

Dedications

I dedicate this work to my family and my dear husband and to my lovely boys Mohammad and Yosef for their encouragement and for being a source of love and support.

Moreover, I dedicate this work to all those who contributed to this work in order to make it an honorable one.

ACKNOWLEDGEMENTS

After thanking the greet ALLAH, I would like to acknowledge. My gratefulness to:-

Dr. Abdelnasser Etorki, my supervisor for his sustained support, guidance, advice, and encouragement during this study.

Dr. Mahmoud Elrais, my supervisor for his sustained support, guidance, advice, and encouragement during this study.

The chemistry department, faculty of science, University of Tripoli and Zawia.

My parents, my sisters and brothers who have been a great source of love and support.

TABLE OF CONTENTS

Subject	Page
DEDICATIONS	I
ACKNOWLEDGMENTS	II
LIST OF FIGURES	VII-VIII
LIST OF TABLES	IX-X
List of symbols.....	XI
ABSTRACT	XII-XIII
CHAPTER (I)	
1.1 Introduction	1
1.2 Environmental problems	1
1.3 Background of Present Research	2
1.4- Toxicity of Dyes.....	2
1.5 Technics available for color removal	3
1.5.1 Biological treatments	3
1.5.2- Chemical methods	3
1.5. 3- Physical methods	4
1.6 Principles of Adsorption	4
1.6.1 Physical adsorption	5
1.6.2 Chemical adsorption	5
1.7 Adsorption Mechanism	6
1.8 Adsorption Isotherms	6
1.9- Adsorption Equilibrium and the Adsorption Isotherm	7
1.10- Dye	9
1.11- Classification systems for dyes	10
1.12- Disadvantages of dyes	12

1.13-Methylene blue Crystal Violet and Methyl Green dyes	12
1.13.1-Methylene blue	12
1.13.2-Crystal violet	13
1.13.3-Methyl Green	14
1.14- Seaweed	15
1.15- Literature Reviews	16-21
1.16- Study Objectives	22
CHAPTER (II)	
2.1 Chemical and Methods	23
2.2-Instrumentation	23
2.3- Procedures	24
2.3.1- Preparation of Adsorbent	24
2.3.2- Preparation of Stock Solution	25
2.3.3-Prapration of mixture salt	25
2.4 Effect of variable parameters	25
2.4.1-Effect of concentration dye on seaweed	25
2.4.2-Effect Contact time on dye removal	25
2.4.3- Effect mass of adsorbent (dose) on dye removal	26
2.4.4-Effect pH on removal of dye	26
2.4.5-Effect of temperature on remove the dye	26
2.4.6- Effect of particle size on dye removal	26
2.4.7- Effect of foreign Ions on the removal	26
2.4.8- Effect photolysis for the dye on seaweed	27
CHAPTER (III)	
RESULTES AND DISCUSSION	28
3.1-FTIR characterization of the seaweed.....	28

3.1.1- FTIR spectra for seaweed before and after addition of Methylene Blue Crystal Violet and Methyl Green.....	29-30
3.2- Scanning Electron Microscope of the seaweed and dyes	31
3.3- (UV/Vis) Spectrophotometer Results for MB, CV and MG.....	33
3.4- Results Removal (Methylene Blue, Crystal violet, and Methyl Green) on the seaweed.....	35
3.4.1- Result Removal of Methylene Blue on the seaweed.....	35
3.4.2- Effect of Contact Time of Methylene Blue on seaweed.....	35
3.4.3- Effect of Initial pH on Methylene Blue removal.....	37
3.4.3.1- Effect of Initial pH on Methylene Blue Removal.....	37
3.4.4- Effect of Initial Dye Concentration.....	38
3.4.5- Effect mass of adsorbent dose on Methylene Blue removal.....	39
3.4.6- Effect of particle size on Methylene Blue removal	41
3.4.7-Effect of Temperature on Methylene Blue removal.....	42
3.4.8- Effect photolysis on Methylene Blue removal	42
3.4.9- Effect foreign ions on Methylene Blue removal	43
3.5- Results Removal of Crystal violet on the seaweed.....	44
3.6- Results Removal of Methyl Green on the seaweed.....	45
3.7-Compare the results of removing MB, CV and MG on seaweed.....	46
3.7.1-Effect of Contact Time of (MB, CV and MG) on seaweed.....	46
3.7.2-Effect of Initial pH on (MB, CV and MG) removal.....	47
3.7.3- Effect of Initial Dye Concentration on MB, CV and MG Removal...48	
3.7.4-Effect of adsorbent dose on (MB, CV and MG) removal	49
3.7.5-Effect of particle size on (MB, CV and MG)removal.....	50
3.7.6-Effect of Temperature on MB, CV and MG removal	51
3.7.7-Effect photolysis on MB, CV and MG removal	52
3.7.8-Effect Foreign Ions on MB, CV and MG removal.....	53

