	----------	-------	-----

Human	Dose	Toxic manifestations
studies	(mg/kg)	
	2-4	Skin desquamation in infants, Hemolytic
		anemia
	7	Fever ,nausea, hemolysis, vomiting, , chest
		pain, abdominal pain
	7.5	Confusion, hyperpyrexia
	20	Hypotension
	80	Bluish discoloration of skin (similar to
		cyanosis)

1.4.3 Uses of methylene blue

1.4.3.1 Medical uses of methylene blue

The main use of MB in toxicology is in the therapy of methemoglobinemia at a dose of 1 to 2 mg/Kg intravenously. Methylene blue has many distinguished utilizations in clinical medicine. It is used in the treatment of herpes simplex, it is also acts as bacteriostatic genitourinary antiseptic, and in combination with vitamin C for the management of chronic urolithiasis. Methylene blue also has a major rule in increasing vascular tone and myocardial function in patients with septic or anaphylactic shock [37]. Its considerable practical importance is also the administration of MB for the prevention and treatment of ifosfamid-induced neurotoxicity in cancer patients [38]. Methylene blue is a generally safe drug with dose – related hemolytic effects [37].

1.4.3.2 Industrial uses of methylene blue

Many dyes including MB are used in different industries, including testile, rubber, plastics, paper, leather, food and pharmaceutical industries [28][29].Various cationic dyes such as methylene blue are used in wool dyeing and paint production. Methylene blue is also used in surgery, microbiology and sensitizer in photo-oxidation of organic pollutants [39].

1.5 Research Objectives

1.5.1 General Objectives

- 1. Extract cellulose from OISW (Jeft)
- 2. Convert the extracted cellulose to nanocrystalline cellulose NCs
- 3. Prepare magnetic nanocrystallinecellulose (MNCs) from NCs.
- 4. Develop a method for removal of MB from waste water using the cellulose, NCs and MNCs.

1.5.2 Specific Objectives

1. Make a comparison between the efficiencies of Cs, NCs and MNCs toward adsorption of methleyene blue from an aqueous solution.

2. Study the effect of pH, temperature, amount of adsorbent, concentration and contact time on the adsorption of methleyene blue dye.

Chapter Two

2.1 Back ground

2.1.1 Adsorption Definition, Features and Types

Adsorption is an adhesion of the adsorbate on the surface of the adsorbent. The ion, atom or molecule which adsorbs on the pores of the surface is called the adsorbate, while the substance on which adsorption occurs is called the adsorbent, Thes surface accumulation of adsorbate on adsorbent is called adsorption. Adsorbate may be liquid, gas, or dissolved solids. While adsorbent may be a solid or a liquid material [40].

Adsorption can also defined as a mass transfer process, that include the transfer of a substance from the liquid phase to the solid surface, and then bounding by physical and/or chemical interactions. Adsorption capacity and surface reactivity increase as surface area increases [41].

Adsorption is a very important process. It has practical applications in technology, biology, industry and environmental protection. The efficiency of this purification method depends on many factors such as the nature of adsorbent and adsorbate, the surface area of the adsorbent and its activation. And also depends on some experimental conditions including pressure, temperature and pH value [42].

Adsorption with comparison to other traditional treatment techniques is very effective and useful. It is also suitable purification method for removing industrial effluents; this is due to its advantages which include low cost, high selectivity, simplicity, safety with respect to hazardous samples, possibility of adsorbent recovery, ability to combine with different modern detection techniques, high efficiency in minimization of many chemical and biological wastes and successful operation over a wide range of pH values and temperatures [43] [44].

This adsorption process involves the formation of new intermolecular attraction forces between the adsorbate and the adsorbent [45]. The exact nature of the bonding depends on the type of functional groups present on adsorbate and adsorbent, the adsorption process itself is mostly classified as Physiosorption (characteristic of van der Waals forces) or chemisorption(characteristic of covalent bonding). It also occur as a result of electrostatic attraction [42].

Physiosorption generally takes place at low temperatures and can be easily reversed by decreasing the pressure or by heating [43], while chemisorption is irreversible, specific and taking place at high temperatures [44].

2.2 Equilibrium Isotherm Models

Adsorption phenomenon is generally described by an invaluable non-linear curve known as adsorption isotherm. Which represents the amount of the adsorbate on the adsorbent as a function of its concentration (if liquid) or pressure (if gas) at constant temperature and pH [45] [46]. The

mathematical correlation that drawn by the adsorption modeling analysis is important for applicable practice and operational design of large scale adsorption systems [47].

Adsorption equilibrium is confirmed when an adsorbate become in contact with the adsorbent for certain period of time, and in the presence of adsorbate concentration in the bulk solution that allows a dynamic equilibrium with the interface concentration [48].

Analysis of the isotherm data is important to develop an equation that exactly explain the observed results. The most known isotherms which are applied in liquid /solid systems are the theoretical equilibrium isotherm models, including Langmuir and Freundlich isotherms [49].

2.2.1 Langmuir Adsorption Isotherm

After the formation of a monolayer adsorbate on the outer surface of the adsorbent, no more adsorption occurs[50], so it is called the ideal localized monolayer model; it was developed to represent chemisorption. Adsorption is limited to monolayer coverage, and so the adsorbed molecule cannot migrate across the surface or interact with neighboring molecules. Furthermore, the surface of the adsorbent is uniform, and so all the adsorption sites are energy equivalent [51].

The Langmuir equation relates the coverage of molecules on a solid surface to the concentration of a medium above the solid surface at a fixed temperature. This equation can be written as:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_{eK_{LC_e}}} \qquad (2.1)$$

Where:

 C_e = the equilibrium concentration of adsorbate (mg/L)

 $q_o = maximum$ monolayer coverage capacity (mg/g)

 K_L = Langmuir isotherm constant (L/mg).

 q_e is the amount of adsorbate per unit mass of adsorbent (mg/g) [52], and it can be calculated using the following relation:

$$q_e = (C_o - C_e) \frac{V}{m}$$
 (2.2)

Where:

 C_o is the initial concentration of the adsorbate (mg/L).

V is the volume of the solution (L).

m is the mass of the adsorbent (g).

 $(C_o - C_e)$ represents the adsorbed amount (ppm). A graph of (C_e/q_e) values versus C_e is used to find the Langmuir parameters. That are, $(1/K_LQ_o)$ as y-intercept and $(1/q_o)$ as slope [53].

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L which is given by the following equation :

$$R_L = \frac{1}{1 + K_{LC_0}}$$
(2.3)

Where:

 C_0 = initial concentration.

 K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the isotherm shape to be unfavorable if ($R_L > 1$) Linear if ($R_L = 1$), favorable if ($0 < R_L < 1$), or irreversible if ($R_L = 0$) [54].

2.2.2 Freundlich Adsorption Isotherm

This adsorption to surfaces supporting sites depends on different affinities or to heterogeneous surfaces. Freundlich isotherm supposes that stronger binding sites are occupied first, so; the binding strength reduces with increasing degree of site occupation. Related to this articulation, the adsorbed mass per mass of adsorbent can be represents this equation [55].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$
 (2.4)

Where:

 K_F is the Freundlich constant which indicates the adsorption capacity of the sorbent (mg/g).

n is the heterogeneity coefficient that gives an indication of the Favorable way

of the adsorption process (g/L)m if the value of 1/n is less than one then the adsorption is normal ,and if n is between one and 10, the sorption process is favorable [56].

A plot of Lnqe values versus LnCe is used to find Freundlich parameters. That are, LnK_F as y-intercept and (1/n) as a slope.

2.3 Adsorption Kinetic Models

The kinetic of adsorption is the process which represents the transportation of the adsorbate molecules from bulk solution to a boundary layer of the water surrounding of the adsorbent particle by molecular diffusion through the stationary layer of water. So, the adsorbate particles are transported into an available site. And formation of an adsorption bond will occur between the adsorbate and the adsorbent [57] [11].

There are many adsorption kinetic models that describe adsorption kinetics and rate-limiting step. These models give information about the adsorption system behavior and determine whether the adsorption process is a chemical or a physical one, and also which is the rate determining step. These adsorption kinetic models include, external mass transfer model, pseudo first-order and pseudo second-order rate models, Adam–Bohart– Thomas relation, Weber and Morris sorption kinetics, first-order reversible reaction model, first-order equation of Bhattacharya and Venkobachar and Elovich's model [58] [59].
2.3.1 Pseudo First–Order Kinetics

This kinetic model is the first model developed to describe adsorption kinetics.

The rate equation for pseudo first-order kinetic model can be written as:

 $\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (2.5)$

Where:

 q_e and q_t are the amounts of adsorbate adsorbed per unit mass of adsorbent at equilibrium, and at time t respectively (mg/g).

 k_1 is the pseudo first-order rate constant for adsorption (min⁻¹).

A plot of $Ln(q_e-q_t)$ versus t should give a linear relationship that allows the computation of a first-order rate constants, k2 and qe[60].

2.3.2 Pseudo Second–Order Kinetics

This kinetic model assumes that the rate-determining step may be chemical adsorption which involve valence forces through sharing or exchange of electrons between the adsorbate and the adsorbent.

The final integrated equation for this kinetic model is:

$$\frac{t}{q_t} = \frac{1}{K_{2q_e^2}} = \frac{t}{q_e}$$
(2.6)

Where;

 k_2 is the pseudo second-order rate constant for adsorption (g.mg⁻¹.min¹).

