Biosorption of cationic textile dyes by a forest industry residue: *Pinus pinaster* bark

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Abstract

The potential of *Pinus pinaster* bark (PP) for the removal of methylene blue (MB) and malachite green (MG) dyes from aqueous solutions in single and binary systems was investigated. In the single systems, batch experiments were carried out to study kinetics and equilibrium of MB and MG adsorption by pine bark. The influence of contact time (till 8h), adsorbent dose (2.5-5-10 g/L), temperature (25-40-60ºC), pH (2-4-6), particle size (0.1-0.5, 0.5-1 and 1.6-2 mm) and initial dye concentration (10-100 mg/L) on adsorption percentage and capacity was analysed. More than 70% of both dyes could be removed in less than 1 h and almost completely when equilibrium was reached. Temperature was the less significant variable. In the binary system, MB and MG exhibited competitive adsorption. Kinetics and equilibrium data were described by the pseudo-second order and Langmuir models, respectively. Adsorbent morphology and functional groups present were characterized before and after adsorption by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. Maximum adsorption capacities (22.2-41.7 mg/g for MG and 31.3-50.0 mg/g for MB) revealed that pine bark can be used as an effective adsorbent for removing cationic dyes.

Keywords: Biosorption, Cationic dyes, Pine bark, Wastewaters.

1. Introduction

The discharge of coloured effluents into the environment is not only detrimental for the environment but affects many biological cycles (Moursli and Bengueddach, 2010). Dye effluents represent a real danger to humans and their environment because of their stability and low biodegradability (Kadirvelu *et al*., 2003; Jain *et al*., 2003).

Methylene blue (MB) and malachite green (MG) are both cationic dyes as they form positively charged molecules when dissolved in water. MB is a thiazine dye whereas MG is a triarylmethane one. They are used in several industries such as paper, leather, cotton, pulp, wool etc., for colouring their final products.

Various physical, chemical and biological processes have been used for the removal of dyes from aqueous solutions (Barka *et al*., 2010; Bielska and Szymanowski, 2006; Elahmadi *et al*., 2009; Karim *et al*., 2009; Khadhraoui *et al*., 2009; Lodha and Chaudhari, 2007). Among them, adsorption has been found to be one of the most economical and effective treatment methods for wastewater decolourization. The efficiency of the adsorption process mainly depends on the cost and removal capacity of the adsorbent used. Nowadays, agricultural and forest biomass residues are receiving an increasing attention due to its low cost and high availability. Thus, the objective of the present work was to study *Pinus pinaster* bark (PP), an abundant residue of the wood industry, as a low-cost adsorbent for the removal of MB and MG from aqueous solutions in single and binary systems.

2. Materials and Methods

Malachite green oxalate (MG) and Methylene blue (MB) were used as cationic dyes. *Pinus pinaster* bark (PP) was supplied by the company Aserpal S.A. (Grupo Losán S.A., Galicia, NW Spain). It was air-dried to a moisture content close to equilibrium and ground in a hammer mill. The fraction of particles with size between 0.1 and 2 mm was selected. In order to extract soluble compounds that could colour the water and interfere with the dye analytical determination, the bark was pre-treated twice with water at 25°C for 4 h at a solid/liquid ratio of 1/10 g/mL. The bark, once filtered and dried, was stored until their use for adsorption experiments.

FTIR spectra of the bark were recorded with the KBr pellet method. Morphological and surface bark characteristics were investigated by scanning electron microscopy (SEM) at a magnification of 200x.

Adsorption experiments were conducted in a thermostatic orbital water bath shaker at 100 rpm. 100 mL of the dye solution (~50 mg/L) were put in contact with the selected amount of PP. The effect of contact time, particle size (0.1-0.5, 0.5-1 and 1.6-2 mm), initial pH (2, 4 (natural pH) and 6), adsorbent dose (2.5, 5 and 10 g/L) and temperature (25, 40 and 60ºC) on adsorption performance was studied.