3.8- Isotherm analysis	54
3.8.1. Langmuir Isotherm.....	54
3.8.2. Freundlich Isotherm	57
3.9- Determination of thermodynamic functions.....	59
3.10- Comparison this results with previous studies.....	62
Conclusions	63-64
Future work.....	65
Appendix.....	66-68
Reference.....	69-75

LIST OF FIGURES

Figure	Page
Figure (1.1) Mechanism of Adsorption.....	6
Figure (1.2) structure of methylene blue.....	13
Figure (1.3) Structure of Crystal Violet.....	14
Figure (1.4) Structure of Methyl Green.....	14
Figure (2.1) dead leaves of seaweed were collected from coast Subrata.....	19
Figure (2.2) Ground dead leaves of seaweed.....	19
Figure (3.1) FTIR spectra for Seaweed before addition of dye.....	29
Figure (3.2) FTIR spectra for Seaweed after addition of MB.....	30
Figure (3.3) FTIR spectra for Seaweed after addition of CV.....	30
Figure (3.4) FTIR spectra for Seaweed after addition of MG.....	30
Figure (3.5). Scanning electron microscopy of the surface of seaweed before (a) and after (b, c, d) MB, CV, MG dye treatment.....	31
Figure (3.6) (UV/Vis) for MB before add seaweed (UV/Vis) for MB and after add seaweed. At 10ppm from MB, 3h, pH =3, 0.15g of seaweed.....	33
Figure (3.7)(UV/Vis) for CV before add seaweed (UV/Vis) for CV after add seaweed. At 10ppm from CV, 3h, pH =3, 0.15g of seaweed.....	33
Figure (3.8) (UV/Vis) for MG before add seaweed (UV/Vis) for MG after add seaweed. At 10ppm from MB, 3h, pH =3, 0.15g of seaweed.....	33
Figure (3.9) UV-VIS spectrum and Calibration curve of MB dye. At 0.15g of seaweed, pH 3, 3h, 25°C.....	35
Figure (3.10) Effect Contact time on MB removal.....	37
Figure (3.11) Effect of pH on MB removal.....	38
Figure (3.12) effect initial dye concentration on MB removal.....	39
Figure (3.13) effect adsorbent dose on MB removal.....	41

Figure (3.14) effect particle size on MB removal.....	41
Figure (3.15) effect Temperature on MB removal.....	42
Figure (3.16) effect photolysis on MB removal.....	43
Figure (3.17) Effect foreign ions on MB removal.....	44
Figure (3.18). UV-VIS spectrum and Calibration curve of CV dye. At 0.15g of seaweed, pH 3, 3h, 25°C	45
Figure (3.19). UV-VIS spectrum and Calibration curve of MG dye. At 0.15g of seaweed, pH 3, 3h, 25°C	45
Figure (3.20) Effect of Contact Time of (MB, CV and MG) on seaweed.....	47
Figure (3.21) Effect of Initial pH on removal of (MB, CV and MG).....	48
Figure (3.22) Effect of Initial Concentration on removal MB, MG and CV.	49
Figure (3.23) Effect of adsorbent dose on removal of (MB, CV and MG)....	50
Figure (3.24) Effect of particle size on removal of (MB, CV and MG)	51
Figure (3.25) Effect of Temperature on MB, CV and MG removal.....	52
Figure (3.26) Effect photolysis on MB, CV and MG removal.....	53
Figure (3.27) Effect foreign Salt on removal of MB, CV and MG.....	54
Figure (3.28) langemyer isotherm for MB onto 0.15g seaweed at 25°C.....	55
Figure (3.29) langemyer isotherm for CV onto 0.15g seaweed at 25°C.....	56
Figure (3.30) langemyer isotherm for MG onto 0.15g seaweed at 25°C.....	56
Figure (3.31) freundlich isotherm for MB onto 0.15g seaweed at 25°C.....	57
Figure (3.32) freundlich isotherm for CV onto 0.15g seaweed at 25°C.....	58
Figure (3.33) freundlich isotherm for MG onto 0.15g seaweed at 25°C.....	58
Figure (3.34) show the van't Hoff polts in Ln Kd versus 1/T	60