The plot of t/q_t versus t will give a straight line for the pseudo second order adsorption with $(1/K_2 q_e^2)$ as y-intercept and $(1/q_e)$ as the slope of the graph [61].

2.3.3 Intra-Particle Diffusion Kinetic Model

This model is established on the theory suggested by Weber and Morris. The final equation of this adsorption kinetic model can be written as:

$$q_t = K_{id} t^{1/2} + Z$$
 (2.7)

Where;

 K_{id} is the Intra-Particle diffusion rate constant (mg/g.min^{1/2}).

Z is a constant that gives an information about the thickness of the boundary layer (mg/g) [62].

A plot of q_t versus $t^{1/2}$ will give a linear relationship for intra-particle diffusion kinetic model with constant Z as a y-intercept and K_{id} as a slope.

2.4 Adsorption Thermodynamics

Adsorption thermodynamics of a process are necessary to determine whether the process is favorable or not. The adsorption characteristics of a material can be expressed in terms of thermodynamic parameters such as the change in Gibbs free energy (ΔG), enthalpy change (ΔH) and the change in entropy (Δ S). Where; Δ G and Δ H are in (J) and the unit of Δ S is (J/K).

The general equation which connects between the adsorption parameters can be written as: [63]

 $\Delta G = \Delta H - T \Delta S \qquad (2.8)$

Where:

T is the absolute temperature (K).

The change in Gibbs free energy can be also calculated by the following

equation:

 $\Delta G = -R T \ln K_d \tag{2.9}$

Where:

R is the universal gas constant that equals 8.314 J.mol^{-1} .K⁻¹.

 K_d is the thermodynamic equilibrium constant that equals (q_e/C_e) with a unit of mol or (L/g).

The combination of the previous two equations will give the following equation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (2.10)$$

The plot of LnK_d versus (1/T) will give a straight line with (- Δ H/R) as slope and (Δ S/R) as y-intercept. The resulting graph is known as Van't Hoff plot.

2.5 Adsorption as an effective method for removing dyes from wastewater

Toxic Dyes can be removed from waste water using several treatment methods, Which can be classified as chemical, physical, and biological methods. According to the different methods, adsorption is an effective separation process for many applications. Economically it is suitable for removal of both organic and inorganic pollutents from waste water [64].

Adsorption is a common technique used to remove dyes from aqueous solution, this is because of many advantages of this method such as low in cost, simple, and environmentally friendly [65].

A synthetic dye in waste water cannot efficiently decolorized by traditional methods. This is due to the high cost and disposal problems for treating dye waste water at large scale industries, Adsorption is a well-Known equilibrium separation process for water decontamination applications. It is the best technique for water reuse because of flexibility, simplicity of design, initial cost and ease of operation [66].

Chapter Three Experimental Part

3.1 Chemicals and Materials

All reagents were purchased from Aldrich Chemical Company, and used without any further purification unless otherwise specified. All chemicals like HCL, H_2SO_4 , NH_4OH , $FeCl_3.6H_2O$, $FeSO_4.7H_2O$ and methylene blue were of analytical grade. Methylene blue dye was used as adsorbate. Distilled water was used to prepare stock solutions like HNO₃ (0.1M) and KOH (0.1M) for pH adjustment were used.

3.2 Instrumentations

The required instrumentations for this research include the following: shaking water bath (DaihanLabtech, 20 to 250 rpm Digital Speed Control), pH meter (model: 3510, JENWAY), glassware, thermometer, AAS instrument (model ZicE-3000 SERIES Serial number c113500021 designed in UK AA Spectrometer), UV spectrometry (model: UV-1601, SHIMADZU), IR Spectrometer (Nicolet iS5, iD3 ATR, Thermo Scientific), TGA (Q50 V20.10 Build 36 instrument at a heating rate of 10° C/min and in N₂ gaseous atmosphere).

3.3. Preparation of adsorbents(Cs, NCs and MNCs)

3.3.1 Cellulose nanocrystalline

Cellulose powder was extracted from OISW using a process developed previously at our laboratory [1]. Extracted cellulose was converted to cellulose nanocrystalline as follows: cellulose (5.0 gram) was added to a beaker (500 mL) containing distilled water (180 mL) and stirred magnetically for 30 min. To the beaker content was added 20 g of concentrated H_2SO_4 to produce a solution with 10 wt% of sulfuric acid. The mixture was stirred at 60 °C for 2 hr. The hot mixture was diluted with ice cold distilled water. The colloidal suspension was centrifuged at 10,000 rpm and decanted. To the residue was added a 100 mL, mixed then centrifuged and decanted. The process was repeated three times to remove the hydrolysis product and sulfuric acid completely.

3.3.2 Magnetic cellulose nanocomposite

Extracted cellulose nanocrystalline was then converted to magnetic cellulose. Cellulose nanocrystalline (1.5 g) was added to 200 mL distilled water in a 500 mL beaker and stirred for 20 min. Then FeCl₃.6H₂O (1.49 g) and FeSO₄.7H₂O (0.75 g) were added to CNC in the beaker. The mixture was heated at 60 °C for 20 min. The manetic cellulose was precipitated by adding 8.0 M ammonium hydroxide dropwise with stirring. The addition was continued until the pH of the solution reached about 10. At this pH the color of the precipitate was changed from orange to black.

The precipitate was left to cool overnight and magnetic nanocellulose was separated magnetically. The precipitate was washed several times with distilled water, ethanol and left to dry at room temperature **[67, 68]**.

3.3.3 Characterization of adsorbents (Cs, NCs and MNCs)

A SEM study was carried out to provide information about the physical morphology of Cs, NCs and MNCs. The desired matrix was examined by FT-IR spectroscopy. Thermal stability of Cs, NCs and MNCs have been determined by thermogravimetric analysis (TGA).

3.4 Statistical Analysis

In this study, all analysis experiments were conducted in duplicate. The mean was taken for each duplicate. The coefficient of variance was mostly less than 1%. The error range was determined using a certainty interval of 95% which was used for data analysis using Excel Microsoft software. The collected data were analyzed using t-test. All variations were considered statistically when p < 0.05 for the analysis of t-test.

3.5 Preparation of methylene blue solutions

A stock solution of MB with a concentration of 1000 mg/L MBwas prepared by dissolving 0.5 g of MB in 500 mL water in a volumetric flask. A set of solutions of MB with various concentrations: 0.5 to 200 mg/L were prepared by dilution.

3.6 Calibration Curve

The absorbenc of the prepared solutions in section 3.5 were measured by UV-visible Spectrophotometer (UV-1601 SHIMADZU) at 640 nm wavelength. The absorbenc was plotted versus concentration, a Linear calibration curve between absorbance and concentration was obtained with MB concentrations in the range 0.5-50 mg/L ($R^2 = 0.9852$) as shown in Figure 3.1(a) and in the range 50-200 mg/L ($R^2 = 0.999$) as shown in Figure 3.1(b).



Figure 3.1(a): Linear calibration curve between absorbance and concentration for MB concentrations in the range 0.5- 50 mg/L



Figure 3.1 (b): Linear calibration curve between absorbance and concentration for MB concentrations in the range 50-200 mg/L

3.7 Adsorption Experiments

The experimental parts were performed using different concentrations of methylene blue in 100 mL solutions using different weight of cellulose adsorbent samples depending on the experiment. The pH of solutions was adjusted using 0.1M HNO₃ and 0.1M KOH solutions. All the measurement of adsorption were performed at 640 nm using UV–Vis spectrophotometer (Perkin Elmer, Model 550S with a 1 cm path length) at different temperatures depending on the experiment like effect of contact time, pH, dose, adsorption isotherm, kinetics or thermodynamics. Before the adsorbate concentration was measured in solution, a calibration curve was made using a range from zero to 300 mg/L. All of the concentrations were made from a stock solution of 1000 mg/L by dilution in double distilled water. The removal ratio percentage (E %) is defined as the ratio of difference in dye concentration before and after adsorption (C_0 - C_f) to the initial concentration of dye in the aqueous solution (C_0) and was calculated using Eq. (3.1):

$$E(\%) = \frac{c_{0-c_f}}{c_0} * 100\%$$
(3.1)

Where C_0 is the initial concentration of MB and C_{f} is the final concentration. All of the experiments were done twice and the means were taken unless there was a difference more than 5% between the readings then a third measurement was taken.

For the experiment of effect of contact time which was carried at 298K and different concentrations (5, 10, 20 mg/L) and time range from 5 to 250 min the adsorption capacity was calculated using Eq. (3.2):

$$q_t = \frac{C_0 - C_t}{m} X V$$
(3.2)

Where qt (mg/g) the adsorbed amount of MB at time t. C_t was MB concentration at time t, m is the mass of cellulose (g) and V is the volume of solution in L.

In working on this study a replicate experiments were conducted on the whole experimental part. The mean was taken for each duplicate. In our study the coefficient of variance was mostly less than 1%. We determined the margin of error using a confidence interval of 95% was used for the data of experiment using ExcelMicrosoft software and the data were

analyzed using t – test. All differences were considered statistically when p < 0.05 for the analysis of t- test.

3.7.1 Optimization of contact time and initial concentration of MB dye

The adsorption of MB dye on the adsorbent was studied as a function of shaking time at 25°C.Asample of 50 mL of dye (5, 10, 20 mg/L) solution at pH 10 was and added to 100 mL a beaker with 0.1 g of adsorbent. At different time intervals the supernatant was carefully removed by a thin plastic dropper and absorbance was measured by UV-visible Spectrophotometer at wavelength 664 nm.

