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Removal of Methylene Blue Dye by Adsorption on Natural Sand

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Abstract

Synthetic dyes are widely used in industries such as rubber, textiles, plastics, paper, and cosmetics to color their products. The effectiveness of adsorption for dye removal from wastewater has made it an ideal alternative to other expensive treatment methods. The purpose of this study was to investigate the feasibility of optimization and removal of dye Methylene Blue (MB) from aqueous solutions by using beach sand as an extremely low cost adsorbent. The sand was collected from south of Morocco. The adsorption of Methylene blue on sand has found to be dependent of contact time. Under the optimum conditions: A pH = 6.5 and T = 20°C, the sorbent could remove more than 99%. According to the results of experiments in this research, adsorption kinetic was found to adopt the pseudo-second order kinetic model, which was the best appropriate model to describe the adsorption process. The maximum adsorption capacity was found to be 0.25mg.g^{-1} and a kinetic constant K_2 of 1.99 g.mg^{-1}min^{-1}. This makes it an interesting option for dye removal from aqueous solution of dye.

Keywords

Wastewater, Adsorption, Methylene Blue, Natural Sand

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1. Introduction

Industrial wastewater is one of the major pollutants of the environment. Colored wastewaters are produced in many industries such as textile, pharmaceutical, food, cosmetic and leather industries [1, 2]. The discharge of organic color containing effluent cause huge damage to environment: colored wastewater prevents the penetration of sunlight into the water and reduces the speed of photosynthetic process [3–6]. More importantly, their carcinogenic effects and genetic mutations in living organisms are proved [7, 8]. Therefore, it is of importance to maintain human and environmental healthy by removing dyes using cheap and economical methods. However the harmful effect of dyes in aquatic ecosystem and human health require the development of treatment techniques for their elimination.

Hence their removal has recently become the subject of interest [9], but dye is not easily removed by conventional water treatment processes due to its complex molecular structure [10]. Various methods have been evaluated for this purpose, such as electrochemical coagulation, using membranes, photocatalytic techniques, electrochemical methods, ultrasonic, mineralization, electrolysis, advanced oxidation and chemical reduction. Biological techniques include bacterial and fungal biosorption and biodegradation in aerobic anaerobic or combined anaerobic/aerobic treatment processes [9]. Since adsorption process is the most economical method doesn't require high energy consumption and has a simpler operational capability and is a unit operation, easily feasible technically. In most cases, it is

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preferred to other techniques [11-13]. Excellent adsorbents can be used such as activated char coal, silica gel, activated alumina, zeolites, etc. However a recently reviewed literature

interestingly highlights the adsorption by zirconium oxide [14], silicon oxide [15], titanium oxide [16, 17] and other oxides like titaniferous sand [18].

One of the most widely used adsorbents is activated carbon due to its high adsorptive properties. However, activated carbon is not easily and economically available because of its expensive cost that hinders its application at a large scale [19]. Therefore, many studies have been conducted to find out inexpensive alternative adsorbent. That's what inspired us to use natural sand as adsorbent since the latter has a very low commercial value. Natural sands contain active components that can strongly adsorb positively charged organic material from an aqueous solution. Generally the phenomenon of adsorption of a dye on a support is influenced by several factors: electronic structure of the adsorbed molecule [20], size and shape of the molecule [21], hydrophobicity and water solubility of the molecule [22], composition of the adsorbent [23]…etc.

This paper aims to determine the beach sand (this is sand that is black in color) as a potential low-cost and easily available adsorbent in removing the Methylene Blue from aqueous solution.

2. Materials and Methods

2.1. Presentation of the Study Area

The Beach sand which was used in this study as dye sorbent was collected from Taghazout beach, 24 km away from Agadir city, Morocco. It is black and metallic aspect (Figure 1). The sand contains 60% Silicon oxide. In addition to SiO_2, it contains other oxides such as: Al_2O_3, $CaCO_3$, Fe_2O_3, TiO_2... The characteristics of the natural sand were a porosity of 34% and a density of 2.56 g/m3. Methylene Blue (cationic dye) was used for the adsorption studies. MB dye was purchased from TECHNIPHARMA Morocco.

2.2. Methods

Stock solution of dye was prepared by dissolving 10 mg of dye in distilled water in 1000 mL volumetric flask. Batch experiment was carried out to determine the optimum adsorption isotherm. Trials of adsorption were carried out by a VELPA SCIENTIFICA agitator and a series of Erlenmeyer flasks. The experiment was based on making contact with agitation for a given time the mass of natural sand (2g) and the given volume dye in solution (50 ml). When the contact between the sand and the pollutant was established, the run time was set. In order to determine the residual concentration of Methylene Blue after adsorption, UV–Visible spectrophotometer (Jenway, Serial: 67XX) was used at a wave length corresponding to the maximum absorbance for the dye solution (max = 664 nm).

