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Potential adsorption of methylene blue from aqueous solution using green macroalgae *Posidonia oceanica.*

F-N Allouche and N Yassaa

Centre de Développement des Energies Renouvelables, B.P. 62, Route de l'Observatoire, Bouzaréah 16340-Algiers, Algeria.

*E-mail: n.allouche@cder.dz

Abstract. The use of inexpensive biological materials, such as marine algae for removing dyes from contaminated industrial effluents appears as a potential alternative method. The aim of this study is to investigate the aptitude of marine macroalgae Posidonia Oceanica local biomass abundant on the coasts of Algeria for selective sorption of methylene blue (MB) from an aqueous solution in batch experiments at 20 °C. A maximum percentage removal of Posidonia oceanica occurs at pH 5. Equilibrium isotherm data were analyzed using the Langmuir and the Freundlich isotherms. The adsorption equilibrium of methylene blue was best describe by Langmuir model than the Freundlich model. The maximum sorption capacity was 357 mgg^{-1} at pH 5. The sorption data were very well described by the pseudo-second-order model. Keywords: Posidonia oceanica, Methylene blue (MB), Biosorption, Isotherm Equilibrium, Kinetics; Modelling.

1. Introduction

In recent years, much attention has focused on various natural solids material, which are able to remove pollution from contaminated wastewater at low cost. *Posidinia oceanica* was an important part of the marine ecosystem and can be developed for number of application. *Posidonia oceanica* are among the most macroalgae in studies of dyes pollution due to their ubiquitous environment and readily available in Mediterranean coast. The marine green macroalgae *Posidonia oceanica* are a renewable natural biomass and are very abundant in the Algerian littoral. Considerable research has been carried out by numbers of studies in Posidonia oceanica biosorbent, for their ability to sequester dye from aqueous solutions [1-5]. This study is intended to highlight on the possibility to use *Posidonia oceanica* as new material to remove and adsorb hazardous pollutants from industrial effluents. Nowadays, it's well known that the pollution due to synthetic dyes is considered as a serious public concern. An untreated dyes cause chemical and biological changes and lead a number of environmental and health hazards. Nearly, 10.000 dyes available commercially and different group of dyes can be discerned [6]. Consequently, approximately 1000000 kg/year of dyes are discharged into waste streams by the textile industry [7]. Most of the industrial activities use synthetic dyestuffs in a great number of operations, they consumes large quantities of water and they generate a considerable amount of colored wastewater. They can be highly toxic and carcinogenic to human health. Methylene bleu (MB) 3,7-bis(dimethylamino)- phenazathionium chloride (a thiazine cationic dye) (figure 1) is commonly used for coloring paper, temporary hair colorant, dyeing cotton, wools and so on [8]. Several physicochemical wastewater treatment techniques were developed for dyes recovery from

industrial effluents including physical and chemical processes such as precipitation, sedimentation, ultrafiltration, flotation, color irradiation, ozonation and coagulation. For the above-mentioned technologies are sometimes inappropriate especially for low-concentration solutions due to economic, technical or environmental reasons. Adsorption is an effective alternative process for treatment of contaminated wastewater in terms of simplicity of design and operation, and insensitivity of toxic substances [9]. Considerable amount of researches have been done on the development of effective, low cost and easily available alternative biosorbents [10-16]. The main objective of this research is to study the ability of Posidonia for removing methylene blue (MB) from aqueous solutions. A laboratory study was conducted to investigate the feasibility of the use of *Posidonia oceanica* as biosorbent on batch experiments. The effect of pH value and various concentrations on biosorption capacity of *Posidonia oceanica* were evaluate. Biosorption kinetics and isotherms equilibrium were examined.

2. Materials and methods

2.1. Preparation of the biomass

Fresh samples of the local *P.oceanica* biomass were harvested from the west coast of Algiers. Sample preparation consist on preliminary cleaning, the raw material was rinsed with tap water to remove impurities (sand and salt of the surface), and then it was rinsed with distilled water and dried on sun light. Before use, the biomass was cuts into segments of 2-4 cm. A pre-treatment of biomass was carried with 0.1 mol HCL for 1 h under stirring, and then washed thoroughly with distilled water at several time to remove excess of salts from the biomass and finally dried in oven at 60°C for 24 h. Then, they were ground in laboratory blender and stored at ambient temperature.

2.2. Chemicals

All chemicals used in this study were of analytical grade and solutions were prepared using deionized and distilled water. Stock solution of methylene blue was prepared by dissolving $C_{16}H_{18}ClN_3S$ x H_2OX in water figure 1. The concentration of unadsorbed methylene blue dyes in the aqueous solution were measured colorimetrically using a spectrophotometer. The absorbance of the color of methylene blue was read at 665 nm.