3.7.2 Effect of pH

Effect of initial pH on adsorption was investigated in the pH range 2.0-12. The pH was adjusted using roughly concentrations of 0.1M HNO₃ and 0.1M KOH. 0. 1 g adsorbent samples were added to 50 mL of MB dye solutions with concentration 10 mg/L. The mixtures were placed in Shaking Water Bath at constant temperature (35°C) for 55 min. At the end of time intervals, adsorbent was removed by filtration in the case of Cs and NCs or by external magnet in the case of MNCs and supernatant was analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 640 nm wavelength.

3.7.3 Effect of adsorbent dose

To study the effect of dose of adsorbent on the removal of MB on the cellulose surfaces different experiment were done using different dose of cellulose substrates ranging between 5–300 mg. This experiment was studied using 10 mg/L solution of MB and pH of 10 at 25 °C. The samples were placed in Shaking Water Bath at constant temperature (25°C) for 50 min. The absorbance of supernatant was measured by UV-visible for the residual concentration of MB dye.

3.7.4 Effect of temperature

The effect of temperature on adsorption was also evalauted, 0.1 g adsorbent samples were added to 50 mL of methylene blue dye solutions with concentration 10 mg/L at pH 10. Each mixture was shaked in a water bath (DaihanLabtech) at desired temperature (the range was 15-55°C) for 50 min. At the end of time intervals, adsorbent was removed by filtration in the case of Cs and NCs or by external magnet in the case of MNCs and supernatant was analyzed by UV-visible spectrophotometer (UV-1601, SHIMADZU) for the residual concentration of MB, at 664 nm wavelength.

3.8 Thermodynamics and Kinetics of Adsorption

The removal of methylene blue dye was studied by adsorption technique using the prepared adsorbent (Cs, NCs and MNCs). The batch technique was adopted under the optimize condition of dose of adsorbent, contact time, initial concentration of MB, temperature and pH. By using UV-spectrophotometer, concentration of dye was measured before and after adsorption. Langmuir, Freundlich adsorption isotherm equations were studied. The values of their corresponding parameters were determined. Thermodynamic parameters like free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the systems were calculated by using Van't Hoff's plot. The values of % removal and K_d for dye systems were calculated at different temperatures ranging (15 – 55°C).

Adsorbent (0.1 g) was added to 50 mL of (5,10,20 mg/L) of MB dye solution at pH 10. The mixture was placed in Shaking Water Bath at constant temperature (25°C). The adsorption rate was monitored by studying the contact time up to 6 h and compared to theoretical models. Pseudo first order and pseudo second order kinetic models were tested in this study where the experimental data obtained for various contact time were used. Pseudo first order and pseudo second order kinetic model parameters (K, Q_e and R^2) for MB dye adsorption on Cs, NCs and MNCs were determined. The values of the calculated and experimental Q_e were compared.

Chapter Four Results and Discussion

4.1 Cs, NCs and MNCs Characterization

4.1.1 SEM Analysis of the CS:

Scanning electronic microscope analysis was performed on OISW. Images were collected at various magnifications are shown in Fig. 4.1. The image exposes the existence of two morphology structures in OISW the main one is the spongy which related to the olive pith and the other one which is the hard part related to the seeds. For this reason, the steps of pulping and bleaching used in this works are a moderate version to those used in the timber industry.



Figure 4.1: SEM Image of OISW at a) 250x. b) 500 x. c) 1000 x.

The x-ray analysis of OISW detects the existence of some metals as shown in Fig. 4.2. The metals are: Ca, K, Cu. Au is existed due to the sample coating which is performed in sample preparation for SEM.



Figure 4.2: X-Ray Spectra of OISW

4.1.2 FT-IR Characterization

FT-IR of cellulose is shown in Fig.4.3. The spectrum shows a broad bandat 3293.09 cm⁻¹ which corresponds to the OH-stretching vibration. The peak at 2895.17 cm⁻¹ corresponds to the C–H stretching vibration, the band at 1427.05 cm⁻¹ corresponds to the CH₂ bending vibration, the band at 1314.38 cm⁻¹ corresponds to the C-O,C-H stretching, the band at 1159.62 cm⁻¹ corresponds to the O-C-O,C-O stretching.



Figure 4.3: FT-IR of Cellulose Extracted from OISW

4.1.3 Analysis cellulose substrates by TEM and Variable Scanning Magnetometry (VSM).

The TEM and VSM of nanocellulose and the magnetic particles of Fe_3O_4 are shown in Fig. 4.4. From Fig. 4.4a shows a good distribution of the magnetic particles on thenanocellulosestracuture and by measurement we can see the spherical size of those particles using a two-parameter fit of magnetization and the diameters are between 15 -20 nm. Fig. 4.4b represents the magnetization of both Fe_3O_4 and MNCs– Fe_3O_4 as a function of applied magnetics field at 298K. In both samples the hysteresis loops were not observed which means they are super-paramagnetic particles. The saturation magnetization for both Fe_3O_4 and $MNCS - Fe_3O_4$ were 44.6 and 21.4 emu/g, respectively. The saturation magnetization for MNCs – Fe_3O_4 were 44.6 mB.



Figure 4.4 (a): TEM and (b) Variable Scanning Magnetometry (VSM).

4.1.4 TGA Analysis and Thermal Stability

The TGA curves are shown in Fig. 4.5. (Fig.4.4b and 4.4c) we can see that both cellulose and nanocellulose showed one sharp stage degradation at 380 °C for the cellulose and at 350 °C for the nanocellulose, respectively. The magnetic nanocellulose(Fig. 4.4a) showed three phases of thermal degradation: I) 110 -400 °C. II) 400 – 600 °C. III) 650 -850 °C. For both cellulose and nanocellulose 80% and 85% weight loss were observed due to degradation and decomposition at temperature range 110-400 °C . For the magnetic nanocellulose most of the steps came from the cleavage of MNCs to carbon residues such as CO_2 and CO. After 650 ° C just 7% of the weight loss came from the oxidation of char [68].



Figure 4.5: Thermo gravimetric curves of (a) MNCs. (b) Cs. (C) NCs.

4.2 Investigation of adsorption parameters

4.2.1 Effect of contact time and MB dye concentration

The amount of methylene blue adsorbed (q_t) at different concentrations (5, 10, 20 mg/L) and different contact times(5 -250 min) were studied, results are shown in Fig 4.6. The adsorption of MB on the cellulose samples were very fast in the first 5 to 10 min and it was faster in both the nanocellules and magnetic nanocellulose and reached more than 73, 79%, respectively.

This was attributed to the available sites on the surfaces of cellulose substrates and due to the small activation energies which has been calculated in the section of thermodynamics. The slow subsequent step (25 -150 min) was due to the rearrangement of methylene blue ions to find available adsorption sites on the cellulose. Also, from the figure we can see the equilibrium adsorption capacity increased from 22 to70 mg/g for MNc as we increased the concentration from 5 to 20 mg/L. So, when we increased the initial concentration, the mass transfer driving force will accelerate the MB ions diffusion from the bulk solution to cellulose surfaces and this will increase the equilibrium adsorption capacity [69]. In our study we used 50 min as a contact time when we studied pH, dose effect etc.



Figure 4.6: Effect of contact time and MB dye concentration to determine the time of maximum adsorption of MB dye. (Temperature= 25° C, pH= 10, concentration Of MB dye= (a) 5 mg/L, (b)10 mg/L, (c) 20 mg/L respectively sontitue Volume= 50 mL, adsorbent dose= 0.1 g).

4.2.2 Effect of pH on MB dye adsorption

The studied effect of pH on the adsorption of MB on the cellulose surface showed dramatic effect. That effect was studied over arrange of 2.0 - 12. The results are shown in Fig.4.7. All of the cellulose substrates showed very high removal of MB at high pH (12). The percentage of removal reached almost 100% for the MNCs at pH of 12. The active sites of cellulose compounds were almost empty at the beginning and by the removal of MB starts filling those sites. Also, it depends on the chemistry of solutes in the solution. At higher pH the active sites of cellulose carries negatively charge and the MB are cations which cause an electrostatic force and this will attract most of MB cations from the solution [70]. There also may be another type of adsorption, e.g., ion exchange [71].

To evaluate the effect of pH on the adsorption capacity of the Cs, NCs and MNCs, the adsorption experiments were carried out in solutions having different pH values. Figure 4.4 shows the effect of the pH value on the uptake of MB dye from its water by Cs, NCs and MNCs. The results show an increase of MB dye uptake as the pH value is increased. The uptake reached its maximum at pH 12. Low uptake capacity occurs at lower pH values, this is probably due to protonation of alcohol oxygen atoms on Cs. At low pH, the retention of MB dye by the Cs, NCs and MNCs is not significant since the cellulose is entirely in its protonated form.



Figure 4.7: Effect of pH on MB dye adsorption. ($C_0 = 10$ ppm, T=25^oC, time= 50 min., adsorbent dose= 0.1 g, solution Volume= 50 mL).