Equilibrium experiments were conducted using initial dye concentrations from 10 to 100 mg/L with an adsorbent dose of 5 g/L at 25, 40 and 60ºC for 8 h. The remaining dye concentration was measured by UV–visible spectrophotometry at the wavelength corresponding to the maximum absorbance, 616 nm for MG and 663 nm for MB.

For the binary system, pine bark at an adsorbent dose of 5 g/L was mixed with 100 mL of a solution containing 50 mg/L of each dye at 25ºC and natural pH. The first-order derivative spectrophotometric method for the simultaneous determination of MG and MB in binary solutions was applied to analyse the remaining dye concentration.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 1 shows the SEM micrographs of PP before and after dyes adsorption. The raw bark (Fig. 1a) shows a heterogeneous surface with available pores. However, after adsorption, the surface was clearly covered by both MG (Fig. 1b) and MB (Fig. 1c), which confirms the adsorption of dyes molecules. FTIR spectra (not shown) revealed that some peaks were shifted or changed in intensity whereas other new peaks appeared. All these changes indicate that different functional groups present in the bark are involved in dyes adsorption.

3.2. Effect of adsorbent particle size on single adsorption

The effect of the sorbent particle size on MG and MB adsorption is shown in Figs. 2a and 2b, respectively. For both dyes, the adsorption rate and the amount of adsorbed dye increased as the particle size decreased. The access to the pores is facilitated as bark particles become smaller, resulting in a higher adsorption (Bhatnagar and Jain, 2005). Equilibrium adsorption percentages from 83.6 to 99.7% were attained. Particle size of 0.5-1 mm was selected to continue experimentation (adsorption percentage 98% for MB and 91.7% for MG) as the adsorbent-solution separation was significantly improved.

3.3. Effect of initial pH on single adsorption

pH is one of the most important variables of adsorption processes. Therefore, its effect on MG and MG adsorption on PP was investigated. As seen in Figs. 2c and 2d, in general, adsorption capacity increased with increasing pH from 2 to 6. The significant lower adsorption rate of MB and MG at pH < 4, especially for MG, may be due to fact that the bark surface becomes positively charged; thereby, adsorption efficiency could decrease due to the electrostatic repulsion between both positive bark surface and dye ions. As there were no significant differences in the adsorption percentages above pH=4 (>90%), natural pH was selected for the subsequent experiments.

3.4. Effect of adsorbent dose on single adsorption

The effect of the bark dose (from 2.5 g/L to 10 g/L) on dyes removal at a fixed dye concentration (~50 mg/L) is shown in Figs. 2e (MG) and 2f (MB). As expected, adsorption capacity increased with decreasing the adsorbent dose. For MB, the adsorption percentage at equilibrium increased from 86.7% (18.6 mg/g) to 98.0% (11.2 mg/g), when the dose was increased from 2.5 g/L to 5 g/L. A further increase up to 10 g/L did not lead to a significant increase in MB removal (98.6% and 5.4 mg/g). Similarly, for MG, the adsorption percentage increased from 84.9% (16.8 mg/g) with 2.5 g/L to 91.7% (9.5 mg/g) with 5 g/L. Using 10 g/L, a value of the same order as that for MB was obtained, 97.5% (5.2 mg/g). The observed rise in dye removal is due to the availability of more active sites on the bark surface when the adsorbent concentration is increased. In view of the results, a dose of 5 g/L was chosen to study the effect of temperature.

3.5. Effect of temperature on single adsorption

Figs. 2g and 2h show the influence of temperature (25, 40 and 60ºC) on MG and MB removal by PP under the conditions previously selected. Adsorption percentages higher than 91% were obtained for both dyes at all temperatures essayed. As observed, temperature hardly influenced dyes adsorption, especially in the case of MG. Accordingly, the lowest temperature, 25ºC was selected.

