SEAWEED BIOMASS FOR THE REMOVAL OF BASIC DYES FROM AQUEOUS SOLUTIONS

Dorothea V. Politi, Odysseas N. Kopsidas, Fragiskos A. Batzias, Dimitrios K. Sidiras
Lab. Simulation of Industrial Processes, Dep. Industrial Management and Technology, University of Piraeus,
80 Karaoli & Dimitriou, GR 18534 Piraeus, Greece, tel. +302104142360, fax +302104142392,
email doritapoliti@unipi.gr, sidiras@unipi.gr

ABSTRACT: The main objective of this study was to evaluate the feasibility of removing methylene blue (taken as representative for dyes) from aqueous solutions, using sea, forest, agricultural and industrial by-products. Specifically seaweed was used, which comes ample in Greece and from many sources. The material was tested in raw form. Adsorption experiments were carried out to investigate the effect of adsorbent dose, pH, contact time and initial adsorbent concentration, on the adsorption process. The adsorption batch kinetics and adsorption equilibrium isotherms were further studied using the data obtained from these experiments. Moreover, adsorption column experiments were carried out and (i) Bohart-Adams and (ii) Clark bed depth column models were successfully used to fit these experimental data.

Keywords: adsorbent, algae, biomass.

1 INTRODUCTION

In industrial water pollution, the color produced by minute amount of organic dyes in water is considered very important because, besides having possible harmful effects, the color in water is aesthetically unpleasant. Colored water can affect plant life, and thus an entire ecosystem can be destroyed by the contamination of various dyes in water. Some dyes are also toxic and even carcinogenic [1-4]. The adsorption technique is proved to be an effective and attractive process for the treatment of dye containing wastewater [5-7]. Also, this method will become inexpensive, if the adsorbent material used is of low cost and does not require any expensive additional pretreatment step.

Different biological, physical and chemical methods have been applied for the cleaning dye wastewater such as adsorption, catalytic oxidation method, traditional biological method, electrochemical process, membrane separation technology and solvent extraction have been developed [8-10].

Among all the techniques for the removal of dyes from wastewater, adsorption method is generally preferred due to its high efficiency, easy handling, and availability of different adsorbents [8].

Methylene Blue (MB) is usually used to gain an understanding of the adsorption kinetics, to describe the rate and mechanism of adsorption, to determine the factors controlling the rate of adsorption [9]. MB, a cationic/basic dye, has wide applications which include colouring paper, dying cottons, wools, silk, leather and coating for paper stock [10].

The present work aims to study a convenient and economic method for MB removal from water by adsorption on a low cost and an abundantly available adsorbent. Specifically, seaweed adsorptivity was tested to investigate the effects of adsorbent dose, pH, contact time and initial adsorbent concentration, on the process. The adsorption batch kinetics, adsorption equilibrium isotherms and continuous adsorption column kinetics were further studied.

2 MATERIALS AND METHODS

2.1 Adsorbent

In this study, a low-cost material, seaweed, was used as adsorbent. This material was acquired from beaches of the Lefkada Island in Greece. Seaweed was washed with distilled water. Also the material was dried for 10 days at room temperature to minimize the humidity.

2.2 Adsorbate

The dye used in batch and column experiments was Methylene Blue. MB has a chemical formula of $C_{16}H_{18}ClN_3S._xH_2O$ with molecular weight of 373.9 10^{-3} g mol^{-1}. A stock solution was prepared by dissolving 5 g of MB in 25L distilled water. Working solutions were 180-1.6 mg L^{-1}. MB concentrations were analyzed by measuring the absorbent values in each experiments with a HACH DR4000U UV-VIS spectrophotometer at λ=664 nm.

2.3 Adsorption isotherm studies

Isotherms obtained from batch experiments. After the batch process, weigh accurately the quantities of tissue were transferred to 0.8-L bottles, where V = 0.5 L adsorbate solution were added. The adsorbent weight ranging from 0.5g, the temperature was T = 23 ^oC, the original MB (Merck, CI 52015) concentration ranged from C_0 = 3.7 mg L^{-1} to 180 mg L^{-1}. The bottles are sealed and mechanically fell for a period of 7 days. This time period was chosen after pilot studies (the time varies from 4 hours to 14 days) to ensure that nearly equilibrium conditions are achieved. The resulting solution was determined concentrations and balance data from each bottle represented one point on the adsorption isotherm plots. The values of solution pH were near 7.5.