4.2.3 Effect of amount of adsorbent

To study the effect of dose of adsorbent on the removal of MB on the cellulose surfaces different experiment were done using different dose of cellulose substrates ranging between 5 – 300 mg as shown in Fig.4.8. This experiment was studied using 10 mg/L solution of MB and pH of 10 at 25 °C. From the figure we can see the adsorption efficiency increases as the dose increased. This can be explained by the available of vacant sites and the unsaturation of adsorption sites. Also, at 150 the three samples (Cs, NCs and MNCs) showed the same percentage of removal which means the vacant sites are almost saturated with MB ions. For this reason we chose 100 mg of adsorbent dose.

The removal efficiency (% Removal) was calculated using the equation [31, 62]:

Removal efficiency(%) =
$$\left[\frac{(C_o - C_f)}{C_o}\right] \times 100$$
 (4.1)

Where, C_o is the concentration of methylene blue in the sample solution before treatment and C_e is the concentration of methylene blue in the sample solution after treatment. Removal efficiency also can be calculated using absorbance of methylene blue in the sample solution before treatment A_o and absorbance of methylene blue in the sample solution after treatment A_f instead of C_o and C_f respectively.



Figure 4.8: Effect of amount of adsorbent on the removal of MB dye. (Temperature= 25° C, time= 50 min., pH= 10, concentration Of MB dye= 10 mg/L, solution Volume= 50 mL).

4.2.4 Effect of temperature on MB dye adsorption

The effect of temperature on the uptake of MB dye by (Cs, NCs and MNCs) was studied at (15-55°C) as shown in Figure 4.9. This figure shows that in general the % removal of MB dye increases with increasing the

temperature to some extent. Increasing the temperature above the room temperature has slight influence on increasing the adsorption capacity of the new modified surface. The maximum adsorption was achieved at 55 $^{\circ}$ C. This indicates that the adsorption of MB dye on (Cs,NCs and MNCs) follows endothermic process.



Figure 4.9: Effect of temperature on MB dye adsorption. ($C_0 = 10$ ppm, time= 50 min., adsorbent dose= 0.1 g, solution Volume = 50 mL).

4.3 Adsorption isotherm of MB dye

An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to find the maximum adsorption capacity [53].To have an idea about the adsorption equilibrium between the concentration of MB in liquid phase and the cellulose particles (Cs, NCs and MNCs); two adsorption isotherm models were used in our study ,the Langmuir and Freundlich models.

4.3.1 Langmuir Adsorption Isotherm

Langmuir isotherm based on the kinetic principle and it describes the monolayer surface adsorption on the solid with definite localized sites that are energetically identical [30]. It assumes that the adsorbate molecules can only accumulate on one localized site without lateral interaction between the adsorbed molecules, even on the nearby sites. Also, it assumes that no further adsorption can occurs after equilibrium. Based upon these assumptions, Langmuir represented the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max}K_L} \tag{4.2}$$

Where:

 C_e : the equilibrium concentration of adsorbate (MB) (mg/L)

 q_e : the amount of MB dye adsorbed per unit mass of adsorbent(Cs,NCs and MNCs) at equilibrium (mg/g)

 q_{max} : is the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g)

 K_L : the Langmuir isotherm constant related to the adsorption energy (L/mg).

The values of q_m and K_L were find from the slope and intercept of the Langmuir plot of C_e/q_e versus C_e . From Langmuir plots which is shown in Figure 4.11 amount adsorbed for monolayer formation (q_{max}), Langmuir

adsorption-desorption equilibrium constant (K_L) and regression constant (R^2) were determined and values are shown in Table 4.1(a,b and c).

From Langmuir isotherm we can also predict if the adsorption is favorable or not using the dimensionless constant separation factor in Eq. 4.3

$$R_L = \frac{1}{1 + K_{LC_0}} \tag{4.3}$$

Where K_L is the Langmuir constant and C_o is the initial adsorbate concentration. If R_L is greater than 1 it means the adsorption is not favorable. But if 0 < RL < 1 it means the adsorption is favorable and of course if $R_L = 1$ means linear adsorption.



Figure 4.10: Langmuir plot for MB dye adsorption on (Cs,NCs and MNCs). Temperature= $(a)15^{\circ}$ C, (b) 30° C,(c) 45° C, (d) 55° C, pH= 10, time= 50 min., solution Volume= 50 mL, adsorbent dose= 0.1 g.

Model	Parameter	Temperature(°C)						
		15	30	45	55			
Langmuir	$q_{max}(mg/g)$	114.9	161.3	163.9	166.6			
isotherm	$K_L(L/mg)$	0.180	0.230	0.270	0.320			
(Cs)	R _L	0.052	0.041	0.035	0.030			
	\mathbb{R}^2	0.983	0.984	0.980	0.980			

Table 4.1 (a): Langmuir isotherm model parameters and correlation coefficient for adsorption of MB dye on Cs at 15, 30, 45 and 55° C.

Table 4.1 (b): Langmuir isotherm model parameters and corre

Model	Parameter	Temperature(C°)							
		15	30	45	55				
Langmuir	q _{max} (mg/g)	126.6	158.73	163.90	175.4				
isotherm	$K_L(L/mg)$	0.280	0.320	0.360	0.430				
(NCs)	R _L	0.034	0.030	0.027	0.022				
	\mathbb{R}^2	0.988	0.991	0.992	0.981				

coefficient for adsorption of MB	dye on I	NCs at 15,	30, 45	and 55	5 C°.

Table 4.1 (c): Lang	muir isotherm	model parameter	s and correlation
coefficient for adsor	ption of MB dy	e on MNCs at 15,	30, 45 and 55 C°.

Model	Parameter	Temperature(C°)						
		15	30	45	55			
Langmuir	$q_{max}(mg/g)$	144.92	166.67	185.18	196			
(MNCs)	$K_L(L/mg)$	0.410	0.450	0.490	0.570			
(1011(05)	R _L	0.023	0.021	0.020	0.017			
	R^2	0.994	0.995	0.990	0.993			

4.3.2 Freundlich model Isotherm

Freundlich model includes interaction between the adsorbed molecules and represents the non- ideal adsorption that includes heterogeneous surface energy system and reported in Eq. 4.4

$$q_e = K_F C_e^{1/n} \tag{4.4}$$

The linear form of this equation can be written as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$
 (4.5)

Where K_F (L /mg) is the Freundlich constant, 1/n is the adsorption intensity, If value of 1/n is below one it indicates a normal adsorption and If n lies between one and ten, this indicates a favorable sorption process [51].

To determine the constants K_F and n, the linear form of the equation may be used to produce a graph of $ln(q_e)$ against $ln(C_e)$ as shown in Figure 4.10:

If value of 1/n is below one it indicates a normal adsorption



Figure 4.11: Freundlichplot for MB dye adsorption on (Cs,NCs and MNCs). Temperature= $(a)15^{\circ}C$, (b) $30^{\circ}C$,(c) $45^{\circ}C$, (d) $55^{\circ}C$, pH= 10, time= 50 min., solution Volume= 50 mL, adsorbent dose= 0.1 g.

Freundlich constants K_F , n and regression constant (R^2) were determined and values are shown in Table 4.2 (a,b and c):

coefficient for adsorption of MB dye on Cs at 15, 30, 45 and 55 C° .

Freundlich	1/n	0.446	0.419	0.376	0.339
isotherm	$K_F(L/mg)$	10.8	16.76	21.12	26.23
(Cs)	R^2	0.9985	0.991	0.9828	0.9724

Tuble fill (b) Treananch ibotherin model parameters and correlation

coefficient for adsorption of MB dye on NCs at 15, 30, 45 and 55 $^\circ C.$

Freundlich	1/n	0.416	0.366	0.346	0.340
isotherm	$K_F(L/mg)$	14.15	22.51	25.8	29.22
(NCs)	R^2	0.9964	0.986	0.9901	0.9927

Table 4.2	(c):	Freundlich	isotherm	model	parameters	and	correlation
-----------	------	------------	----------	-------	------------	-----	-------------

coefficient for adsorption of MB dye on MNCs at 15, 30, 45 and 55 $^\circ C.$

Freundlich	1/n	0.390	0.3419	0.3516	0.334
isotherm	$K_F(L/mg)$	18.54	28.78	30.26	35.16
(MNCs)	R^2	0.9852	0.959	0.9815	0.9877

Table 4.3 ((a): Para	meters a	and co	rrela	tion	coe	ffici	ient	t of	La	ngn	uir,
Freundlich	and for	adsorpti	ion of	MB	dye	on	Cs	at	15,	30,	45	and
55 °C.												

Model	Parameter	Temperature(°C)			
		15	30	45	55
Langmuir	q _{max} (mg/g)	114.9	161.3	163.9	166.6
isotherm	$K_L(L/mg)$	0.180	0.230	0.270	0.320
(Cs)	R _L	0.052	0.041	0.035	0.030
	\mathbb{R}^2	0.983	0.984	0.980	0.980
Freundlich	1/n	0.446	0.419	0.376	0.339
isotherm	$K_F(L/mg)$	10.82	16.76	21.12	26.23
(Cs)	R^2	0.968	0.961	0.962	0.962

Table 4.3 (b): Parameters and correlation control	efficient of	Langmuir,
Freundlich and for adsorption of MB dye on	NCs at 15,	30, 45 and
55°C.		

