

Acidic and Basic Dyes Removal by Adsorption on Chemically Treated Mangrove Barks

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Abstract

The purpose of this study is to investigate the adsorption characteristics of acidic and basic dyes onto chemically treated mangrove bark. The *Rhizophora Apiculata* barks, an industrial waste lignocellulosic product was obtained from the charcoal industry. The bark powder was chemically treated in an acidic formaldehyde solution to produce non-soluble adsorbent and used for the adsorption of dyes. Batch experiments were carried out for the adsorption of dyes molecules onto modified barks at room temperature (30 ± 2) °C. Various factors such as pH, contact time, initial dyes concentrations, and amount of adsorbent were taken into account, and promising results were obtained. The applicability of the Langmuir as well as Freundlich adsorption isotherms for the present system was tested. The equilibrium data were found to be well represented by the Langmuir isotherm equation. The monolayer adsorption capacity of modified barks for Malachite Green (basic dye) and Sunset Yellow FCF (acidic dye) adsorption was found to be 129.87 mg g^{-1} and 12.72 mg g^{-1} , respectively. The adsorption kinetics was found to follow pseudo-second order kinetic model for both dyes. These results indicate that mangrove bark could be employed as a low-cost material for the removal of the textile dyes from effluents.

Keywords: mangrove bark, adsorption, acidic dye, basic dye, adsorption isotherm, adsorption kinetics

1. Introduction

Water pollution by dyes is a worldwide problem particularly in textile industry where large quantities of dye effluents are discharged from the dyeing process. Considering both volume and composition, effluent from the textile industry was declared as one of the major sources of wastewater in ASEAN countries. Dyes are also widely used in other industries such as rubber, paper, plastic, cosmetic etc. There are more than 10,000 commercially available dyes with over 7×10^5 tonnes of dyestuff being produced annually across the world (Robinson *et al.*, 2001). The total dye consumption of the textile industry worldwide is more than 107 kg/year, and about 90% ending up on fabrics. Dye producers and consumers are interested in the stability and fastness of dyes and consequently, are producing dyestuffs which are more difficult to degrade after being used. It is estimated that 10–15% of the dye is lost during the dyeing process and released with the effluent (Ezgi *et al.*, 2009).

Various urban and industrial wastewaters are directly discharged into the environment. The dye-based effluent is a considerable source of non-aesthetic pollution since the presence of small amounts of dyes (below 1 ppm) is clearly visible. The chemical structure of dyes varies enormously, and some have complicated aromatic structures that resist degradation in conventional wastewater treatment process because of their stability to sunlight, oxidizing agents and microorganism. Many of the organic dyes are hazardous and may affect the aquatic life and even the food chain. Dyes are broadly classified as anionic (direct, acid and reactive dyes), cationic (basic dyes), non-ionic and zwitterionic depending on the ionic charge on the dye molecules. Cationic dyes are more toxic than anionic dyes (Nandi *et al.*, 2009).

In our century, waste disposal has become an increasing worldwide concern. The use of waste materials for different purposes can play a significant role in helping to solve disposal problems. In addition, utilization of waste materials can contribute to the wise and efficient use of materials, and to protect our environment. Many efforts, however, have been made to investigate the use of various low cost organic adsorbents.

A variety of materials are used as adsorbents for dyes, and various studies have been published on its adsorption on activated carbon, starch xanthate, alumina, low-grade manganese ore, crushed coconut shell, fly ash, sawdust, rice husk carbon, wood charcoal, bituminous coal, and lignite (Huseyin *et al.*, 2007). Therefore, the aim of this study was to investigate the potential of mangrove bark, an abundantly available solid waste, as a non-conventional adsorbent in the removal of a basic dye (malachite green) and acidic dye (sunset yellow) from aqueous solutions.