2.4 Adsorption Kinetic studies

Batch experiments were carried out at various stirring speed values (65-664 rpm), pH values (1.54-12.9) and initial dye concentration values (3.7-180 mg L^{-1}) for a contact time up to 95 min. Every 5 min was selected a sample to determine the concentration of MB in the effluent solutions. The reactor, containing V = 1 L aqueous solution of dye was placed in a water bath to maintain constant temperature at the desired level.

2.5 Adsorption Column studies

Column experiments were conducted in 15 cm x 2,5 cm and 25 cm x 2,5 cm stainless steel columns. The bed height was x = 15 and 25 cm, respectively. The flow rate was controlled at about 20 mL min^{-1} and the initial concentration of MB was 163 mg L^{-1}. Every 200 ml output was selected a sample to determine the concentration of MB in the effluent solutions. At the end of every adsorption experiment desorption experiments with distilled water was performed.

3 RESULTS AND DISCUSSION

3.1 Adsorption isotherms

The comparison of the adsorption capacity of the seaweed samples was based on the Freundlich [11], Langmuir [12] and Sips [13] isotherm models. The first two models are both widely used for investigating the adsorption of a plethora of dyes on various lignocellulosic materials and activated carbons.

The Freundlich [11] isotherm is given by the following equation:

$$q = K_F \cdot (C_e)^{\frac{1}{n}} \qquad (1)$$

where q is the amount adsorbed per unit mass of the adsorbent (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/L) and KF [(mg/g)(L/mg)$^{1/n}$], n are the Freundlich constants related to adsorption capacity and intensity, respectively. Deriving the logarithmic form of eq. (1):

$$\log q = \log K_F + \frac{1}{n}\log C_e \qquad (2)$$

The K_F and n values were estimated by non-linear regression analysis (NLRA) from the experimental adsorption data obtained at 23^0C for MB. MB adsorption isotherms for untreated seaweed are presented in Fig. 1. The theoretical curves were estimated according to the Freundlich equation. The standard error of estimates (SEE)-values was calculated by the following equation:

$$\text{SEE} = \sqrt{\sum_{i=1}^{n'} (y_i - y_{i,theor})^2 /(n'-p')} \qquad (3)$$

where: y_i is the experimental value of the depended variable, $y_{i,\text{theor}}$ is the theoretical (estimated) value of the depended variable, n' is the number of the experimental measurements and p' is the number of parameters, i.e., (n' – p') is the number of the degrees of freedom.

The Langmuir isotherm equation [12] is based on the following 'pseudo-monolayer' adsorption model.

$$q = \frac{K_L q_m C_e}{1 + K_L C_e} \qquad (4)$$

or

$$\frac{1}{q} = \left(\frac{1}{q_m}\right) + \left(\frac{1}{K_L \cdot q_m}\right) \cdot \left(\frac{1}{C_e}\right) \qquad (5)$$

where K_L is the Langmuir constant related to the energy of adsorption (L.mg^{-1}) and q_m the amount of dye adsorbed (mg.g^{-1}) when saturation is attained. In cases where the isotherm experimental data approximates the Langmuir equation, the parameters K_L and q_m can be estimated either by plotting 1/q versus 1/Ce either by NLRA.

The essential characteristics of the Langmuir isotherm can be described by a dimensionless constant called 'equilibrium parameter' or 'separation factor' R_L, defined by the following equation:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \qquad (6)$$

where C_0 is the initial dye concentration (mg/L) and KL is the Langmuir constant (L/mg). The value of RL indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < RL < 1$) or irreversible ($R_L = 0$). At the present work, the RL values were found $0 < R_L < 1$ for all dye concentrations C_0 in the range of 3.7-180 mg/L for MB indicating favorable adsorption.

The Sips (Langmuir – Freundlich) [13] isotherm equation, also examined in the present work, is based on the following adsorption model:

$$q = \frac{q_m \cdot (K_L \cdot C_e)^{1/n}}{1 + (K_L \cdot C_e)^{1/n}} \qquad (7)$$

where K_L , q_m is the Langmuir constants and n the Freundlich constant.

The parameters of the three isotherm models can be obtained by NLRA. Table I presents the estimated parameter values for the experimental data obtained in the present study. The fitting of the Sips' adsorption model to the present data (see theoretical curves in Fig.3) was satisfactory for MB adsorption, as shown by the corresponding SEE-values given in Table I.