Model	Parameter	Temperature(°C)			
		15	30	45	55
Langmuir	q _{max} (mg/g)	126.6	158.73	163.90	175.4
isotherm	$K_L(L/mg)$	0.280	0.320	0.360	0.430
(NCs)	R _L	0.034	0.030	0.027	0.022
	R^2	0.988	0.991	0.992	0.981
Freundlich	1/n	0.41	0.36	0.34	0.34
isotherm	$K_F(L/mg)$	14.15	22.51	25.8	29.22
(NCs)	\mathbb{R}^2	0.986	0.986	0.990	0.982

Table 4.3 (c): Parameters and correlation coefficient of Langmuir, Freundlich and for adsorption of MB dye on MNCs at 15, 30, 45 and 55 $^{\circ}$ C.

Model	Parameter	Temperature(°C)			
		15	30	45	55
Langmuir isotherm (MNCs)	q _{max} (mg/g)	144.92	166.67	185.18	196
	$K_L(L/mg)$	0.410	0.450	0.490	0.570
	R _L	0.023	0.021	0.020	0.017
	\mathbb{R}^2	0.994	0.995	0.990	0.993
Freundlich	1/n	0.390	0.3419	0.3516	0.334
isotherm	$K_F(L/mg)$	18.54	28.78	30.26	35.16
(MNCs)	R^2	0.9852	0.959	0.9815	0.9877

All fitting parameters using the equations are listed in Table 4. From the values of the correlation coefficients (> 0.99) and the separation factor R_L which was calculated for all the cellulose substrates (1.74 x 10⁻⁴ – 2.2 x 10⁻⁴) while the values of 1/n (0.39 – 0.446) which indicates high adsorption intensity, that the adsorption approach conformed to Langmuir isotherm model. This indicates that all the functional groups of MB are equally and homogeneously spread over the outer porous surfaces of all cellulose substrates. Another observation is that the magnetic nanocellulose (MNCs) has the highest sorption capacity among the others.

4.4 Adsorption kinetics of MB dye

The adsorption kinetics of MB on the cellulose samples were studied for each cellulose sample at four various concentrations of 50, 100, 150 and 200 mg/L. The dynamic experimental data were fitted for pseudo first order, pseudo second order and the intraparticle diffusion model using the following equations (4.6 - 4.8):

The pseudo-first ordere quation is :

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$
 (4.6)

The pseudo second-order equation is:

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{K_2 q_e^2}$$
(4.7)

The intraparticle diffusion modelequation is

$$q_t = K_{id}t^{1/2} + Z$$
 (4.8)

where q_e and q_t are adsorption capacities (mg/g) at equilibrium and at different time t (min), respectively, K_1 is the pseudo-first-order rate constant (min⁻¹), K_2 is the pseudo-second-order rate constant (g /mg.min). The K_{id} is the intraparticle diffusion rate constant (mg/ g.min^{1/2}) and Z

(mg/ g) which gives information about the thickness of boundary layer [72]. The values of all these parameters are shown in Tables (4.4 -4.5) and Figs (4.11-4.13). The value of K₁ was obtained by plotting $\ln(q_e - q_t)$ vs t (Fig. 4.11); while K₂ and the adsorption capacity q_e where calculated from the slope and the intercept of plotting t/qtvs t (Fig. 4.12). While K_{id} and Z obtained from plotting q_t vs t^{1/2} (Fig 4.13). When the experimental data were plotted for both the pseudo-first-order and the second-pseudo-order kinetics, the correlation coefficients (R²) for the pseudo second order was higher than the pseudo-first-order and it reached 1 in most of the cellulose samples. Other indication also came from the calculated q_e values for the pseudo-second-order were very close to the experimental qe values indicating that the adsorption process of MB on the surfaces of Cs, NCs and MNCs were followed and described by the pseudo-second-order see Table (4.5) and Fig. 4.12.

From Table(4.4) we can see the values for K_1 were decreasing with increasing the concentrations of MB which can be explained by the fact that the number of vacant and easy accessible sites were reduced while the concentration of MB increased. This will take a lot of time for the equilibrium to be achieved and this will reduce the values for the rate constant. This phenomenon was also observed for the pseudo-second-order.



Figure 4.12: Pseudo first order sorption kinetics of MB dye on (a) Cs, (b) NCs and (c) MNCs. (Temperature= 25° C, pH= 10, solution Volume= 50 mL, adsorbent dose= 0.2 g).



Figure 4.13: Pseudo second order adsorption kinetics of MB dye on (a) Cs, (b) NCs and (c) MNCs). (Temperature= 25° C, pH= 10, solution Volume= 50 mL, adsorbent dose= 0.1 g).

C ₀ (mg/L)	q_e (exp) (mg/g)	Pseudo-first -order model		
		$K_1 (min^{-1})$	$q_{cal}(mg/g)$	\mathbb{R}^2
50	32.27	0.0396	10.42	0.967
100	52.13	0.0347	8.93	0.972
150	63.15	0.073	4.17	0.951
200	93.14	0.041	11.24	0.973
C ₀ (mg/L)	q _e (exp) (mg/g)	Pseudo-s	econd -order	model
C ₀ (mg/L)	q_e (exp) (mg/g)	Pseudo-s K ₂ (g/mg.min))	econd -order $q_{cal}(mg/g)$	model R ²
C ₀ (mg/L)	q _e (exp) (mg/g) 32.27	Pseudo-s K_2 (g/mg.min)) $6.73 * 10^{-3}$	econd -order q _{cal} (mg/g) 34.48	model <u> </u>
C ₀ (mg/L) 50 100	q _e (exp) (mg/g) 32.27 52.15	Pseudo-s K_2 (g/mg.min)) $6.73 * 10^{-3}$ $3.17 * 10^{-3}$	econd -order $q_{cal}(mg/g)$ 34.48 50.32	model R ² 0.998 0.999
C ₀ (mg/L) 50 100 150	q _e (exp) (mg/g) 32.27 52.15 63.15	$\begin{tabular}{ c c c c c } \hline Pseudo-s \\ \hline K_2 (g/mg.min)) \\ \hline 6.73 * 10^{-3} \\ \hline 3.17 * 10^{-3} \\ \hline 1.8 * 10^{-2} \end{tabular}$	econd -order q _{cal} (mg/g) 34.48 50.32 61.17	model R ² 0.998 0.999 0.999

Table 4.4 (a): Pseudo first order and pseudo second order kinetic model parameters for MB dye adsorption on Cs at 25°C.

Table 4.4(b): Pseud	o first order and	l pseudo second	order kinetic model

parameters for MB dye adsorption NCs at 25°C.

C ₀ (mg/L)	q _e (exp)	Pseudo-first -order model			
	(mg/g)	$K_1 (min^{-1})$	q _{cal} (mg/g)	R^2	
50	36.5	0.0415	8.75	0.923	
100	57.2	0.0313	7.76	0.942	
150	70.5	0.028	5.69	0.943	
200	99.4	0.047	14.28	0.971	
C ₀ (mg/L)	q _e (exp)	Pseudo-second -order model			
	(mg/g)	K_2	$q_{cal}(mg/g)$	\mathbb{R}^2	
		(g/mg.min))			
50	36.5	$7.63 * 10^{-3}$	37.12	0.9997	
100	57.2	9.76 * 10 ⁻³	56.23	1	
150	70.5	$1.7 * 10^{-2}$	68.13	0.9999	
200	99.4	$8.4 * 10^{-3}$	98.57	1	

C ₀ (mg/L)	$q_e(exp)(mg/g)$	Pseudo-first -order model		
		$K_1 (min^{-1})$	q _{cal} (mg/g)	\mathbb{R}^2
50	38.7	0.045	11.58	0.9678
100	61.32	0.0313	11.94	0.979
150	73.5	0.028	9.40	0.979
200	102.65	0.047	12.76	0.954
C ₀ (mg/L)	$q_e(exp)(mg/g)$	Pseudo-second -order model		
		K_2 (g/mg.min))	$q_{cal}(mg/g)$	\mathbb{R}^2
50	38.7	$8.8 * 10^{-3}$	36.9	0.9998
100	61.3	9.6 * 10 ⁻³	60.87	1
150	73.5	$1.71 * 10^{-2}$	71.62	0.9999
200	102.65	$5.7 * 10^{-3}$	100.8	1

Table 4.4(c): Pseudo first order and pseudo second order kinetic model parameters for MB dye adsorption MNCs at 25°C.

We studied the mechanism of the diffusion behavior of the adsorbed MB on cellulose samples at different concentrations (50, 100, 150 and 200 mg/L) using the calculations and the theory proposed by Weber and Morris and the model they suggested using Eq. (4.8).

From plotting qtvs $t^{1/2}$ (Fig. 4.13) we can obtain the values of K_{id} and Z. The values are presented in Table (4.5). All plots were linear and did not passing through the origin indicating that the rate limiting process is not the only rate-limiting step. From Fig. 4.13 we see that for cellulose and the magnetic nanocellulose has first linear part which represents the adsorption on the exterior surface or sometimes represents the instant adsorption stages. The rest of stages were also linear and they were describing the gradual adsorption of MB and they showed the intraparticle diffusion rate limiting steps. The nanocellulose showed different behaviour and all of the plots were almost linear without two stages (Fig.4.13). [73]. Other
conclusion from the values of Z that they were increasing with the increase of concentration indicating augmentation in the density of outer layer and dwindling in external mass transfer [74] while the potential of internal mas transfer increased. Several studies showed the same behaviour we obtained [75].



