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Application of chemically modified beach sand as low cost efficient adsorbent for dye removal

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In the current work, beach sand (BS) and beach sand coated with polyaniline (BS/Pani) were used as an efficient green adsorbent for dye removal from aqueous solutions. Methylene blue (MB) was chosen as a test probe for the evaluation of the selected adsorbents for dye removal efficiency. The adsorption experiments were carried out in batch system and the effect of some important empirical parameters affecting adsorption processes were then investigated. The experimental data were also analyzed by Langmuir and Freundlich adsorption models. Based on the correlation coefficient values obtained (R^2), it was found that equilibrium data for both adsorbents fitted well with both models. Adsorption data were also examined by pseudo-first-order and pseudo-second-order models and their respective rate constants were estimated. It was found that sorption of MB dye onto BS/Pani is fitted very well with pseudo-second-order kinetic model. Using the equilibrium concentration constants obtained at different temperatures, important thermodynamic parameters of the sorption process were calculated. It was found that the chemically modified beach sand is an effective and low cost adsorbent for dye removal from aqueous solutions.

1. Introduction

Industrial developments in recent years have left their impression on the environmental society. Many industries like the textile industries use dyes to color their products and thus produce huge wastewater containing various dyes. The removal of dyes from waste effluents becomes environmentally important because even a small quantity of dye in water can be toxic and highly visible[1,2]. Real textile wastewater is a mixture of dyes, organic compounds, heavy metals, dissolved solids, surfactants, salts, and chlorinated compounds[3]. The cationic dyes are commonly used initially for dyeing of silk, leather, plastics, paper, cotton mordanted with tannin and also in manufacturing of paints and printing inks[4]. In the dyeing processes consider amount of dyes are lost because of the low

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levels of dye-fiber fixation. Acute exposure to MB may cause serious hazards such as increased heart rate, shock, vomiting, cyanosis, jaundice, and tissue necrosis in humans[5]. In the recent years, several works have appeared in the scientific literature reporting adsorption of several dyes, most notably among them, MB by natural and synthetic adsorbents.

Adsorption process provides an optimum technical alternative to remove various chemicals such as dyestuff and pigments from wastewater due to their simple design, easy operation, low-cost, and high efficiency even in their more concentrated form[6-9]. In this study, beach sand, a very available and cheap natural material was selected as adsorbent for its application for dye removal. In order to improve its sorption capacity, it was also modified with polyaniline via simple cast solution technique. The effect of some important parameters such as initial dye concentration, pH, adsorbent dosage, temperature, salt and contact time on the adsorption of MB onto both treated and untreated beach sand were compared.

2. Materials and Methods

2.1. Chemicals and instruments

All of the chemicals and reagents employed in this work were purchased from Merck and were used as received. Beach sand (BS) was collected from Bandar Anzali seaside (North of Iran). They first washed with copious tap water for removing any dirt, dust and other impurities and were finally washed with distilled water, dried in an oven (at 100 °C) and sieved before use (50-70 mesh). The stock solutions of MB dye were prepared in distilled water and the working solutions were prepared by diluting the stock solution with distilled water to the needed concentrations. MB analysis was carried out spectrophotometrically using a single beam Perkin-Elmer UV-vis spectrophotometer.

A calibration curve was obtained at a wavelength of 660 nm for quantitative measurement of unadsorbed MB dye. A Metrohm pH meter (model 827) with a combined double junction glass electrode was used for showing pH values. The pH was changed by gradual addition of incremental amounts of either dilute HCl or NaOH to test solution. A shaker equipped with a water bath (Grant Operation C100196) was used for controlling of temperature. Scanning electron micrograph (SEM) characterization was carried out using XL30 (Philips Co, Netherlands) apparatus operated at a 25 kV accelerating potential.