The best fitting was by the Freundlich model which has the lower SEE value (Table I).

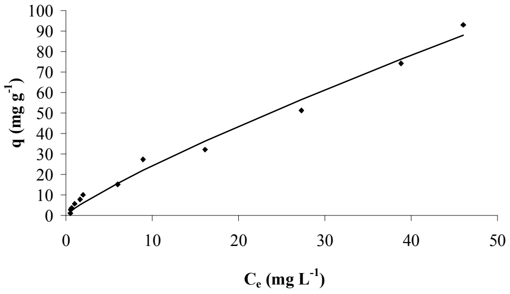

Figure 1: The Freundlich isotherm curves of MB adsorption on seaweed. Adsorption process: temperature 23oC, MB initial concentration C_0=3.7-180 mg L^{-1}, m/V=1 g L^{-1}

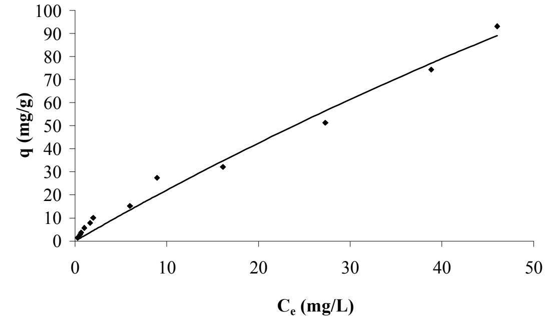

Figure 2: The Langmuir isotherm curves of MB adsorption on seaweed as affected by MB initial concentration. Adsorption process: temperature 23^{o}C, MB initial concentration C_0=3.7-180 mg L^{-1}, m/V=1 g L^{-1}

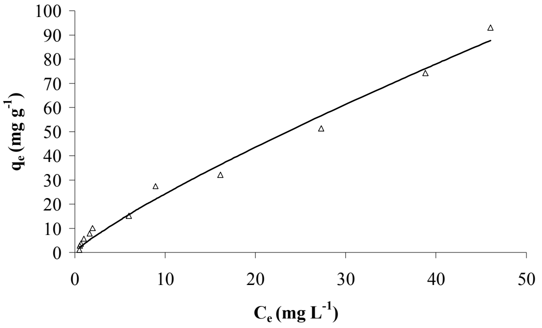

Figure 3: The Sips isotherm curves of MB adsorption on seaweed as affected by MB initial concentration. Adsorption process: temperature 23^{o}C, MB initial concentration C_0=3.7-180 mg L^{-1}, m/V=1 g L^{-1}

Table I: Isotherms models' parameters of Methylene Blue adsorption on seaweed

	K_F [(mg g^{-1})(L mg^{-1})$^{1/n}$]	*n*	K_L (L mg^{-1})	q_m (mg/g)	*SEE*
Freundlich	3.47	1.19	-	-	3.649
Langmuir	-	-	0.004	557	4.303
Sips	-	-	0.0002	4303	3.902

3.2 Kinetics of adsorption

Kinetic models' equations: The kinetics of adsorption of MB on various materials has been extensively studied using four kinetic equations. The widely used Lagergren equation [14] is shown below:

$$q - q_t = q \cdot e^{-k \cdot t} \qquad (8)$$

where q and qt are the amounts of MB adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium time ($t \rightarrow \infty$) and adsorption time t, respectively, while k is the pseudo-first order rate constant for the adsorption process (in min^{-1}). Furthermore,

$$q = (C_0 - C_e)V/m \text{ and } q_t = (C_0 - C)V/m \qquad (9)$$

where C, C_0 , C_e are the concentrations of MB in the bulk solution at time t, 0, and , respectively, while m is the weight of the adsorbent used (in g), and V is the solution volume (in mL). Further modification of eq. (9) in logarithmic form gives:

$$ln(q - q_t) = ln\,q - k \cdot t \qquad (10)$$

The commonly used second order kinetic model [15] is as follows:

$$q_t = q - \left[q^{-1} + k_2 t\right]^{-1} \qquad (11)$$

or

$$q_t = q - \frac{1}{\frac{1}{q} + k_2 t} \qquad (12)$$

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [16]:

$$q_t = c + k_p \cdot \sqrt{t} \qquad (13)$$

where qt is the amount of MB adsorbed at time t, c is a constant (mg g^{-1}) and kp is the intra-particle diffusion rate constant in mg g-1 $min^{-0.5}$.