Figure 4.14: The intraparticle diffusion of MB dye on (a) Cs, (b) NCs and (c) MNCs). (Temperature= 25° C, pH= 10, solution Volume= 50 mL, adsorbent dose= 0.1 g).

Table 4.5(a): Intraparticle diffusion for adsorption of different initialconcentrations of MB by Cs.

$C_0 (mg/L)$	Intraparticle diffusion model			
	K _{id} Z			
50	1.04	21.5		
100	0.0905	42.17		
150	0.67	57.91		
200	1.09	81.88		

Table 4.5(b): Intraparticle diffusion for adsorption of different initial

concentrations of MB by NCs.

$C_0 (mg/L)$	Intraparticle diffusion model		
	K _{id} Z		
50	1.03	4.55	
100	1	5.5	
150	0.9356	8.0392	
200	1	9.8	

Table 4.5(c): Intraparticle diffusion for adsorption of different initialconcentrations of MB by MNCs.

$C_0 (mg/L)$	Intraparticle diffusion model		
	K _{id}	Z	
50	1.047	27.58	
100	0.907	51.67	
150	0.67	66.8	
200	1.1	90.78	

Finally, the activation energy was calculated for the sorption process at 303 and 318 K, respectively using Eq.4.9.

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{Ea}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$
(4.9)

The idea is to see the impact of temperature on adsorption behavior of MB on Cs, NCs and MNCs. Activation energy (E_a) values for CS, NCs and

MNCs were 0.523, 0.11 and 0.437 kJ/mole, respectively. These values give an idea about the type of adsorption. In non-activated chemical sorption, the activation energy is close to zero and this is what we obtained [76]. Usually low activation energy values suggest that the energy barrier toward ion adsorption is always easier to overcome and the adsorption process takes place very fast.

4.5 Adsorption Thermodynamics

To understand the thermodynamics behaviour of the adsorption of MB dye using Cs, NCs and MNCs we obtain the thermodynamics parameters likeequilibrium rate constant (K) (L/g), the standard Gibbs free energy (ΔG^0) (J/mol), the standard entropy (ΔS^0) (J/mol.K), the standard enthalpy (ΔH^0) (J/mol) using different ranges of temperatures T(K) and the gas constant R (J/K.mol).

All of these parameters where calculated using van't Hoffs equation (Eq.4.10 and 4.11) [46].

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4.10}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{4.11}$$

From the graph of lnKd versus 1/T (Fig. 4.14) the slopes and intercept will give us the values of these parameters. The values are shown in Table (4.6). From this table the values of ΔS^0 and ΔH^0 are positive which denote

that the entropy increased at the solid/solution interface through the adsorption process, while ΔH^0 values were positive for the cellulose particles due to their endothermic nature [74]. Also, from the table we found all the Gibbs free energies (ΔG^0) for the cellulose were negative indicating spontaneous nature of the adsorption process at different temperatures.



Figure 4.15: Plot of lnK_d versus 1/T for MB dye adsorption on (Cs, NCs and MNCs). (Temperature= $15^{\circ}C$, pH= 10, time= 50 min., solution Volume= 20 mL, adsorbent dose= 0.1 g)

onto Cs (C $_{\circ}$ = 10 ppm, pH = 10 ,adsorbent dose = 100 mg , t = 50 min.

Temperature (K)	ΔG°	$\Delta \mathrm{H}^{\circ}$	ΔS° (J/K.mol)
	(KJ/mol)	(KJ/mol)	
288	-11.008	12.78	82.6
303	-12.24		
318	-13.48		
328	-14.312		

Table 4.6 (b): Thermodynamic parameters for the adsorption of MB onto NCs ($C_{\circ} = 10$ ppm, pH = 10, adsorbent dose = 100 mg , time = 50 min.

Temperature (K)	ΔG°	ΔH°	ΔS°
	(KJ/mol)	(KJ/mol)	(J/K.mol)
288	-11.82	7.92	68.55
303	-12.85		
318	-13.87		
328	-14.56		

Table 4.6(c) Thermodynamic parameters for the adsorption of MB onto MNCs ($C_{\circ} = 10$ ppm, pH = 10, adsorbent dose = 100 mg, time = 50 min.

Temperature (K)	ΔG°	ΔH°	ΔS°	
	(KJ/mol)	(KJ/mol)	(J/K.mol)	
288	-12.03	7.11	66.48	
303	-12.85			
318	14.63			
328	-14.78			

4.6 Recovery of MB dye and reusability of the adsorbent

This part of experiment was done to see how many times we can use the adsorbents and see their efficiencies. The experiment was repeated 4 times using the same adsorbent and the results are summarized in Table 4.7.

From the whole cycles we could not see any remarkable decrease in the sorption capacities. The desorption efficiency of MB was maintained almost the same thing in MNCs. From the magnetic field study (Fig. 4.3) it is not difficult to see that the used sorbent can be recycled easily from the waste water using magnetic field. This will enhance the industrial application to avoid secondary pollution during the wastewater treatment.

Table 4.7: Percentage of MB dye removal by the regenerated adsorbent compared with a fresh one at (Temperature= 25°C, pH= 10, solution Volume= 50 mL, adsorbent dose= 0.1 g, contact time= 50 min).

Recycling times	1	2	3	4
Cs (MB removal efficiencies, %)	98.8	98.6	98.5	98.2
NCS (MB removal efficiencies, %)	99.3	99.3	99.1	99.0
MNCs (MB removal efficiencies, %)	99.9	99.8	99.6	99.5

The results and the studies show that, the tendency of the three polymers, cellulose, NCs and the prepared MNCs for extracting methylene blue (MB) from water were evaluated. The base polymers cellulose and NCs showed acceptable tendency for methylene blue. However, MNCs showed excellent extraction efficiency toward MB. The thermodynamic studies revealed a spontaneous adsorption of MB by MNCs at different temperature. The spontaneous adsorption could be attributed to the electrostatic interaction and H-bonding between MNCs and MB. However the interaction between cellulose NCs and MB is limited to the H-bonding. A representative structure showing the interaction between MNCs and MB

is shown the following figure. The figure shows the aromatic ring and iron complextaion and the dipole-dipole interaction between the OH group and the iron.



Figure 4.16: A representative structure showing the interaction between MNCs and MB.

Conclusions

Olive Industry Solid Waste (OISW) consists of cellulose, hemicelluloses, lignin and extractives. The cellulosic part was extracted and purified then converted to cellulose nanocrystalline. Cellulose nanocrystalline as then converted to magnetic cellulose nanocrystalline by reacting it with solution of FeC₁₃.6H₂O and FeSO₄.7H₂O. Different techniques and instrumentations were used to analyze the cellulosic materials such as IR, SEM, TEM, XRD, TGA and others. In thermal analysis both cellulose and nanocellulose showed one sharp stage degradation at 380 °C and 350 °C for cellulose and CNC, respectively. The MCNC showed three stages of thermal degradation due to degradation and oxidation of iron. The ability of the cellulosic material to extract MB from waste water was evaluated. Results showed that cellulose has a moderate efficiency toward MB in the first 5 to 10 min relative to CNC and MCNC, for the latest the efficiency reached about 73 to 79%, respectively. The results all show that, the adsorption efficiency increases as the dosage increased which can be explained by the availability of vacant sites and the unsaturation of adsorption sites. The highest efficiency of the three cellulosic materials toward MB was shown pH 12. At this pH the percentage of removal of MB was quantitative 100% for the MCNC. The value of the correlation coefficients (> 0.99), the separation factor R_L (1.74 x 10⁻⁴ – 2.2 x 10⁻⁴) and the 1/n (0.39 – 0.446) indicate high adsorption intensity. The adsorption mechanism was predicted to follow Langmuir isotherm model. When the experimental data were plotted for both the pseudo-first-order and the second-pseudo-order kinetics, the correlation coefficients (\mathbb{R}^2) for the pseudo second order was higher than that for the pseudo-first-order and it reached 1 for all cellulosic samples. The calculated q_e values for the pseudo-second-order were very close to the experimental q_e values indicating that the adsorption process of MB on the surfaces of cellulose, CNC and MCNC were followed and described by the pseudo-second-order.

The ΔS^0 and ΔH^0 value for the adsorption process were positive indicating that the randomness at the solid/solution interface increased during adsorption process, while ΔH^0 values were positive for the cellulose particles due to their endothermic nature. The free energies for the cellulose were negative indicating spontaneous nature of the adsorption process at different temperatures.

67 **References**

[1] Hamed O., Jodeh S., Al-Hajj N., Abo-Obeid A., E. M. Hamed E.M.,
Fouad Y.,2015, *Cellulose acetate from biomass waste of olive industry*,
Journal of Wood Science, Vol.61(1): 45-52.

[2] Hamed O., Abo-Obeid A., Fouad Y., Hamed E.M., Al-Hajj N., 2012,
Cellulose Powder from Olive Industry Solid Waste, Bioresources, Vol. 7
(3) :4190-4201.

[3] Roger Rowell M., 1984 May. 5, The Chemistry of Solid Wood, Advances in Chemistry, Vol. 207: 48-126.

[4] Bradford A., Pollution Facts & Types of Pollution, 2015 Mar. 10, Live Science Contributor.

[5] Hamed BH, Din ATM, Ahmed AL, 2006, Adsorption of methyleneblue onto bamboo-based activated carbon kinetics and equilibrium studies.J Hazardous Mater, Vol. 7: 49.