2. Materials and Methods

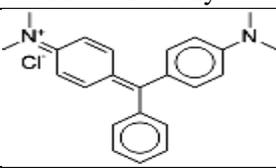
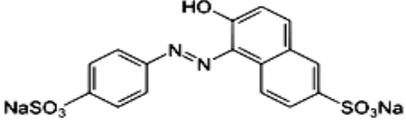
2.1. Adsorbent

The mangrove barks were collected from the charcoal factory in Kuala Sepetang, Perak, Malaysia. The collected barks were extensively washed with distilled water and air-dried. Air dried bark was crushed to small pieces before grinding into powder. After grinding, the bark powder was sieved using 250 mesh sieve. The adsorbent was produced based on formaldehyde pretreatment in acidic medium. Four gram of ground bark was added to a mixture of 37% formaldehyde and 0.10 M sulphuric acid (5/20, v/v). The mixture was refluxed at 50°C for 2 hours and filtered. The treated bark was washed with distilled water to remove excess acid and formaldehyde. Finally the treated bark was dried in the oven until constant weight and kept in a well-sealed container for further use (Tan *et al.*, 2010).

2.2 Adsorbate

Basic dye malachite green (MG) and acidic dye sunset yellow FCF (SY) were purchased from Merck Chemicals and their structures are illustrated in Table 1. Table I shows the characteristics of these dyes. The dyes were used as commercial salts without purification. Stock solution of 1000 ppm of dye was prepared by dissolving an accurately weighed quantity of dye, in deionised water. Experimental solutions of desired concentration were prepared by diluting this stock solution with deionised water.

Table 1 Characteristics of selected dyes

Dye	Structure of dye	λ_{max} (nm)	Molecular weight (g/mol)
Malachite Green (MG)		617	927.02
Sunset Yellow FCF		481.5	452.37

2.3 Point of zero charge

The determination of point of zero charge of treated mangrove bark was performed according to the batch equilibrium method in 0.01 M NaCl. The graph of difference in pH ($\Delta pH = pH_i - pH_f$) was plotted against pH_i . The pH_{ZPC} value of the adsorbent can be determined from the point of intersection of the curve to x-axis.

2.4 Sorption experiments

The batch adsorption studies were performed by adding a fixed amount of adsorbent into a number of 250 mL stoppered Erlenmeyers flasks containing 50mL of fixed initial concentration (100 mg/L) of dye solution with an optimum pH at a temperature of 30 °C. The flasks were placed on a shaker and agitation was provided at 150 rpm for 360 min. The dye concentrations were measured at equilibrium. The effect of pH on the amount of dye adsorbed onto modified bark was studied in the pH range from 2 to 10. The pH was carefully adjusted by adding a 0.10 M of HCl or NaOH solution using a pH meter (Denver Instrument, BASIC). The optimum pH was then determined and used throughout all adsorption experiments, which were conducted at various time intervals to determine the adsorption equilibrium time and the maximum removal of dyes.

The effect of adsorbent dose on the amount of dyes adsorbed was studied by adding different amounts (0.05, 0.10, 0.20, 0.40, 0.60, 0.80, and 1.00 g) of adsorbent. At time $t = 0$ and equilibrium, the dye concentrations were measured using a double beam UV–vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at the wavelength of maximum absorbance (see Table 1). Prior to the measurement, a calibration curve was obtained by using the standard dye solution with known concentrations.

3. Results and discussion

3.1. Point of zero charge of the adsorbent

The value of pH affected a net zero charge on a solid in the absence of specific biosorption is called the pH_{zpc} . The pH_{zpc} is found to be at pH 3.50 for the H_2SO_4 treated adsorbent. This is a convenient index of a surface when the latter becomes either positively charged or negatively charged as a function of pH. When the pH of the aqueous solution is below the pH_{zpc} , the surface of the adsorbent will become positively charged. Meanwhile, the surface of the adsorbent will become negatively charged when the solution pH is greater than pH_{zpc} (Shukla *et al.*, 2002).