In Fig. 4 the effect of the MB initial concentration for the MB adsorption on seaweed is presented. The adsorption process conditions were: temperature 23^{o}C, MB initial concentration C_0=3.7-180 mg L^{-1}, m/V=1 g L^{-1}. The second order kinetics, for the same experimental data, is presented in Fig. 5. Finally, the intra-particle diffusion kinetics is presented in Fig. 6.

As regards the three models, the kinetic parameters of Methylene Blue adsorption on seaweed, are given in Table II for C_o = 36-180 mg L^{-1} and in Table III for C_o = 3.7-11 mg L^{-1}.

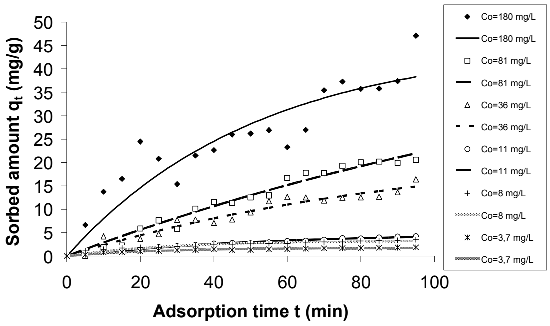

Figure 4: Lagergren curves of MB adsorption on seaweed as affected by MB initial concentration. Adsorption process: temperature 23^{o}C, MB initial concentration C_0=3.7-180 mg L^{-1}, m/V=1 g L^{-1}

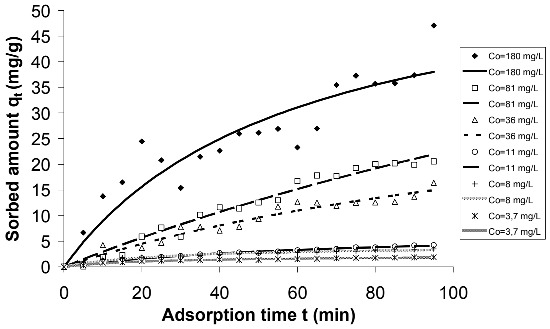

Figure 5: Second order curves of MB adsorption on seaweed as affected by MB initial concentration. Adsorption process: temperature 23^{o}C, MB initial concentration C_0=3.7-180 mg L^{-1}, m/V=1 g L^{-1}

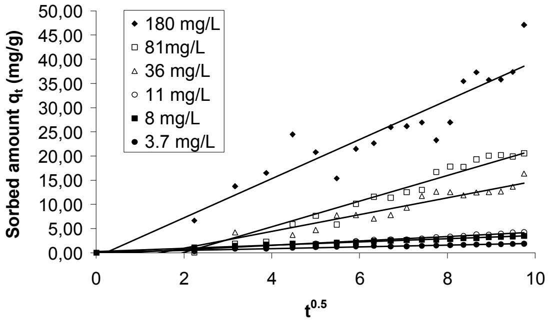

Figure 6: MB amount adsorbent on seaweed vs. t 0.5 for MB initial concentration C_0=3.7-180 mg L^{-1}. The theoretical lines are according the intra-particle diffusion model. Adsorption process: temperature 23°C, m/V=1 g L^{-1}

Table II: Kinetic parameters of Methylene Blue adsorption on seaweed, for C_o = 36-180 mg L^{-1}.

C_o (mg L^{-1})	180	81	36
First order kinetic model parameters			
k	0.0194	0.0056	0.0104
qe	45.52	53.40	23.70
SEE	4.6805	1.2127	1.1408
Second order kinetic model parameters			
k	0.0003	0.000035	0.0002
qe	61.63	93.24	39.97
SEE	4.4742	1.2216	1.1444
Intra-particle diffusion kinetic model parameters			
c	-0.8474	-5.2001	-2.557
k_p	4.0400	2.6458	1.7377
SEE	3.9211	1.9067	1.3920

Table III: Kinetic parameters of Methylene Blue adsorption on seaweed, for C_o = 3.7-11 mg L^{-1}.