2.2. *Preparation of BS/Pani adsorbent*

Polyaniline was first synthesized chemically using 0.20 M freshly distilled aniline in HCl 1 M solution. Ammonium persulfate 0.20 M was employed as chemical oxidant. EB was prepared by treatment of the synthesized Pani/HCl powder with 0.50 M NH_3. The solvent allowed to evaporating at 50–60 ºC using an air circulating oven. For coating of BS particles, BS particles were first washed with enough distilled water for removing any impurities such as dust. The dried BS particles was then treated with a solution of paraffin oil in 1, 2 dichloroethane solvent (10% v/v) in order to stabilize the BS substrate in polymer cast solution during coating. The polymer solution was prepared by dissolving of polyaniline (Emeraldine Base form, EB) in concentrated formic acid with a concentration of 1% (w/w) as described previously[10,11]. The solution was agitated for 1 h using a magnetic stirrer operated at a constant speed and at room temperature. BS particles previously coated by paraffin were added into the polymer solution and the mixture allowed stirring for duration of 5 h and left overnight without stirring. The polymer coated sand particles (BS/Pani) were filtered, washed with sufficient distilled water, and then dried in an oven at temperature about 60 °C before use.

2.3. Adsorption experiments

The data obtained in batch model studies were used to calculate the equilibrium MB uptake quantity. The amount of MB dye removal was calculated using the following equations[7]:

$$\%\text{Sorption}=\frac{(C_0-C_e)}{C_0}\times 100, \quad (1)$$

$$\frac{x}{m}=\frac{(C_0-C_e)V}{m}, \quad (2)$$

where C_o and C_e are the initial and equilibrium MB concentration (mg L^{-1}) respectively, x/m is the adsorption equilibrium MB uptake quantity per unit mass value (mg g^{-1}), V the sample volume (L), and m is the dry weight of the used adsorbent (g).

3. Results and discussion

3.1. SEM characterization

The surface morphology of an adsorbent can be extensively characterized using scanning electron microscopy (SEM). It is useful for determining the particle shape, porosity and appropriate size distribution of an adsorbent. The surface morphologies of BS before and after coating were characterized by SEM (Figs. 2a and 2b). As the SEM images show, BS particles were coated by polyaniline layer and there are many pores and pleats on the surface of the BS/Pani which provided active sites for dye entrapment.