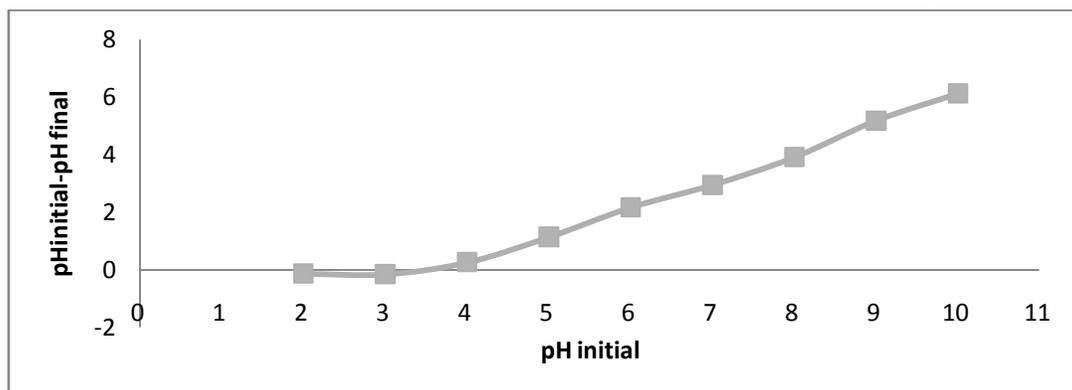


Fig. 1. Determination of point of zero charge of the sorbents.

3.2. Effect of solution initial pH

In order to determine the effect of pH on the adsorption capacity, solutions were prepared at different pH values ranging from 2.0 to 10.0. Fig. 2 shows that the percentage removal of MG was minimum at the initial pH 2 and increased with pH up to 4.0 and then remained nearly constant over the initial pH ranges of 4–10. The surface charge of the adsorbent is positive below 3.50. The removal of basic dye MG decreased with decreasing pH is possibly because the surface is positively charged, thus making (H^+) ions to compete with the dye cations thus a decrease in the amount of dye adsorbed. At higher solution pH, the surface charge of the adsorbent may get negatively charged, which enhances the positively charged MG cation through electrostatic forces of attraction. The removal of acidic dye SY, on the other hand, decreased monotonously with increasing pH over the whole examined pH range, probably due to increasing coulombic repulsions (Poots and McKay, 1979). The optimum pH for MG and SY was pH 8 and pH 2 respectively and was used for further studies. Precipitation formed at pH 10 due to some chemical reactions other than adsorption might take place. For this reason, the pH 8 was selected as optimum pH for MG.

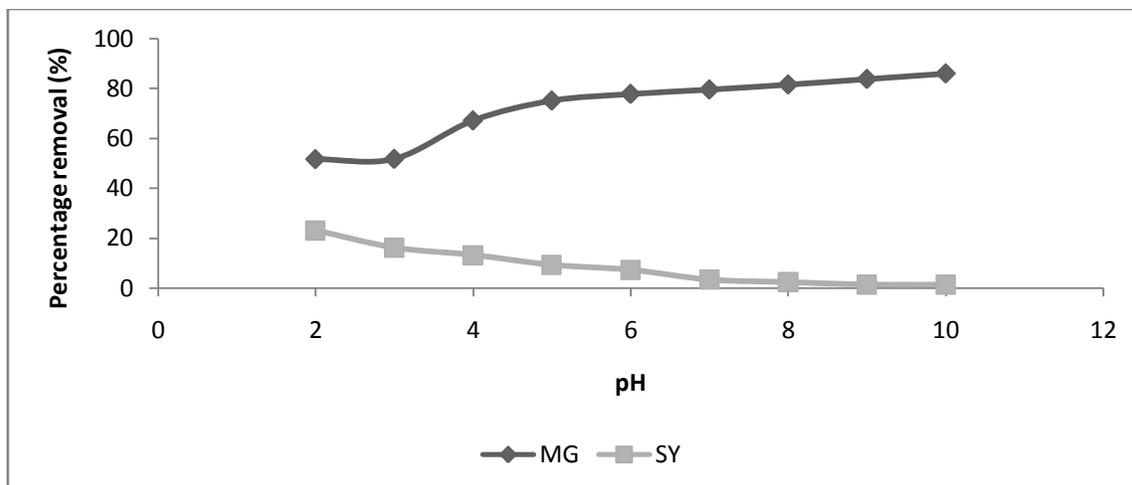


Fig. 2. Effect of solution pH on the percentage removal of MG and SY.