C_o (mg L^{-1})	11	8	3.7
First order kinetic model parameters			
k	0.0190	0.0366	0.0405
qe	4.88	3.29	1.76
SEE	0.1440	0.2358	0.1052
Second order kinetic model parameters			
k	0.0020	0.0095	0.0188
qe	7.09	4.11	2.22
SEE	0.1219	0.1855	0.0825
Intra-particle diffusion kinetic model parameters			
c	-0.3048	0.2653	0.1171
k_p	0.4562	0.3288	0.1845
SEE	0.1195	0.1031	0.1007

3.3 Adsorption column studies

The 'bed depth service model' developed by Bohart and Adams [17] is as follows:

$$\ln\left(\frac{C_i}{C}-1\right)=\frac{K\cdot N\cdot x}{u}-K\cdot C_i\cdot t \qquad (14)$$

in which C=effluent concentration (mg L^{-1}); C_i=influent concentration (mg L^{-1}); K=adsorption rate coefficient (L^{-1} mg^{-1} min^{-1}); N=adsorption capacity coefficient (mg L^{-1}); x=bed depth (cm); u=linear velocity ($cm.min^{-1}$); and t=time (min). This model, expressed as non-linearized equation has the form of the 'simple logistic function':

$$C=\frac{C_i}{1+Ae^{-rt}} \qquad (15)$$

where ; $A=e^{K\cdot N\cdot x/u}$; $r=K\cdot C_i$

Clark [18] has developed an alternative to the 'simple logistic function', called the 'generalized logistic function', which incorporates the parameter n of the Freundlich adsorption isotherm:

$$C=\left[\frac{C_i^{\,n-1}}{1+Ae^{-rt}}\right]^{\frac{1}{n-1}} \qquad (16)$$

where n=inverse of the slope of the Freundlich isotherm. This expression coincides with Eq. (16) for n=2. Evidently, we can estimate the parameters K and N by applying linear and non-linear regression analysis (NLRA). The SEE has a lower value in the case NLRA. The equations used to calculate the parameter-values after having performe non-linear regression are K=r/Ci and N=u.lnA/(x.K)= Ci.u.lnA/(x.r).

The values of A and r according to the Bohart–Adams model can thus be estimated by NLRA from the column MB effluent data for the cases presented in Fig. 7 and 8. The effluent dye solution volume V (in L) is V=Q.t, where Q is the dye solution flow rate.

The theoretical estimations, according to the Bohart–Adams model, sufficiently simulate the experimental data in the examples given in these figures.

According to them, the fitting of the Bohart–Adams model to experimental data was found to be better than the fitting of the Clark model for the dye used herein.

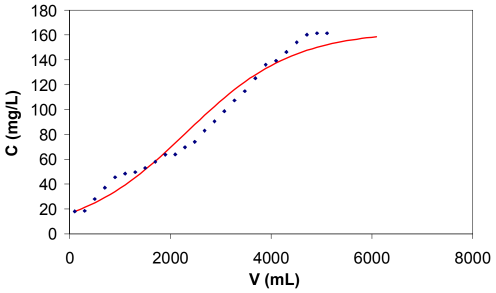

Figure 7: Breakthrough curves of effluent MB concentration C vs. effluent volume V according to the Bohart-Adams model; bed depth x=15 cm, flow rate Q=20 ml min^{-1}, filling adsorbent m=20 g seaweed,

influent MB concentration C_i=162 mg L^{-1} MB.

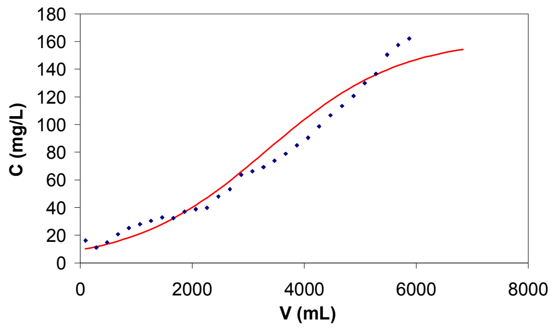

Figure 8: Breakthrough curves of effluent MB concentration C vs. effluent volume V according to the Bohart-Adams model; bed depth x=25 cm, flow rate Q=20 ml min^{-1}, filling adsorbent m=20 g seaweed, influent MB concentration C_i=162 mg L^{-1} MB.

4 CONCLUSIONS

The present work deals with the evaluation of the feasibility of removing MB from aqueous solutions, using seaweed, which comes ample in Greece and from many sources. Adsorption experiments were carried out and the effect of adsorbent dose, pH, contact time and initial adsorbent concentration was investigated. The adsorption batch kinetics and isotherms were studied. In addition, the adsorption column kinetics was investigated and the (i) Bohart-Adams and (ii) Clark models were successfully applied to fit the corresponding experimental data.

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