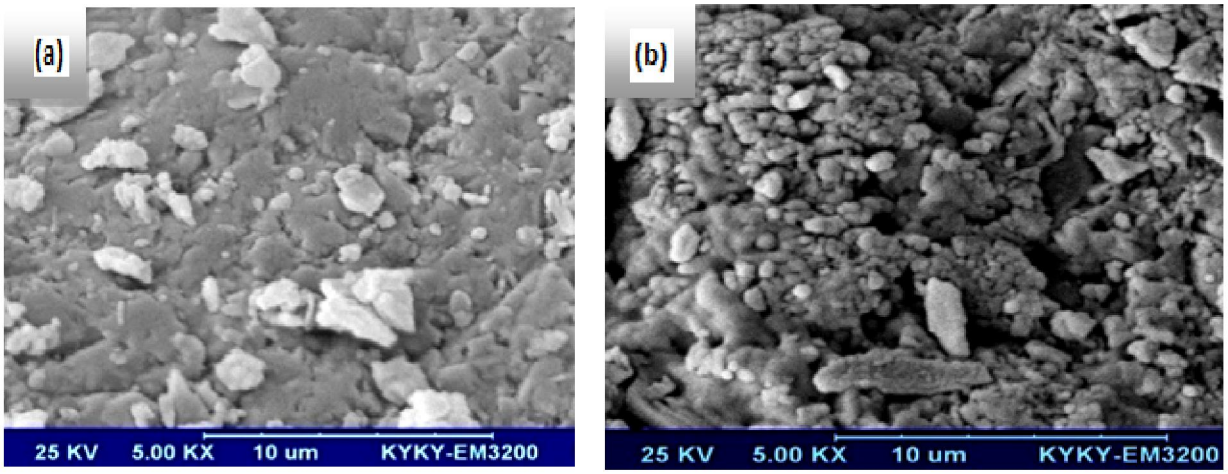

Fig. 1. SEM images of treated and unmodified beach sand: (a) BS, (b) BS/Pani

3.2. Effect of pH

The pH is usually an important factor affecting many adsorption processes. The pH of a medium will control the magnitude of electrostatic charges which are imparted by ionizable adsorbates. The hydrogen ion affects the degree of ionization of ionizable dye molecules and also the surface charge of the adsorbents[13]. In this study, the effect of pH on the amount of MB removal was analyzed over the pH range from 2-12. The pH was adjusted using 0.10 M NaOH and HCl solutions. In this study, 50 mL of 100 mg L^{-1} MB dye solution was agitated with 0.50 g of adsorbent under a constant agitation speed of 170 rpm at room temperature for duration of 60 min. As shown in Table.1 with increasing of pH, sorption of MB onto BS/Pani is increased. However, the improvement was not very considerable. On the other hand, it could be concluded that MB dye uptake by the used adsorbents was not very pH dependent.

Table 1. Effect of initial solution pH solution on dye removal percentage

pH	2	4	6	8	10	12
BS	51.6	52.0	52.0	53.5	53.8	58.0
BS/Pani	89.3	90.8	91.0	91.2	96.8	97.1

3.3. Effect of initial concentration

To study the effect of initial concentration of MB on its adsorption, aliquots of 50 mL MB solutions with different initial concentrations (20-140 mg L^{-1}) were treated with fixed amounts of adsorbents (0.50 g) under a constant agitation speed of 170 rpm at room temperature for constant exposure time (60 min). As the results show, a great improvement in dye removal is observed in the case of BS/pani. With increasing the initial concentration of MB, sorption capacity increases linearly up to 120 mg L^{-1} (Fig. 2). However, after the initial concentration of 120 mg L^{-1} some desorption was observed especially in the case of BS adsorbent. The improved sorption of MB by polymer modified BS can be due to the strong electrostatic interactions between charged dyes molecules and charged coating on the surface of BS particles.

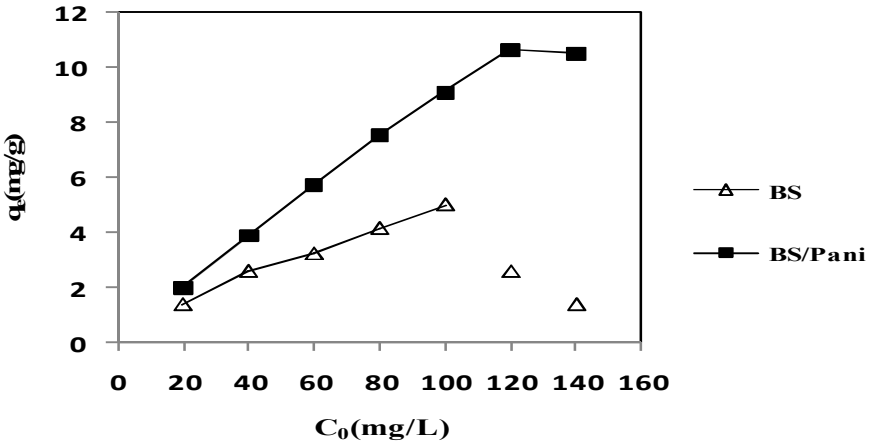

Fig. 2. Effect of initial MB dye concentration on sorption by BS and BS/Pani

3.4. Adsorption isotherms

The analysis of adsorption process requires equilibrium to better understand the adsorption process. Equilibrium isotherm equations are used to describe the experimental sorption data. Sorption isotherms provide fundamental physiochemical data for evaluating the applicability of sorption process at constant temperature and equilibrium state[13-15]. The sorption process is usually described by the Langmuir and the Freundlich isotherm[16]. In the present investigation, the equilibrium data were analyzed using this two equilibrium models for describing solid–liquid sorption systems. The Langmuir equation assumes that there is no interaction between the adsorbate molecules and the sorption is localized in a monolayer where q_m is the monolayer capacity[15-17]. It is then assumed that once a dye molecule occupies a site, no further sorption can take place at that site. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. The Langmuir isotherm as an important model has been used for the sorption of variety of compounds. The linear form of Langmuir is expressed as:

$$\frac{1}{q_e} = \frac{1}{K_L C_e q_m} + \frac{1}{q_m} \tag{3}$$

where, q_e is the amount of dye sorbed (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), q_m is the maximum adsorption capacity for a complete monolayer (mg g^{-1}), and K_L is the sorption equilibrium constant related to energy of adsorption (L mg^{-1}). A plot of $1/q_e$ versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(K_L C_e q_m)$. The Freundlich model is often applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The linear for of Freundlich isotherm is represented by:

$$\log\frac{x}{m} = \log K_F + \frac{1}{n}\log C_e, \quad (4)$$

where, q_e is the equilibrium dye concentration on the adsorbent (mg L^{-1}); C_e (mg L^{-1}) the equilibrium dye concentration in solution, K_F (mg g^{-1} (L $mg^{-1})^{1/n}$), the Freundlich constant which represents the adsorption capacity and n is the heterogeneity factor. Freundlich empirical parameters were calculated from the slope and y axis intersection of the linear plot of log q_e versus log C_e. The data obtained were summarized in Table 2.

Table 2. Isotherm parameters obtained from adsorption of MB onto BS and BS/Pani

Adsorbent	Langmuir Parameters			Freundlich parameters		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F	n	R^2
BS	6.45	0.046	0.989	3.2	0.58	0.982
BS/Pani	11.24	0.499	0.988	4.0	2.60	0.987

A comparison of maximum monolayer adsorption capacity of MB onto the two examined adsorbents indicates BS/Pani has a relatively larger adsorption capacity compared to untreated BS. This shows that modification of BS by Pani improves its sorption properties toward MB dye removal considerably.

3.5. Effect of contact time

Batch tests were done at different contacting times at the initial concentration of MB 100 mg L^{-1} and adsorbent dose 0.50 g in 50 mL solution of MB at the room temperature. Agitation was made at a constant agitation speed of 170 rpm for duration of 60 min. The samples were then collected at 10, 20, 30, 40, 60 min and were centrifuged. The left out concentration in the supernatant solution was analyzed using a UV-Vis spectrophotometer. The adsorption capacities for BS and BS/Pani toward MB dye removal reached about 5.0 and 9.1 mg g^{-1} respectively (Fig. 3).

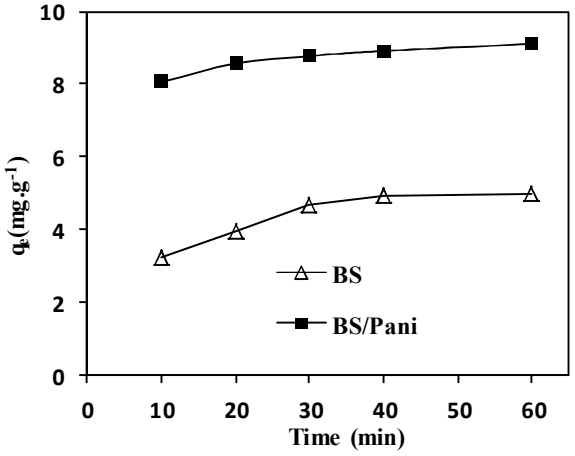

Fig. 3. Effect of contact time on sorption of MB onto BS and BS/Pani

3.6. Effect of adsorbent dose

Adsorbent amount is an important parameter in the determination of adsorption capacity. In addition, study of the effect of adsorbent dosage gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum dosage. Batch adsorption tests were done at