3.3. Effect of adsorbent dosage

The percentage removal of dyes was studied by varying the adsorbent dose between 0.02 g and 1.00 g at a dye concentration of 100 mg/L. An attempt to enhance dyes removal was evaluated by examining the effect of adsorbent dosage. As shown in Fig. 3, it is apparent that the removal percentage of dye increases as the adsorbent amount increases and then becomes constant. The removal increased with increased amount of TBA up to a maximum efficiency (>90%), after which an increase in adsorbent dosage does not further improve the dye removal, implying that a complete dye removal could not be achieved even though using large amount of the adsorbents (Gode and Pehlivan, 2005). When too much adsorbent was added into the dye solution, the transportation of dye ions to the active adsorption sites will be limited as well, hence reduced the adsorption efficiency (Araujo and Teixeira, 1997).

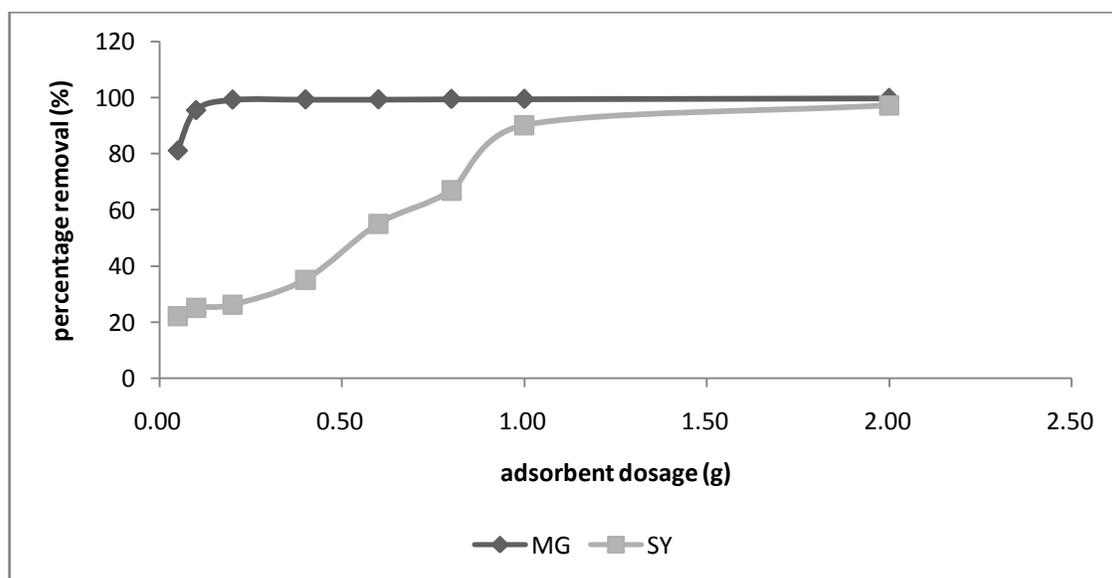


Fig. 3. Effect of adsorbent dosage on the amount of SY and MG dyes uptake.

3.4. Effect of contact time and initial concentration

The effect of contact time on the removal of SY and MG by modified bark at different initial concentration is given in Fig. 4. It indicates that the rate of color removal increased depending on the contact time. For the first 30 minutes, the percentage removal for both dyes by the adsorbent is rapid and thereafter it proceeds at a slower rate and finally attains saturation at different contact time for different initial concentration of dyes. The higher concentration solution of dyes employed, the longer equilibrium time was needed.

The rate of removal of the adsorbate is higher in the beginning due to the large surface area of the adsorbent available for the adsorption of dye ions (Hameed and Ahmad, 2009). After a certain period, only a very low increase in the dye uptake was observed because there are few active sites on the surface of sorbent. From the contact time studied, it was revealed that 4 hours of agitation time is sufficient to reach equilibrium when 100 mg/L of dyes concentration was employed. Therefore, equilibrium time of 4 hours was selected for the adsorption of both dyes for further studies. It was found that an increase in the dye concentration had caused a decrease in the percentage of dye removal. This is due to the saturation of the sorption sites on the adsorbents as the concentration of the dye increased. A similar observation was reported for the adsorption of MG on oil palm trunk fibre (Hameed and Khaiary, 2008).