LIST OF TABLES

Table (1.1) Application Classes of Dyes and Their Chemical Types	11
Table(1.2) Disadvantages of different dye class.....	12
Table(2.1) list of all instruments used.....	23
Table (3.1). Functional groups of dried seaweed with adsorbed MB, CV and MG and their corresponding wavenumber	29
Table (3.2) the effect of Contact time on MB removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.....	36
Table (3.3) the effect of pH on MB removal. At 10 ppm, 0.15g of seaweed, 3h, 25°C.....	38
Table (3.4) the effect of initial dye concentration on MB removal. At 0.15g of seaweed, pH 3, 3h, 25°C.....	39
Table (3.5)the effect of adsorbent dose on MB removal. At 10 ppm, pH 3, 3h, 25°C.....	40
Table (3.6)the effect of particle size on MB removal. At 10 ppm, pH 3, 3h, 25°C.....	41
Table (3.7)the effect of temperature on MB removal. At 10 ppm, pH 3, 3h, 25°C.....	42
Table (3.8)the effect of photolysis on MB removal. At 10 ppm, pH 3, 3h, 25°C.....	43
Table (3.9)the effect of foreign ions on MB removal. At 10 ppm, pH 3, 3h, 25°C.....	44
Table (3.10) the effect of Contact time on MB,CV and MG removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.....	46
Table (3.11) the effect of pH on MB,CV and MG removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.....	47

Table (3. 12) the effect of Concentration on MB,CV and MG removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.....	48
Table (3.13)the effect of adsorbent dose on MB, CV and MG removal. At 10 ppm, pH 3, 3h, 25°C.....	49
Table (3.14) the effect of particle size on MB,CV and MG removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.....	50
Table (3.15) the effect of temperature on MB,CV and MG removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.....	51
Table (3.16) the effect of photolysis on MB,CV and MG removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.....	52
Table (3.17) the effect of foreign ions on MB,CV and MG removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.....	53
Table (3.18) Effect of concentration value on adsorption 0.15g seaweed, connect time 3h and at 25° C for MB.....	55
Table (3.19) Effect of concentration value on adsorption 0.15g seaweed, connect time 3h and at 25° C for CV.....	55
Table (3.20) Effect of concentration value on adsorption 0.15g seaweed, connect time 3h and at 25° C for MG.....	56
Table (3.21) the isothermal model adsorption data for MB, CV, and MG dyes.....	59
Table(3.22) C_e , Q_e and T values of the three dyes(CV, MG, MB) on seaweed.....	60
Table(3.23). Thermodynamic parameters for adsorption of MB, CV and MG dye onto Seaweed ($T = 293, 303, 313$ and 323 K).....	61
Table (3.24) Results of some scientific studies related to organic dyes removal.....	62

List of symbols

Parameter	
q_e	The adsorption density mg of adsorbate per gram of adsorbent.
C_e	The concentration of adsorbate in solution (mg/L).
C_o	Final equilibrium concentration of adsorbate after adsorption has occurred, (mg/l).
V	Volume of liquid in the reactor, (L).
M	Mass of adsorbent, (g).
MB	Methylene Blue dye.
CV	Crystal Violet dye.
MG	Methyl Green dye.
SEM	Scanning Electron Microscope.
FT-IR	Fourier Transform infrared spectroscopy.
ppm	Parts per million.
nm	Nano meter.
R^2	Correlation coefficient
R_L	Dimensionless separation factor
K_L	Langmuir equilibrium constant (L/g)
K_F	Constant in Freundlich Isotherm
n	Freundlich exponent
P.S	Particle Size

Abstract

Dyes in the aquatic systems is really a serious environmental problem, which may affect the environmental awareness and the economical point of view. The use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing textile dyes from wastewater. This study try to find out the feasibility of using seaweed for removal of synthetic dye from aqueous solutions. The characteristics of adsorption of methylene blue (MB), Crystal Violet (CV) and Methyl Green (MG) dyes onto seaweed as bio adsorbents were investigated. UV spectrophotometer technique was used for the measurement of concentration of dye before and after adsorption. A spectroscopic analysis was done to a fourier transform of the seaweed the results showed the existence of hydroxyls, thiol, carbonyls, alkyl, Sulfonyl, carboxylic acid and amines. While the scanning electron microscopic image displayed the gradual formation of cavities and open pores on the surface. Batch adsorption experiments were carried out for the adsorption of the dyes molecule from aqueous solution onto the seaweed at a variable effect of different parameters like pH (2-9), initial concentration of dye (2.5 to 80 mg/L), contact time (5 to 180 min), adsorbent dosage (0.05 to 0.3 g), temperature (20, 30, 40, 50 °C), and particle size (100, 150, 300 micron). The effect of light and foreign ions on the adsorption process was also studied. The results of this study showed that the seaweed was able to remove up to (96.9% of MB, 92.6% of CV, and 80.62% of MG) from solutions with initial dye concentrations 10 ppm and 0.15g mass of adsorbent, time average of 3h, 100 micron of seaweed and initial pH of 3. The effect of temperature on adsorption process was also studied and the results showed that the adsorption decreases when temperature increasing. The best temperature for best adsorption was 20°C.