the initial concentration of MB 100 mg L^{-1} and the various amounts of the adsorbent dose were contacted with 50 mL of dye solution. Agitation was made for 60 min at a constant agitation speed of 170 rpm at room temperature. The samples were then centrifuged and the left out concentration in the supernatant solution was analyzed as said before. As the results indicate (Fig. 4), BS/Pani is more effective for dye removal at all sorbent dosages. With increasing the amount of sorbent, dye removal percentage is increased too. The enhancement of sorption with higher amount of sorbent can be attributed to the increased surface area and availability of more sorption sites. The highest dye removal capacity was achieved when sorbent dosage of 0.50 g of BS/Pani was used. The further increase of the adsorbent dose did not make any important change concerning the sorption capacity.

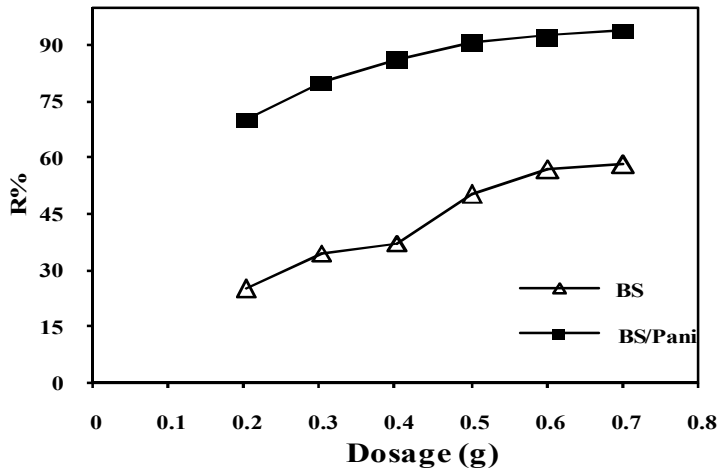

Fig. 4. Effect of adsorbent dosage on sorption of MB dye onto BS and BS/Pani

3.7. Effect of temperature

Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. If the adsorption capacity increases with increasing temperature then the adsorption is an endothermic process and the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process[18]. The effect of temperature on sorption capacity of BS and BS/Pani was investigated at temperature range from (0-100 ºC). The results show that an increase in temperature leads to a slight increase in adsorption values (Table 3). It might be concluded that adsorption of MB by BS and BS/Pani is an endothermic process. However, sorption improvement upon temperature rise is not very considerable.

Table 3. Effect of temperature on removal % of MB dye of BS and BS/Pani

T (K)	273	298	323	348	373
BS	47.8	50.0	52.0	54.6	56.5
BS/Pani	90.0	91.0	92.5	92.7	93.5

3.8. Kinetics Study

The rate at which the species are removed from solution onto an adsorbent surface is an important factor for designing treatment plants. Thus in order to characterize the adsorption process of the dyes onto the selected adsorbents, two kinetic models suggested by Lagergren and Mac Kay and HO were investigated namely the pseudo first order and pseudo second order model[19,20]. These two models are commonly used to describe the adsorption behavior of pollutants on solid surfaces. The linear forms

of the pseudo first order and pseudo second order equations (Eqs 5 and 6) can be represented as the following:

$$\log(q_{e1} - q_t) = \log(q_{e1}) - \frac{k_1}{2.303} t, \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}}, \quad (6)$$

where q_t and q_e (mg g^{-1}) are the amount of dye adsorbed at equilibrium and at time t (min) respectively; k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order and second order rate constants. The adsorption rate constant (k_1) and q_{e1} are calculated from the slope and y intercept of the linear plot of plot of log (q_{e1}-q_t) against t. The slopes and intercepts of plots t/q_t versus t were calculated to access the pseudo second-order rate constant K_2 and q_{e2}. Parameters of the kinetic models were extracted from the experimental data of this study and the linear plots of the kinetics equations. The kinetics parameters derived from both Pseudo-first and second order linear plots (not shown) were summarized in Table 4.