[6] O'Mahony T, Guibal E, Tobin JM., 2002, Reactive dye biosorption

by Rhizopus arrhizus biomass, Enzyme Microbiol Technol, Vol. 31: 456-63,:

[7] Rajappa A., Ramesh K., Nandhakumar V., Pugazhenthi M , Sivajiganesan S., 2014 Aug., *Thermodynamics and Instrumental Analysis* of Bismarck Brown R Dye onto Activated Carbon Prepared from Delonix Regia Pods (Flame Tree), Asian Journal of Chemical and Pharmaceutical Research, Vol. 2(2): 145-151.

[8] Rajeshwari S, Sivakumar S, Senthilkumar P, Subburam V., 2001, **Carbon from cassava peel, an agricultural waste, as anadsorbent in the removal of dyes and metal ions from theaqueous solution**, Bioresource Technol, Vol. 80(3): 233-235.

[9] Lee CK, Low KS, Gan P., 1999, Removal of some organic dyes byacid treated spent bleaching earth, Environ Technol, Vol. 20: 99-104, Available from.

[10] Sreejalekshmi KG, Anoop Krishnan K, Anirudhan TS, 2009 Jan. 30 Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies, Journal of Hazardous Materials, Vol. 161 (2–3):1506–1513.

[11] Li Y., Wangb Z., Luanc Z., Dinga J., Xua C, Wua D, 2003, Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes, J. of elsevier Carbon, Vol. 41(5): 1057–1062.

[12] Thygesen LG., Hidayat BJ., Johansen KS., Felby C., 2011 Aug., *Role of supramolecular structures in enzymatic hydrolysis of plant cell walls*, J. Ind. Microbiol. Biotechnol, Vol. 38 (8): 975-983.

[13] Salas C.,Nypelö T., Rodriguez-Abreu C., Carrillo C., Rojas OJ., 2014
Oct., Nanocellulose: Properties and Applications in Colloids and
Interfaces, Current Opinion in Colloid & Interface Science, Vol. 19 (5):
383–396.

[14] Chirayil CJ., Lovely Mathew L., Thomas S., 2014, **Review of Recent Research in Nano Cellulose Preparation From Different Lignocellulosic Fibers**, Rev .Adv. Mater. *Sci*, Vol. 37: 20-28.

[15] Chen Tian C.,Fu S, Lucia LA.,2015, Magnetic $Cu_{0.5}Co_{0.5}Fe_2O_4$ ferrite nanoparticles immobilized in situ on the surfaces of cellulose nanocrystals, Cellulose, Vol. 22: 2571–2587.

[16] Mariño M., Lopes da Silva L., Nelson Durán N., Tasic L., 2015,
 Enhanced Materials from Nature: Nanocellulose from Citrus Waste,
 Molecules, Vol.20: 5908-5923.

[17] Moraisa J., Rosa M., Filho M., Nascimentoa L., Diego Magalhães do Nascimento D., Cassale A.,2013 Jan. 2, **Extraction and characterization of nanocellulose structures from raw cotton linter,** Carbohydrate Polymers,Vol. 91(1): 229–235.

[18] Zain N., Yusop S., Ahmad I., 2014, Preparation and Characterization of Cellulose and Nanocellulose From Pomelo (Citrus grandis) Albedo, J Nutr Food Sci, Vol.5 (1): 334 , [19] Kampeerapappun P., 2015, Extraction and Characterization of Cellulose Nanocrystals Produced by Acid Hydrolysis from Corn Husk,
Journal of Metals, Materials and Minerals, Vol.25 (1): 19-26.

[20] Hokkanen S., Repo E., Loub S., Sillanpää M., 2015 Jan. 15, *Removal* of arsenic(V) by magnetic nanoparticle activated microfibrillated cellulose, Chemical Engineering Journal, Vol. 260: 886–894.

[21] Luo X., Lina Zhang L., High effective adsorption of organic dyes on magnetic cellulose beads entrapping activated carbon, 2009 Nov. 15,
Journal of Hazardous Materials, Vol.171(1–3): 340–347.

[22] Abdul Khalil HPS., Chaturbhuj K., Adnan AS., M.R. Nurul Fazita MR.,Syakir MI., Davoudpour Y., M. Rafatullah M., C.K. Abdullah CK., Haafiz MKM.,Dunganid R. *2016*, **A review on chitosan-cellulose blends and nanocellulose reinforcedchitosan biocomposites: Properties and their applications,** Carbohydrate Polymers, Vol. 150: 216–226.

[23] Kongliang Xie, Weiguo Zhao, Xuemei He,2011 Feb., Adsorption properties of nano-cellulose hybrid containing polyhedral oligomeric silsesquioxane and removal of reactive dyes from aqueous solution, Carbohydrate Polymers, Vol. 83 (4): 1516–1520.

[24] Yagub MT, Sen TK, Afroze S, Ang HM1, Ang H.M., 2014 Jul., Dye and its removal from aqueous solution by adsorption: A review, Advances in Colloid and Interface Science, Vol. 209: 172–184. [25] Gupta VK., Kumar R., Nayak A., Saleh TA., Barakat M.,2013 Jun., Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review, Adv Colloid Interface Sci, Vol. 193-194: 24-34.

[26] Tahir H., Sultan M., Jahanzeb Q., 2008 Aug. 4, *Removal of basic dye methylene blue by using bioabsorbents Ulva lactuca and Sargassum*,
African Journal of Biotechnology, Vol. 7 (15): 2649-2655.

[27] Bulut Y., Aydın H., 2006, **A kinetics and thermodynamics study of methylene blue adsorption on wheat shells,** Desalination, Vol. 194: 259–267.

[28] Shehata A., 2013 December, *Removal of Methylene Blue Dye from Aqueous Solutions by Using Treated Animal Bone As A Cheap Natural Adsorbent,* International Journal of Emerging Technology and Advanced Engineeringm, Vol. 3(12): 507-513.

[29] Wong Y., Senan M., Atiqah N., 2013 Mar. 21, *Removal of Methylene Blue and Malachite Green Dye Using Different Form of coconut Fiber as Adsorbent*, Journal of Basic & Applied Science, Vol. 9: 172-177.

[30] Miclecu A., Wiklund L. 2010, *Methylene blue, an old drug with new indications*, Romanian journal of Anesthesiology and Intensive Therapy, Vol.17 (1): 35-41. [31] Tani A., Thomson A., Butt J.2001 Oct., **Methylene blue as an** electrochemical discriminator of single- and double-stranded oligonucleotides immobilised on gold substrates, Analyst, Vol. 126 (10): 1756-1759.

[32] Miclescu A., 2009, Cerebral Protection in Experimental Cardiopulmonary Resuscitation - With Special Reference to the Effects of Methylene Blue, Acta Universitatis Upsaliensis, Digital Comprehensive Summaries of Uppsala Dissertations from the facultu of Medicine, Vol. 466: 79.

[33] Gillman k., Methylene Blue and Serotonin Toxicity Syndrome,2014 Dec.4,

[34] Medsafe, Data sheet: Methylene Blue Solution for Injection, 2010Dec.,

[35] Carlson J., 1999 May. 3, Re: Students asked if methylene blue put into cookies as a prank was dangerous,

[36] Shopes E., Gerard W., Baughman J., 2013 Jun., Methylene Blue Encephalopathy: A Case Report and Review of Published Cases, AAN Journal, Vol. 81 (3): 216-221.

[37] Clifton J., Leikin JB., 2003 Aug., *Methylene Blue*, American Journal of Therapeutics, Vol. 10 (4): 289-291.

[38] Schirmer RH., Adler H., Pickhardt M., Mandelkow E., 2011 Dec.,Lest we forget you--methylene blue, Elsevier Neurobiology of Aging,Vol. 32(12): 2325.e7-16.

[39] Visa M., Bogatu C, Duta A., 2010 Jun. 15, Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash, Applied Surface Science, Vol. 256(17): 5486-5491.

[40] Rashed MN., 2013 Jan. 30 Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater, Organic Pollutants Monitoring, Risk and Treatment. Prof. M. Nageeb Rashed (Ed.).

[41] Worch E., 2012 Aug., Adsorption Technology in water Treatment-Fundamentals, Processes, and Modeling, Germany, Water de Gruyter GmbH & Co.KG, 345p.

[42] Dabrowski A., 2001 Oct., Adsorption—From Theory to Practice,Advances in a Colloid and Interface Science, Vol. 93 (1–3): 135–224.

[43] Piccin JS., Dotto GL., Pinto LAA.,2011, Adsorption Isotherms and Thermochemical Data of FD&C RED N[•] 40 Binding by Chitosan, Brazilian Journal of Chemical Engineering, Vol. 28(2): 295-304.

[44] Tighadouini S., Radi S, El Massaoudi M., Bacquet M., Zaghiroui M.,
2015, Adsorption of Cu(II) onto novel silica gel-immobilized bithiophene
tripodal receptor, J. Mater. Environ. Sci., Vol. 6 (5): 1457-1468.

[45] Ghiaci M., Abbaspur A., Kia R., Seyedeyn-Azad F., 2004, *Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto Organozeolites and as-synthesized MCM-41*, Separation and **Purification Technology J.**, Vol. 40 (3): 217–229.

[46] Ferraria L., Kaufmam J., Winnefeld F., Plank J., 2010 Jul., *Interaction* of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements, Journal of Colloid and Interface Science, Vol. 347 (1): 15–24.