Thermodynamic parameters, ΔG° , ΔH° , and ΔS° , were calculated according to van't Hoff equation. Negative values of Gibbs free energy imply that the process is spontaneous. Also, the equilibrium data were fitted to the Langmuir equilibrium isotherm models. The maximum capacity obtained from Langmuir was (33.64 of MB, 45.35 of CV, and 7.46 of MG) (mg/g), whereas the maximum capacity obtained from Freundlich K_f was (0.2865 of MB, 0.2927 of CV, and of MG 0.1792) of MB, CV, and MG respectively. The results indicate that the data fit with Langmuir and Freundlich. The final results of the study indicate that seaweed may be used as a low cost adsorbent or an alternative for the treatment of effluents that contain MB, CV and MG.

الخلاصة

وجود الأصباغ في النظم المائية تعد مشكلة بيئية خطيرة من شأنها أن تؤثر في الوعي البيئي ووجهة النظر الاقتصادية. فقد تم التحقق من استخدام الممترات منخفضة التكلفة والصديقة للبيئة كبديل مثالي للطرق الباهظة الثمن المستخدمة حاليا لإزالة صبغات النسيج من مياه الصرف الصحي. هذه الدراسة تحاول استكشاف مدى فاعلية استخدام تين البحر في إزالة الصبغات الاصطناعية من المحاليل المائية. حيث تم دراسة خصائص إمتزاز صبغات الميثيلين الأزرق والكريستال البنفسجي والميتيل الأخضر كنوع من الممترات البيولوجية. تم استخدام تقنية الطيف الضوئي بالأشعة فوق البنفسجية لقياس تركيز الصبغة قبل وبعد الإمتزاز. تم إجراء تحليل طيفي بالأشعة تحت الحمراء لتحويل فوربييه لتين البحر وأظهرت النتائج وجود مجموعة الهيدروكسيل ، الألكيل ، الثيول ، الكربونيل ، حمض الكربوكسيل ، السلفونيل والأمينات. بينما أظهرت الصورة المجهرية الإلكترونية تشكيلا تدريجيا للتجاويف والمسام المفتوحة على السطح. تم إجراء تجارب الإمتزاز الدفعي لإمتزاز جزئ الصبغة من المحلول المائي على تين البحر بتأثير متغيرات لمعاملات مختلفة مثل الرقم الهيدروجيني (2-9) ، التركيز الأولي للصبغة (2.5 إلى 80 مجم/لتر)، وقت الرج (5 إلى 180 دقيقة)، وزن تين البحر (0.05 إلى 0.3 جم)، درجة الحرارة (20,30,40,50 م°)، وحجم الجسيمات (100,150، 300 ميكرون). وتم أيضا دراسة تأثير الضوء والأيونات الخارجية على عملية الإمتزاز. أظهرت نتائج هذه الدراسة أن تين البحر قادر على إزالة ما يصل إلى (96.9% من الميثيلين الأزرق، 92.6% من الكريستال البنفسجي و 80.62% من الميتيل الأخضر) من المحاليل ذات التركيز الأولي للصبغة 10 جزء من المليون و 0.15 جم من المادة الممتزة ووقت الرج 3 ساعات ، 100 ميكرون من تين البحر ودرجة الحموضة الأولية 3. تم دراسة تأثير درجة الحرارة على عملية الإمتزاز ، وأظهرت النتائج إن الإمتزاز يتناقص كلما ازدادت درجة الحرارة وأفضل درجة حرارة للإمتزاز كانت 20 درجة مئوية. تم حساب المعاملات الديناميكية والحرارية وفقا لمعادلة فانت هوف حيث تشير القيمة السالبة لطاقة جيبس الحرة أن العملية تلقائية. تم تركيب البيانات التجريبية لنماذج متساوي الحرارة لانجمير وفريندليش. السعة القصوى التي تم الحصول عليها من لانجمير كانت كالاتي 33.64 مجم/جم للميثيلين الأزرق ، 45.35 مجم/جم للكريستال البنفسجي و 7.46 مجم/جم للميتيل الأخضر بينما السعة القصوى التي تم الحصول عليها من معادلة فريندليش كانت كالاتي 0.2866 للميثيلين الأزرق، 0.2927 للكريستال البنفسجي و 0.1792 للميتيل الأخضر. تشير النتائج إلى أن البيانات تتلأم مع

نموذج لانجمير وفرندليش. وتشير النتائج النهائية للدراسة بأنه يمكن استخدام تبن البحر كمادة مازة منخفضة التكلفة وبديل لمعالجة النفايات السائلة التي تحتوي على الميتيلين الأزرق والكريستال البنفسجي والميتيل الأخضر.