From the high regression coefficient (R^2= 0.999) as well as the good agreement between experimental q_e (9.1) and calculated q_{e2} (9.4) from the pseudo second-order kinetic model, it could be concluded that MB sorption onto BS/Pani is mostly happened via chemisorption mechanism. Also for untreated beach sand, the pseudo first-order kinetic model is best fitted, because of the closeness of experimental q_e value with the calculated q_{e1}.

Table 4. Comparison of the different kinetic model parameters at 25 ºC

Adsorbent	Pseudo-first-order model			Pseudo-second order model			
	q_{e1} (mg/g)	k_1 (g/mg.min)	R^2	q_{e2} (mg/g)	k_2 (g/mg.min)	$q_{e\,(exp)}$ (mg/g)	R^2
BS	6.15	0.12	0.992	8	0.030	5.0	0.812
BS/Pani	1.89	0.03	0.962	9.4	0.55	9.1	0.999

3.9. Thermodynamic study

Standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0), of adsorption can be estimated from van't Hoff equation (Eq. (7)) given as following:

$$\ln K_c = \frac{-\Delta H^o_{ads}}{RT} + \frac{\Delta S^o}{R}, \quad (7)$$

where, T is absolute temperature and R is the universal gas constant, K_c is adsorption equilibrium constant. The K_c value is calculated from the Eq. (8):

$$K_c = \frac{C_{Ae}}{C_{Se}}, \quad (8)$$

where C_{Ae} is the amount of dye adsorbed on the adsorbent per liter of the solution at equilibrium (mg L^{-1}) and C_{Se} is the equilibrium concentration of the dye in the solution (mg L^{-1}). The plot of ln K_c against 1/T (T in K) should be linear. Thermodynamic parameters are then obtained from the slope and y intercept of the linear plot. The values associated with the thermo dynamic parameters are listed in Table 5.

In many cases ΔG^0 values are negative for BS/Pani which indicates that adsorption of MB onto this adsorbent is a spontaneous process. While the positive ΔG^0 values for BS shows the non-spontaneous adsorption process and more needed activation energy.

Table 5. Thermodynamic parameters for sorption of MB on BS and BS/Pani

Adsorbent	T (K)	K_c	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	$\Delta S°$ (J/mol.K)
BS	273	0.09	5.426	2.98	-9.06
	298	0.10	5.704		
	323	0.11	5.967		
	348	0.12	6.127		
	373	0.13	6.330		
BS/Pani	273	0.90	0.24	3.94	13.57
	298	1.02	-0.04		
	323	1.23	-0.56		
	348	1.27	-0.69		
	373	1.44	-1.13		

The positive value of $\Delta S°$ also indicates the increased randomness during the uptake of MB dye onto BS/Pani particles and reflects the affinity of this adsorbent for MB dye. With displacement of the adsorbed water molecules by the dye molecules, more translational entropy is gained, thus allowing the prevalence of randomness in the system. Positive value of ΔH^o reveals endothermic nature of adsorption.

4. Conclusion

Application of beach sand is a very cost effective substrate for coating with polyaniline in order to be used as efficient adsorbent for dye removal from aqueous solutions. Based on the adsorption isotherms, the adsorption data fitted well to both Langmuir and Freundlich equations. Sorption kinetic data revealed that the adsorption kinetics for BS followed the pseudo first order equation and BS/Pani conform pseudo second order equation. This suggests a chemisorption mechanism during dye uptake by BS/Pani. Negative values of $\Delta G°$ indicate the spontaneous nature of adsorption. Positive values obtained for $\Delta H°$ and $\Delta S°$ for BS/Pani, indicate that sorption process is endothermic and the spontaneity of the reaction is therefore mainly controlled by entropy factor.

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