3.6. Dye adsorption in binary systems

Industrial wastewaters are generally a mixture of more than a single pollutant. Hence, binary adsorption of MG and MB was also investigated using a solution containing both dyes. Fig. 3 shows the amount of dyes adsorbed on PP in a binary system (50 mg/L MB - 50 mg/L MG) in comparison with the single one at an initial concentration of 50 mg/L. As observed, the capacity of the bark to remove MB (Fig. 3a) or MG (Fig. 3b) was considerably reduced in the presence of the other dye. The maximum adsorption capacities for the single systems (9.5 mg/g for MG and 11.2 mg/g for MG at 8 h) were reduced by 30% in the binary system. This reduction could be attributed to an antagonistic effect due to the competition between both dyes.
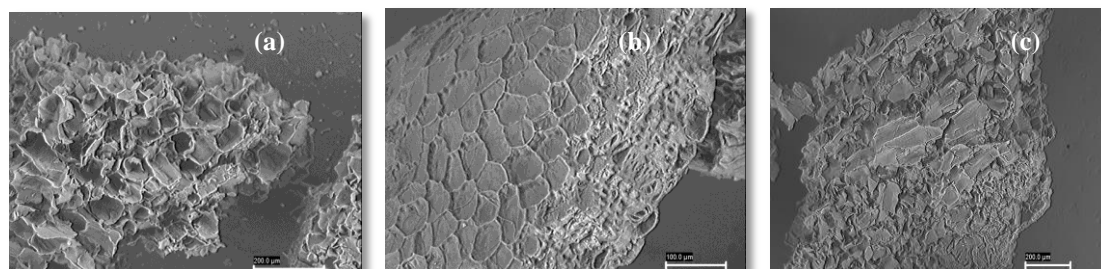
Figure 1. SEM micrographs of *Pinus pinaster* bark before adsorption (a) and after MG (b) and MB (c) adsorption

3.7. Kinetic studies

Fig. 2 shows the time course profile of MG and MB adsorption processes for all conditions studied. High adsorption rates were attained at the beginning but decreased gradually till equilibrium was reached. Lagergren's pseudo-first-order and Ho's pseudo-second-order kinetic models were applied to the experimental data. For both dyes in the whole range of experimental conditions, the Ho's model fitted better to the experimental data than the Lagergren one (not shown) and high correlation coefficients (R^2 >0.99) were obtained (Table 1). Furthermore, the calculated q_e values are in agreement with the experimental data (Fig. 2). The Ho's model was also well fitted to the experimental data in the binary system, with correlation coefficients close to 1 (Fig. 3).

3.8. Equilibrium studies

To study adsorption equilibrium, experiments were conducted at different initial dye concentrations (10-100 mg/L) and at the three temperatures essayed (25, 40 and 60°C) under the conditions previously selected for the other variables. The Langmuir and Freundlich isotherms models were applied to the data and their parameters are presented in Table 2, together the correlation coefficients, R^2. The higher R^2 values for the Langmuir isotherm indicate that MB and MG adsorption by PP occurred by a monolayer type adsorption. The predicted maximum adsorption capacities were found to be 41.7 and 50.0 mg/g for MG and MB, respectively, at 40ºC.

Table 1. Pseudo-second order model parameters for MB and MG adsorption by *Pinus pinaster* bark.

		Methylene blue (MB)			Malachite green (MG)		
		k_2 (g/mg·h)	q_e (mg/g)	R^2	k_2 (g/mg·h)	q_e (mg/g)	R^2
	0.1-0.5	2.29	12.0	0.99	12	10.2	1
Particle size (mm)	0.5-1	0.27	11.8	0.99	0.26	10.2	0.99
	1.6-2	0.22	10.9	0.99	0.16	9.7	0.99
	2	0.13	10.4	0.99	0.46	6.8	0.99
Initial pH	4 (Natural)	0.21	11.9	0.99	0.26	10.2	0.99
	6	0.40	11.3	0.99	0.26	11.1	0.99
	2.5	0.08	20.4	0.99	0.07	18.2	0.99
Adsorbent dose (g/L)	5	0.27	11.8	0.99	0.26	10.2	0.99
	10	3.64	5.5	0.99	0.84	5.4	0.99
	25	0.21	11.9	0.99	0.46	10.2	0.99
Temperature (°C)	40	0.70	9.7	0.99	0.26	10.4	0.99
	60	4.51	10.5	0.99	0.26	9.4	0.99

Table 2. Isotherm parameters for MB and MG adsorption onto *Pinus pinaster* bark.