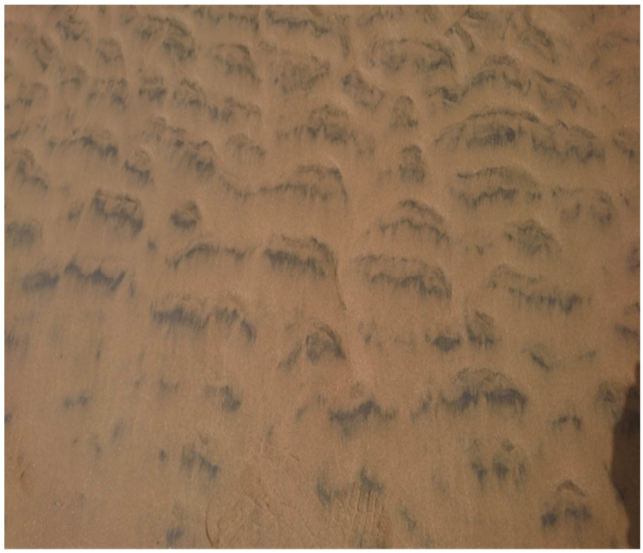
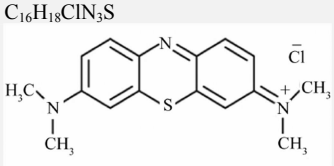


Figure 1. Sample of natural sand used as an adsorbent.

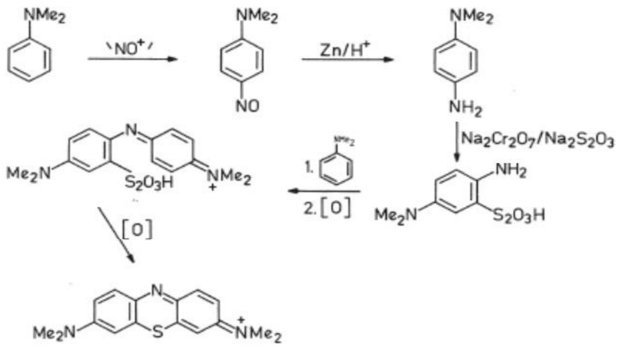
3. Results and Discussion

Methylene Blue is a cationic dye [24], it is a heterocyclic aromatic compound used as a dye for different staining procedures, it is in the form of a dark green powder and is very soluble in water; Table 1shows physical and chemical characteristics of this adsorbent.

Table 1. Chemicaland physical properties of methylene blue.

Chemical names	**methylene blue and Methylthioninium chloride**
C A S Number	61-73-4
Familly	Basic dye
Molecular formula	$C_{16}H_{18}ClN_3S$
Structure chemical	
Molecular weight	319.85g/mol
Maximum Absorbance Max	664 nm
Water Solubility	43.60 g/L (25°C)
Melting point	190°C
pH	5.9
pKa	3.8
Density	1.75 g/cm^3 (22°C)

Methylene blue is prepared following the reaction below (Reaction 1):



3.1. Effect of Contact Time

Removal of dye by sand was carried out after 5, 10, 20, 30, 40 and 60 min of starting the adsorption process. Results are shown in Figure 2. For MB, when contact time increases, removal percent goes up and finally reaches to a constant level which deals with reaching equilibrium after 30 min. After then, the percentage of dye adsorbed was calculated using equation (1) [25].

$$\%\ Removal = \frac{C_0 - C_e}{C_0} X\ 100 \qquad (1)$$

whereCe and C_0 are equilibrium and initial dyes concentration ($mg.L^{-1}$) respectively. In adsorption studies, q_e ($mg.g^{-1}$) is the amount of adsorbed dye on sorbent in equilibrium state and it can be calculated according to equation (2) [26]:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \qquad (2)$$

where C_0 and C_e ($mg.L^{-1}$) are respectively the concentration of dye at initial point and at equilibrium, V (L) isthe volume of the solution and m (g) is the mass of dryadsorbent used.The kinetics highlighted 60 minutes of duration. The retention of MB was 99.% in the operational conditions (pH = 6.5 and T = 20°C) consistent of an adsorption capacity of 0.25 mg/g

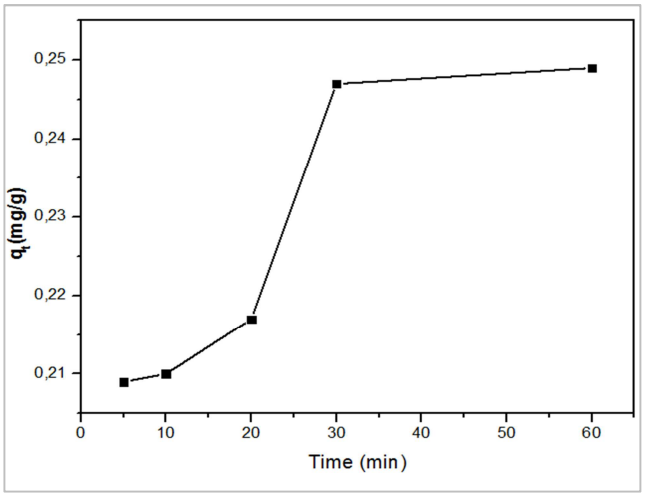


Figure 2. Effect of contact time on the adsorption of the MB: pH=6.5; T=20°C and V=50mL.