2.3. Batch biosorption experiments

2.3.1. Equilibrium studies

The performance of *P.oceanica* is described through the batch experiment. Firstly, adsorption isotherms, 100 mg of biosorbent were mixed with 100 mL of methylene blue solution during 24 h, at 20 °C and 150 rpm stirring rate, at the optimum pH 5. The pH was controlled using molar solutions HCl and NaOH. After this, aliquots were removed from the supernatant and filtered through membranes using 1-2 µm pore size filtration membrane. Filtrates were analyzed by spectrometry (S), using a UV-vis spectrometer (Biomate spectrometer-Thermo electron corporation, Model TM3). The amount of adsorbed by biosorbent at equilibrium was calculated from the mass balance of the equation as given follows:

$$q = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where q is the adsorption amount at equilibrium (mg/g), C_o and C_e are metal concentrations in the initial solution and after adsorption (mg L−1), respectively; V is the volume of solution (L) and W is the mass of biosorbent used (g). For all experiments, the MB concentration was determined by an UV-visible spectrophotometer at wavelength corresponding to the maximum absorbance of the dye solution (λmax=665nm).

2.3.2. Kinetic experiments

Kinetics experiments were carried out to determine equilibrium time for biosorbent, by adding a known amount of *P.oceanica* and methylene blue solution. Samples were taken at fixed time intervals.

The pH and temperature of the solution were maintained at pH 5 and 20 °C respectively. The flasks containing 500 ml of methylene blue solution of known initial concentration with 1 gL^{-1} of algal biomass and stirrer at constant agitation speed 200 rpm to ensure equilibrium was reached.

3. Results and discussion

3.1 Influence of pH

The pH of aqueous solution plays an important role in the adsorption of dyes onto biomass [17]. The pH affects significantly the adsorption capacities of the Methylene Blue onto the biomass. Figure 2. shows the influence of pH on the sorption of methylene blue using P.oceanica for pH ranging between 2 and 7. The adsorption capacity of methylene blue increases sharply when pH is below 3.0, and then the adsorption becomes to reach the equilibrium state at pH 5. The pretreatment of the biomass with HCl allows reducing the variation of pH during dyes sorption taking into account the characteristics of the biosorbent. This is an important parameter for stabilizing the material, and reducing the possible occurrence of local phenomena of dyes micro-precipitation and for comparison of sorption performance.

Hamdaoui [10] showed that adsorption of Methylene Blue on sawdust and crushed brick increased by increasing pH (until a value of 9). For pH lower than 5 both adsorbents were positively charged: in this case, the adsorption decreased because methylene blue is a cationic dye. At pH 2 and 5, a competition occurs between protonated MB and also there exists an electrostatic repulsion between the positively charged surface of biomass and BM [18].

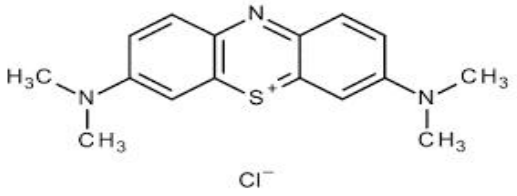

Figure 1. Chemical Structure of Methylene bleu (MB).

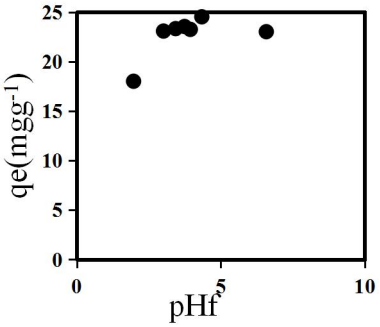

Figure 2. Influence of pH of BM sorption using Posidonia oceanica.

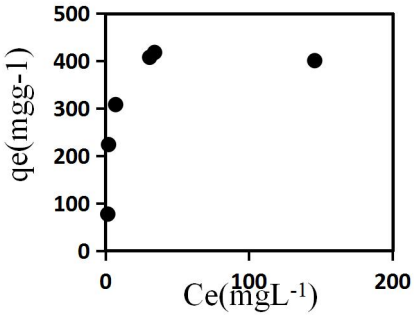

Figure 3. Experimental equilibrium data for modeling with Langmuir isotherm.

3.2. Sorption isotherm

Figure 3 shows the sorption isotherms of the methylene blue biosorption using dried P.oceanica. The isotherms were drawn based on equilibrium concentration. All experiments were carried out initial methylene blue concentration in the range 5-100 ppm and the equilibrium pH was 5. There are numerous reports on dyes biosorption with *P.oceanica* [2-4, 13]. In this study, two models Langmuir (1916) [19] and Freundlich (1906) [20] were commonly used and the appropriate

model was identified to better understand the dye–podidonia interaction. From the best correlation obtained by using Langmuir model [19], it can be concluded that the monolayer adsorption is more suitable to explain the adsorption of (MB) and indicates at the same time that chemisorption might also be involved in the sorption process. The maximum sorption capacity reached 357 mgg^{-1} at pH 5. The affinity coefficient (b coefficient) was close to 1.07 Lmg^{-1} at pH 5(table1).

Table 1. Maximum adsorption capacity (q max) of methylene blue by *P.oceanica*.