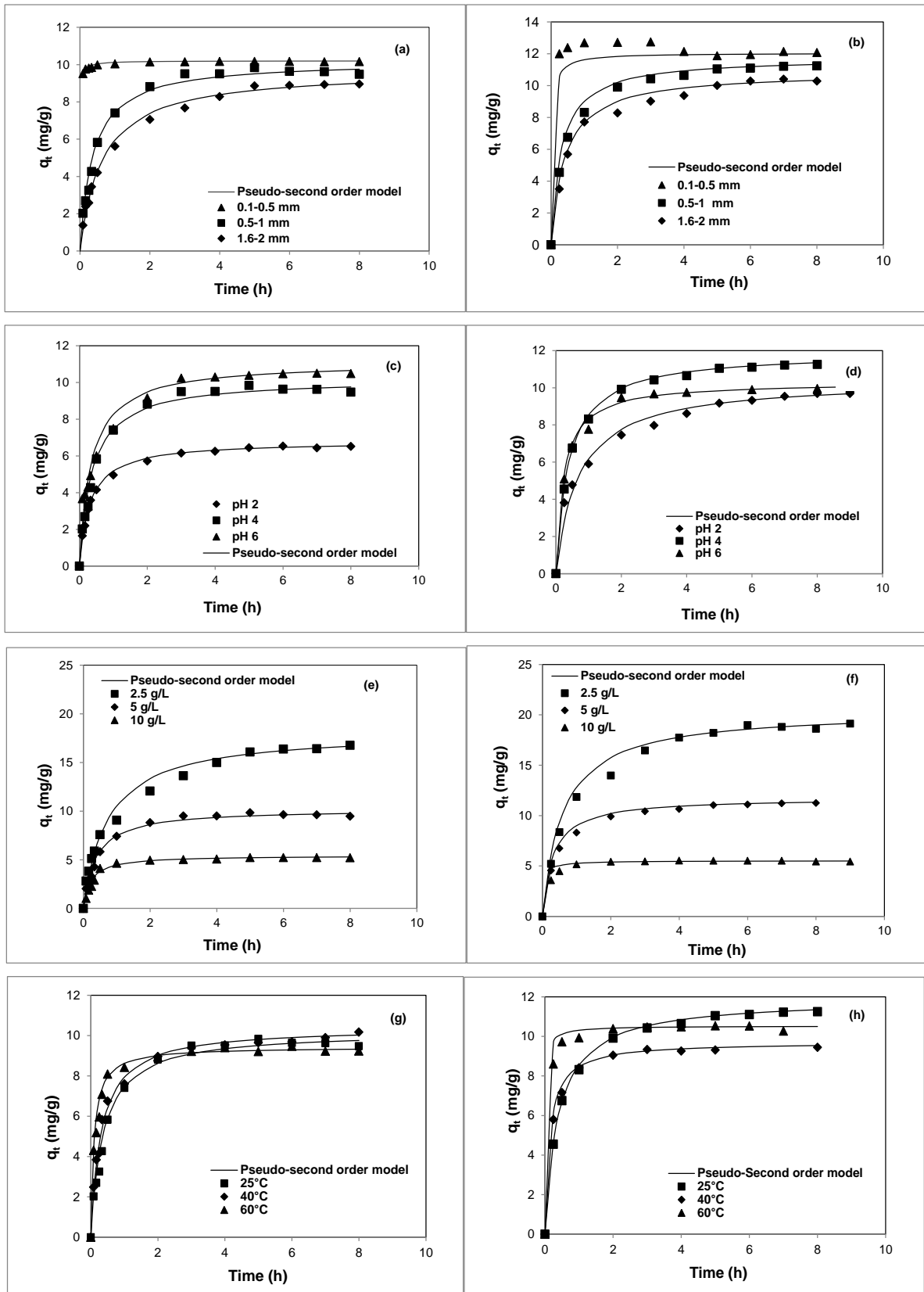|	Malachite green (MG)			Methylene blue (MB)		
Langmuir isotherm						
Temperature (°C)	25	40	60	25	40	60
q_m **(mg/g)**	22.2	41.7	35.7	31.3	50.0	47.6
K_a **(L/mg)**	0.30	0.82	1.04	0.57	0.61	0.41
R^2	0.99	0.99	0.99	0.99	0.99	0.99
Freundlich isotherm						
K_F **(mg$^{1-1/n}$ · L$^{1/n}$ /g)**	4.72	15.30	14.85	12.76	17.90	16.73
n	1.63	1.98	2.75	4.55	3.52	3.69
R^2	0.93	0.91	0.92	0.95	0.93	0.97