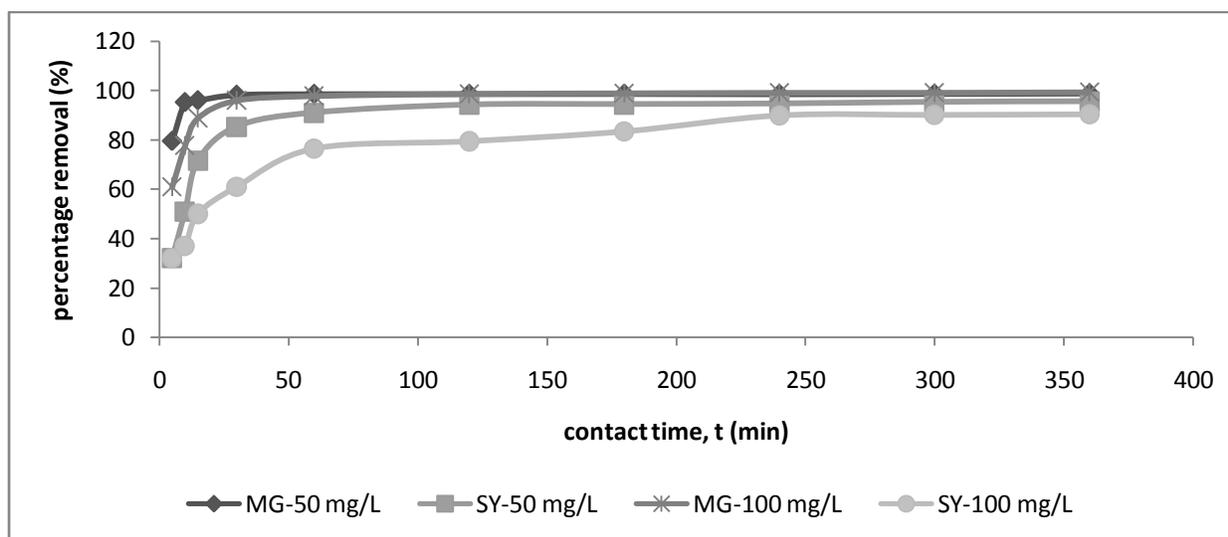


Fig. 4. Effect of contact time on the percentage removal of SY and MG at different initial concentrations

3.5. Kinetic studies

The modeling of the kinetics of adsorption of MG on SY was investigated by two common models, namely, the Lagergren pseudo-first-order model and pseudo-second-order model. The pseudo-first-order model was described by Lagergren as:

$$\log (q_e - q) = \log q_e - kt/2.303 \quad (1)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_t (mg/g) is the amount of dye adsorbed at time t and k_1 (1/min) is the rate constant of pseudo-first-order adsorption. A linear plot of $\log (q_e - q_t)$ against time allows one to obtain the rate constant. The Lagergren's first-order rate constant (k_1) and q_e determined from the model are presented in Table 2. It was found that the calculated q_e values did not agree with the experimental q_e values (Table 2). This suggests that the adsorption of MB and SY did not follow first-order kinetics. Table 2 presents the kinetic parameters resulted by fitting the pseudo-first order equation to the experimental data.