Dye	Langmuir constant		
Methylene blue	q(mgg^{-1})	b	R2
	357	1.07	0.995

The data demonstrated that the biosorbent in this work had relatively high capacities of the methylene blue dyes. Comparative and competitive biosorbents for methylene blue sorption are reported in table 2. *Posidonia oceanica* can be compete with others adsorbents to remove methylene blue such as zeolite [21], rice husk [22], *Caulerpa cemosa* [23], clay [24], and commercial activated carbon [25, 26]. It can be seen that the qm value varies significantly for different biosorbents and that by comparison, the posidonia indicates a good capacity to adsorb (MB) ions from aqueous solutions.

Table 2. Comparison of methylene blue sorption for different sorbents.

Biosorbent	qm or qmax (mgg^{-1})	Reference
Activated charcoal	25.25	[12]
Posidonia oceanica	5.56	[14]
Crosslinked chitosan /bentonite composite	142.86	[15]
Zeolite	10.82	[21]
Rice husk	40.58	[22]
Caulerpa cemosa Var.cylindracea	5.23	[23]
Clay	6.3	[24]
Commercial activated carbon	930.3	[25]
Commercial activated carbon	200	[26]
Posidonia oceanica	357	In this study

3.3. Adsorption Kinetics

3.3.1. Effect of initial dye concentration

The influence of concentration was studied at room temperature by fixing the solution pH and varying the initial concentration in the range of 25-50-100 mg/L for MB dye. Figure .4. shows the effect of contact time of methylene blue adsorption. It can be noticed that the sorption processes at different concentrations are fast in the time within 30 min. In order to describe adsorption kinetics, the two most commonly used kinetic models of pseudo first-order [27], pseudo second-order kinetic [28] were used to test the experiment data, respectively.

The first-order rate model may be represented in Eq. (2):

$$\mathrm{Ln}\,(qe - qt) = \ln qe - k_1 t \tag{2}$$

where qt and qe are the amount of methylene blue adsorbed (mgg^{-1}) at time t (min) and at equilibrium, respectively, and k_1 is the rate constant of the pseudo-first-order adsorption process (min^{-1}).The pseudo-second-order model is expressed in Eq. (3):

$$\frac{\mathbf{1}}{\mathrm{qt}} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\mathrm{t} \tag{3}$$

where k_2 is the constant of pseudo-second-order rate (g mg^{-1} min^{-1}). On the basis of the experimental data of q_t, the equilibrium adsorption capacity qe and k_2 can be determined from the slope and intercept of the plots of t/q_t against t.

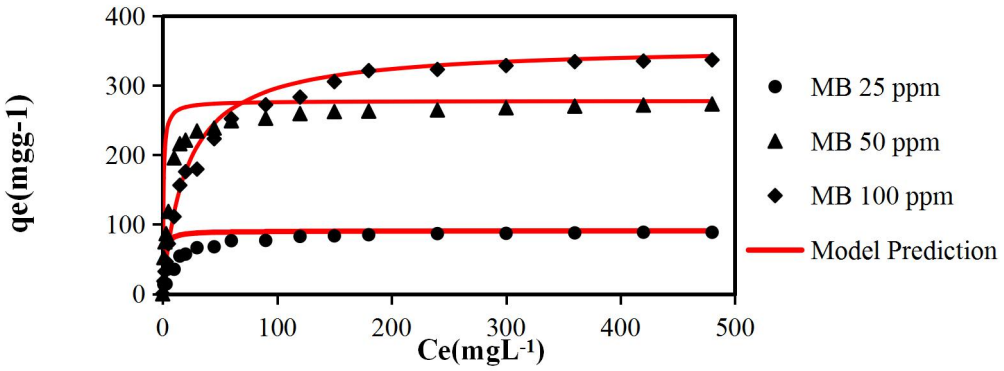

Figure 4. Influence of initial dye concentration (C0, mgMBL^{-1}) on MB uptake kinetics (pH 5; SD: 0.1 gL^{-1}; C0: 50 mg MBL^{-1}; PS: G3; curves represent the modeling of uptake kinetics with the PSORE).

Figure 4 presented the effect of concentration on the dye adsorption capacities of MB dyes on the P.oceanica. An increase in the concentration led to an increase in initial adsorption rate. Based on the obtained R2, of the linear forms of different models, it is observed that pseudo-second-order rate model describes the mechanism of sorption of MB on biomass better than pseudo first-order model.

4. Conclusion

Methylene blue (MB) was selected as a model dye in order to evaluate the capacity of the P.oceanica to remove dyes from aqueous solutions. The pH optimum is found close to pH 5. The biomass P.oceanica can be used as good as new biosorbent for the biosorption of MB. Maximum sorption capacities 357 mgg^{-1} at pH 5 still comparable to the level reached by some biosorbent in the literature. Kinetic experiment can be well represented by the pseudo-second-order kinetic model. The adsorption isotherms could be well fitted by the Langmuir equation confirming that adsorption of (MB) onto P.oceanica ocured by chemisorption. P.oceanica can be developed as cost effective adsorbent from textile and other wastewater.

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