[47] Ncibi MC., 2008, Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis, Journal of Hazardous Materials, Vol. 153: 207–212.

[48] Sylvester O. Adejo and Mbanefo M. Ekwenchi., 2014 Jan., *Proposing a new empirical adsorption isotherm known as Adejo-Ekwenchi isotherm*, Journal of Applied Chemistry, Vol. 6(5): 66-71.

[49] Foo KY. and B.H. Hameed BH.,2010, *Insights into the modeling of adsorption isotherm systems*, Chemical Engineering Journal, Vol. 156,: 2-10.

[50] Chen X.,2015 Jan. 22, Modeling of Experimental Adsorption Isotherm Data, Information, Vol. 6: 14-22. [51] Dada A., Olalekan A., Olatunya A., Dada O., 2012 Nov.-Dec., Langmuir,Freundlich, Temkin and Dubinin – Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{+2} unto phosphoric acid modified Rice Husk, IOSR Journal of Applied Chemistry, Vol. 3 (1): 38-45.

[52] Qiu H., Lv L., Pan B., Zhang Q., Zhang W., 2009, *Critical Review in Adsorption Kinetic Models*, Journal of Zhejiang University Science A., Vol. 10: 716-724.

[53] He J., Hong S., Zhang L., Gan F., Ho Y., 2010, Equilibrium and Thermodynamic Parameters of Adsorption of Methylene Blue onto Rectorite, Fresenius Environmental Bulletin, Vol. 19: 2651-2656.

[54] Sridev D., Rajendran K., 2009, Synthesis and Optical Characteristics of ZnO Nanocrystals, Bulletin of Materials Science, Vol. 32: 165-168.

[55] Ferrari L, Kaufmann J, Winnefeld F, Plank J., 2010 Jul. 1, *Interaction* of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements, J Colloid Interface Sci., Vol. 347 (1): 15-24.

[56] BAI Y., BARTKIEWICZ B.,2009, *Removal of Cadmium from wastewater using ion exchange resin amberjet 1200H columns*, Polish J. of Environ. Stud. Vol. 18(6): 1191-1195. [57] Agrawal A., Sahu K., 2006 Sep. 21, *Kinetics and isotherm studies of cadmium adsorption on manganese nodule residue*, Journal of Hazardous Materials, Vol. 137(2): 915–924.

[58] Lin J., Wang L., 2009 September, **Comparison between linear and non-linear forms of pseudo-first-order and pseudo-second-order adsorption kinetic models for the removal of Methylene blue by activated carbon**, Frontiers of Environmental Science & Engineering in China, Vol. 3(3): 320-324.

[59] Ugurlu M., Gurses A., Acıkyıldız M., 2008 Apr. 15, Comparison of textile dyeing effluent adsorption on commercial activated carbon and activated carbon prepared from olive stone by ZnCl₂ activation, *Microporous and Mesoporous Materials*, Vol. 111(1–3): 228–235.

[60] Elmolla E., Chaudhuri M., 2009, *Improvement of biodegradability of synthetic amoxicillin wastewater by Photo-Fenton process*, World
Applied Science Journal, Vol.5 (special issue for environment): 53-58

[61] Tan I., Hameed B., Ahmad A., 2007 Mar. 1, *Equilibrium and Kinetic studies on basic dye adsorption by oil palm fiber activated carbon*,
Chemical Engineering Journal, Vol. 127(1–3): 111–119.

[62] Ho Y., Malarvizhi R., Sulochann N., 2009, Equilibrium Isotherm Studies of Methylene Blue Adsorption onto Activated Carbon Prepared from Delonix regia Pods, Journal of Environmental Protection Science, Vol. 3: 111 – 116. [63] EL Boujaady H., Mourabet M., Bennani-Ziatni M., Abderrahim T., 2013 Oct., *Adsorption/desorption of Direct Yellow 28 on an apatitic phosphate: Mechanism, Kinetic and thermodynamic studies*, Journal of **the Association of Arab Universities for Basic and Applied Sciences**, Vol. 16: 64-73.

[64] Dargo H., Gabbiye N., Ayalew A., 2014 Sep., *Removal of Methylene Blue Dye from Textile Wastewater using Activated Carbon Prepared from Rice Husk*, International Journal of Innovation and Scientific Research, Vol. 9 (2): 317-325.

[65] Vitz J., ErdmengerT., Haensch C., Schubert US., 2009 Jan. 5 ,Extended dissolution studies of cellulose in imidazolium based ionic liquids, Green Chemistry, Vol. 11 (3): 417-424.

[66] Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J, 2011, *Cellulose Nanomaterials Review: Structure, Properties and Nanocomposites*, Royal Society of Chemistry Journal, Vol. 40, 3941-3994.

[67] Anirudhan T.S., Rejeena S.R., 2012 Adsorption and hydrolytic activity of trypsin on a carboxylate-functionalized cation exchanger prepared from nanocellulose, J.ColloidInterfaceSci, Vol.381: 125-136.

[68] Anirudhan T.S., Rejeena S.R., 2013, Selective adsorption of hemoglobin using polymer-grafted-magnetite nanocellulose composite, Carbohydr.Polym, *Vol.* 93: 518-527.

[69] AnirudhanT.S, Rejeena S.R, Binusree j., 2013, Adsorptive separation of Myoglobin from aquous solution using iron oxide magnetic nanoparticles modified with functionalized nanocrystalline cellulose, J. Chem. Eng. Vol.58: 1329 – 1339.

[70] Vadivelan V., Kumar K.V, 2005, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk,
J. Coll. Interface Sci. Vol.286: 90–100.

[71] Racovita S., Lungan M.A, Bunia I., Popa M., Vasiliu S., 2016, Adsorption and release studies of cefuroxime sodium from acrylic ion exchange resin microparticles coated with gellan. Reactive and Functional Polymers. <u>Vol. 105</u>: 103–113.

[72] Vimonses V., Lei S.M, Jin B., Chow C.W.K, Saint C., 2009, Adsorption of congo Red by three Australian kaolins, Applied Clay Science. Vol.43 (3–4): 465–472.

[73] Guo H., Zhang S., Z. Kou Z., Zhai S., Ma W., Yang Y., 2005,Removal ofcadmium(II) from aqueous solutions by chemically modified maize straw, Carbohydrate Polymers. Vol.115 : 177–185.

[74] Wang L., J. Zhang J., Zhao R, Li C., Li Y., Zhang C.L., 2010, Adsorption of basicDyes on activated carbon prepared from Polygonum orientale linn: Equilibrium, kineticand thermodynamic studies, Desalination. Vol. 254(1–3) 68–74. [75] Gusmão K.A.G., Gurgel L.V.A, T. Melo T., L.F. Gil L.F, 2012, Application of Succinylated sugarcane bagasse as adsorbent to remove methylene blue and gentian violet from aqueous solutions – Kinetic and equilibrium studies. Dyes and Pigments, Vol.92 (3): 967–974.

[76] Aksu Z., 2002 Determination of the equilibrium, kinetic and thermodynamic parametersof the batch biosorption of nickel(II) ions onto Chlorella vulgaris, Process Biochemistry, Vol.38: 89–99.

تحضير وتشخيص مواد نانوسيليولوزية مغناطيسية من الجفت لغاية إزالة صبغة الميثيلين الأزرق من الماء

إعداد

عبير محمد رشيد ملحم

إشراف

أ.د.شحدة جودة

د. عثمان حامد

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء، بكلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس – فلسطين. 2017 تحضير وتشخيص مواد نانوسيليولوزية مغناطيسية من الجفت لغاية إزالة صبغة الميثيلين

الأزرق من الماء إعداد عبير محمد رشيد ملحم إشراف أ.د. شحدة جودة د. عثمان حامد الملخص

تم استخراج السليلوز المستخدم في هذه الدراسة من الجفت (OISW) خلال عملية متعددة الخطوات، والسليلوز المستخرج ثم تحويله الى نانو سيليولوز (CNC) عن طريق التحلل الحمضي. و CNC المصنع ثم تحويله إلى نانوسليلوز المغناطيسي (MCNC) عن طريق معاملته مع محلول FeCl₃.6H₂O و FeCl₃.6H₂O وقد تم تشخيص النانو سيليولوز المصنع عن طريق محلول FeCl₃.6H₂O و FeCl₃.6H₂O وقد تم تشخيص النانو سيليولوز المصنع عن طريق , SEM, TEM, XRD, FTIR VSM محساب قدرة النونوسيليولوز المصنع على استخراج الميثيلين الأزرق (MB) من الماء ت ومقارنته مع السليلوز . أظهر السليلوز والنانو ميل مقبول لاستخلاص الميثيلين الأزرق. ومع ذلك أظهرت MCNC كفاءة استخلاص ممتازة نحو MB. تم رصد ثلاثة متغيرات وتقييمها أثناء عملية الاستخراج: الوقت والجرعة، والتركيز . تم دراسة الديناميكا الحرارية لادمصاص الثلاث مواد السيليولو والنانو سيليولوز والنانو سيليولوز المغناطيسي، كل منهم ريت. Sender order و يعيمها أثناء عملية الاستخراج: الوقت والجرعة، والتركيز . تم دراسة الديناميكا الحرارية لادمصاص الثلاث مواد السيليولو والنانو سيليولوز والنانو المغناطيسي، كل منهم التقاءي للادمصاص في درجة حرارة مختلفة.