Table 2 Pseudo-first-order kinetic model parameters for adsorption of SY and MG at 300 K

Dyes	Concentration (mg/L)	q_e experiment (mg/g)	q_e Calculated (mg/g)	k_1 (g/mg min)	R^2
Malachite Green	50	12.33	1.29	0.076	0.8232
	100	24.79	3.80	0.024	0.8919
Sunset Yellow FCF	50	2.37	0.81	0.025	0.9229
	100	4.42	2.33	0.014	0.9112

The pseudo-second-order model (McKay and Ho, 1999) was expressed as

$$t/q = 1/kq_e^2 + t/q_e = 1/h + t/q_e \quad (2)$$

where q_e is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg g^{-1}), q is the amount of solute adsorbed (mg g^{-1}) at any given time t (min) and k is the rate constant (min^{-1}). $h = kq_e^2$ and is known as initial sorption rate. The pseudo-second order model has been successfully used to fit the kinetic data. When the linearities of the plots of the two kinetic models were compared, the linearities of the chemisorptions pseudo-second-order kinetic model were higher for each concentration than when the Lagergren pseudo-first-order kinetic model was applied (Table 3). This shows that the mechanism of the adsorption of MG and SY by modified bark can be described by the pseudo-second-order kinetic model, based on the assumption that the rate-limiting step may be chemisorptions involving valency forces through sharing or exchange of electrons between the hydrophilic edge sites of barks and dye ions (Gucek *et al.*, 2005).

The value of q_e increased as the initial concentration of the adsorbate increased. The value of the overall rate constant, k , also varied as the initial concentration was varied. The initial adsorption rate (h) also changed with the variation in the initial adsorbate concentration (Table 3).

Table 3 Pseudo-second-order kinetic model parameters for adsorption of SY and MG at 300 K

Dyes	Concentration (mg/L)	q_e experiment (mg/g)	q_e Calculated (mg/g)	k_2 (g/mg min)	h (mg/g min)	R^2
Malachite Green	50	12.32	12.36	0.1562	23.8663	1.0000
	100	24.68	24.94	0.0195	12.1212	1.0000
Sunset Yellow FCF	50	2.37	2.44	0.0641	0.3811	0.9998
	100	4.42	4.69	0.0143	0.3150	0.9990

3.7. Adsorption isotherms

3.7.1 Langmuir isotherm

The Langmuir and the Freundlich isotherm equations were used to interpret the experimental data. The equilibrium data have been analysed on the basis of Langmuir isotherm, expressed as

$$C_e/q_e = 1/x_m K_L + C_e/x_m \quad (3)$$

where C_e is the equilibrium concentration of solution (mg/L), q_e is the amount adsorbed per unit mass of adsorbent (mg/g), m is the mass of the adsorbent (g), x_m and K_L are Langmuir constants which are the adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. A linear graph C_e/q_e versus C_e is plotted with $1/x_m$ as slope and intercept is $\{1/x_m K_L\}$. Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface. The Langmuir isotherm constants, K_L , and equilibrium monolayer capacities, x_m , calculated from the equation are presented in Table 4. The adsorption capacity, x_m was greater for the basic dye than for the acidic dye (Table 4).

Table 4. Analysis of Langmuir isotherms

Dyes	Langmuir isotherm		
	Equilibrium monolayer capacities, x_m (mg/g)	Isotherm Constant, K_L (L/mg)	R^2
Sunset Yellow FCF	12.72	0.0446	0.9913
Malachite Green	129.87	0.0678	0.9868

3.7.2. Freundlich isotherm

Analyses of the experimental data show that the Freundlich model is not appropriate prediction of the isothermal profiles for the sorption of the investigated dyes on modified mangrove barks. The low R^2 shows that the adsorption isotherms do not fit the Freundlich isotherm. It indicates that there is no heterogeneity of the adsorbent surface (Sharma and Forster, 1993).

4. Conclusions

This study showed that treated mangrove bark acts as a good adsorbent for the removal of basic dye from aqueous solutions but was found to be inferior for acidic dye. The amount of dye adsorbed was found to be dependent on solution pH, adsorbent concentration, initial dye concentration, and contact time. The basic dye adsorption decreased at low pH values in accordance with a presupposed ion-exchange mechanism of the adsorption. The adsorption of acid dye, on the other hand, decreased with increasing pH. Equilibrium data fitted the Langmuir isotherm equation. Adsorption of Malachite Green and Sunset Yellow FCF onto modified mangrove bark follows the pseudo-second-order kinetics.

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