3.2. Kinetic Study of Adsorption

In order to find the mechanism of adsorption of dye on the sand, two kinetics models were used. These are the models of the first pseudo order and the second pseudo order. First pseudo order was calculated by equation (3):

$$\ln(q_e - q_t) = -K_1 . t + \ln q_e \qquad (3)$$

where the amount of dye adsorbed at any time is shown as $q_t(mg.g^{-1})$, t is contact time (min) and the pseudo first order constant is K_1 (min^{-1}). By plotting the log ($q_e - q_t$) versus t, K_1 and q_e were calculated from the slope and intercept of the plot, respectively. Pseudo second order was calculated by equation (4):

$$\frac{t}{q_t} = \frac{1}{K_2 . q_e^2} + \frac{1}{q_e} . t \qquad (4)$$

By plotting the ln (q_e - q_t) versus t, K_1 and q_e were calculated from the slope and intercept of the plot, respectively.

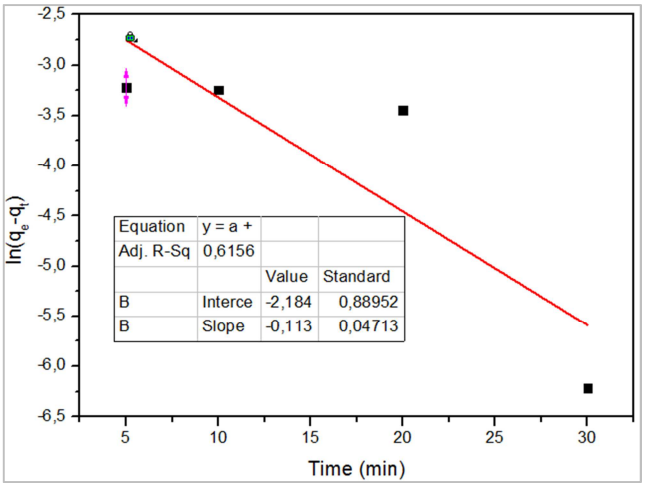


Figure 3. Linearization according to the pseudo first order model.

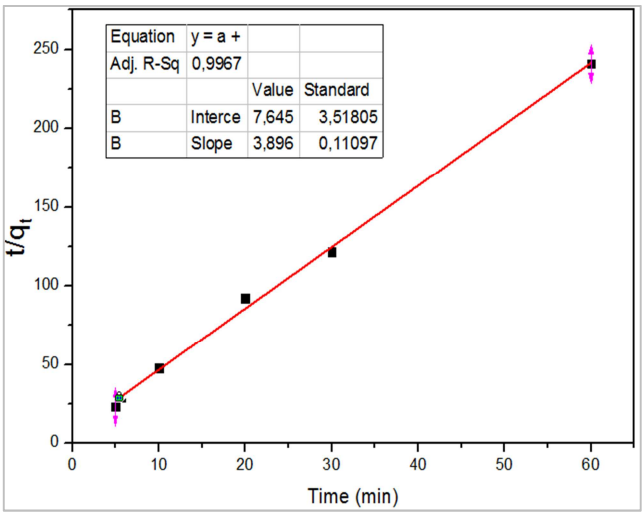


Figure 4. Linearization according to the pseudo second order model.

The adsorption rate constant of this model, K_2 ($g.mg^{-1}.min^{-1}$)

is the pseudo-second order constant which was obtained from the intercept of the plot of t/q_t against t. The slope of this plot shows q_e. The results of the kinetics modeling are displayed in Figure 3 and Figure 4.

Based on the obtained correlation coefficients R^2, the kinetic model of first pseudo order is inconsistent with the experimental results. However, the pseudo second order model better described the adsorption kinetics. Its reveals that pseudo second order is the best fitted model for kinetic of removal of Methylene Blue. The kinetic parameters of the model are displayed in Table 2.

Table 2. Kinetic parameters of the pseudo second order model.

Kinetic parameters	q_e (mg/g)	K_2 ($g.mg^{-1}min^{-1}$)	R^2
Values	0.25	1.99	0.997

4. Conclusion

This work consisted on studying the adsorption of Methylene Blue which is used as a dye by using beach sand as adsorbent. The contact time was investigated. The adsorbed amounts of dye increased with increase in contact time and reached the equilibrium in 30 mins. The equilibrium data have been analyzed using the first pseudo order and the second pseudo order models. The characteristic parameters for each model and related correlation coefficients have been determined from graphs of their linear equations. It was found that the second pseudo order model appears to fit the isotherm data better than the first pseudo order model. It can be concluded that the adsorbent used in this study has the capacity of removing the MB from dye wastewater.

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