Figure 2. Malachite green (MG) and methylene blue (MB) adsorption by pine bark in single system (50 mg/L) as a function of: Particle size at 25ºC, bark dose of 5 g/L and pH=4, (a) MG and (b) MB; pH at 25ºC, bark dose of 5 g/L and 0.5-1 mm of particle size, (c) MG and (d) MB; Adsorbent dose at 25ºC, pH=4 and 0.5-1 mm of particle size, (e) MG and (f) MB and Temperature at pH=4, bark dose of 5 g/L and 0.5-1 mm of particle size, (g) MG and (h) MB.
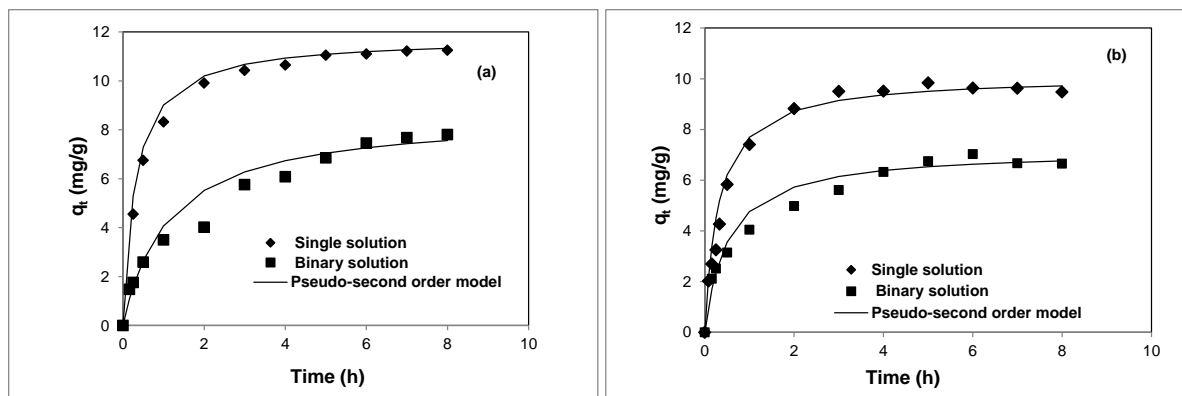
Figure 3. Comparison of MB (a) and MG (b) adsorption on pine bark in single and binary solutions (particle size, 0.5-1 mm; adsorbent dose, 5 g/L; pH=4: T=25ºC; dye concentration, 50 mg/L)

4.   Conclusions

The present work demonstrated that *Pinus pinaster* bark, an abundant and cheap residue from the wood industry, could be used as an effective adsorbent for the removal of MG and MB from industrial wastewaters. Adsorption kinetics of both dyes was satisfactorily explained by the pseudo-second-order model. Langmuir isotherm described the equilibrium data. Pine bark particle size, initial solution pH and adsorbent dose were found to affect significantly MG and MB adsorption, while temperature hardly influenced the adsorption process. The results revealed that pine bark has a higher affinity for MB than for MG. Thus, maximum adsorption capacities predicted were higher for MB than for MG. In binary systems competitive effects between dyes were found and the adsorption capacity of the bark for both dyes diminished.

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