BIOSORPTION OF METHYLENE BLUE AND MALACHITE GREEN FROM SINGLE AND BINARY SOLUTIONS BY Pinus pinaster BARK

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ABSTRACT

Aiming to develop a sustainable separation process reducing the water pollution, in this work Pinus pinaster (cluster pine) bark from a wood veneer industry was used for methylene blue and malachite green removal from aqueous systems. For single adsorption, the influence of time (up to 8 h), adsorbent dose (2.5 - 5 - 10 g·L⁻¹), temperature (25 ºC - 40 ºC - 60 ºC), pH (2 - 4 - 6) and particle size (0.1 mm - 0.5 mm, 0.5 mm - 1 mm and 1.6 mm - 2 mm) on adsorption was investigated. To study the initial concentration effect on binary adsorption, different concentrations (0 - 5 - 25 - 50 mg·L⁻¹) were used at 25 ºC, natural pH and a dose of 5 g·L⁻¹. High efficiency was obtained at pH = 4 (natural pH), dose of 5 g·L⁻¹ and particle size of 0.5 - 1 mm. Adsorption percentages higher than 70 % were reached in less than one hour, with removal almost complete at equilibrium in single systems, without temperature influence. Methylene blue was slightly better adsorbed by bark. In binary systems, dyes exhibited competitive adsorption, decreasing their removal, especially increasing the initial concentration of the other dye. Dyes adsorption followed the pseudo-second order kinetic model, whereas the Langmuir isotherm explained adsorption equilibria in mono-component systems. High adsorption capacities (41.7 mg·g⁻¹ for malachite green and 50.0 mg·g⁻¹ for methylene blue) were obtained at 40 ºC and natural pH indicating that pine bark can be effectively used as biosorbent.

Keywords: Bark, binary solutions, adsorption, Langmuir isotherm, malachite green, methylene blue, Pinus pinaster, wood veneer

INTRODUCTION

The discharge of colored effluents is harmful to the environment, affecting many biological cycles, especially, because dyes are stable and not easily biodegradable (Boakye et al. 2022). Cationic dyes have high toxicity and great resistance to degradation; thus, researchers are looking for efficient removal processes capable of reducing their concentration in effluents (Witek-Krowiak 2011). Methylene blue (MB) and malachite green (MG) are both cationic dyes because they form positive charged molecules when dissolved in water. Their high solubility in water, easy implementation and low cost have turned them into compounds of interest for the productive sectors where they are frequently used (Piccin et al. 2009).
Dyes can be removed from aqueous solutions using different processes, being adsorption, one of the most economic and effective ones (Adeyi et al. 2019, Adeyi et al. 2020, Ho 2022). In general, the adsorbent cost and its removal capacity affect mostly to the adsorption efficiency. Consequently, nowadays, researchers’ attention is focused on agricultural and forest residues, cheaper than the commercial adsorbents and easily available. Thus, the goal of this work was the use of cluster pine (Pinus pinaster Aiton) bark for removing dyes (MB and MG) from aqueous solutions, as it is abundantly produced as residue from the wood industry in Galicia (NW of Spain). Previously, pine bark was used efficiently to eliminate Congo red from aqueous solutions (Litefti et al. 2019).

Most of the investigations have been focused on the evaluation of the best adsorption conditions, but limited to a single dye, either anionic or cationic in batch mode. However, wastewaters from industries that use dyes normally contain mixtures of them. In this regard, there is a limited number of works that include the evaluation of the best conditions to remove mixtures of dyes. Probably, this is due, in part, to the methodological difficulty in quantifying them as determining the individual dye content implies greater analytical complexity due to the superposition of their absorption spectral bands (Turabik 2008), and, therefore, the use of derivative spectrophotometric methods is mandatory. However, as mentioned before, different dyes are present in real wastewaters, and possible interactions could occur among them and affect to the dye adsorption. Thus, in this work, the conditions for an efficient removal of the cationic dyes, methylene blue and malachite green, by cluster pine (Pinus pinaster Aiton) bark were evaluated in single and binary mixtures. Also, adsorption kinetics in both systems and isotherms for the single system were determined. FTIR and SEM analysis were applied to study, respectively, the structure and morphology of pine bark.

MATERIALS AND METHODS

Biosorbent preparation

Cluster pine (Pinus pinaster Aiton) bark (PP) was supplied by Aserpal S.A. (Grupo Losán S.A., Galicia, Spain), a company which manufactures wood veneers. The bark, air-dried to equilibrium moisture content (20%, on a dry basis), ground in a hammer mill and sieved to size of 0.1 - 2 mm, was pretreated for 4 h with water at 25 °C and solid/liquid ratio of 1/10 g·mL⁻¹ as in Litefti et al. (2019).

Preparation of dye solutions

Methylene blue (MB) and Malachite green (MG) were obtained from Panreac (Barcelona, Spain). Dye solutions of the selected concentration were prepared by dilution of stock solutions (1000 mg·L⁻¹), which were obtained by dissolving a weighed amount of the dye in distilled water. pH of each solution was adjusted with NaOH or HCl solutions before mixing with the bark.

Characterization of the adsorbent

Pine bark FTIR spectra, before and after adsorption, was recorded with a VARIAN FTIR 670 spectrometer. KBr pellets (2%, g of sample·100 g of pellet⁻¹) were prepared with samples obtained after grinding in a ball mill and drying under vacuum for a week. Bark surface morphology analysis, before and after dyes adsorption, were carried out by scanning electron microscopy (SEM) using a ZEISS EVO LS 15 microscope. The point of zero charge of the bark was determined in a previous work (Litefti et al. 2019) and found to be 3.4.

Batch adsorption study

For single adsorption experiments, a certain amount of pine bark was put in contact up to 8 h with 100 mL of a dye aqueous solution (50 mg·L⁻¹) in a thermostatic orbital shaking water bath (100 rpm). That time was considered enough to achieve the equilibrium. To determine the parameters influencing the MB and MG removal by the bark, initial pH (2, 4 (natural pH) and 6), particle size (0.1 mm - 0.5 mm, 0.5 mm – 1 mm and 1.6 mm - 2 mm), adsorbent dose (2.5 g·L⁻¹, 5 g·L⁻¹ and 10 g·L⁻¹) and temperature (25 °C, 40 °C and 60°C) were studied. The dye remaining concentration in solution was determined spectrophotometrically by measuring the absorbance for each dye at the maximum wavelength, using a VIS JASCO (V-630 UV) spectrophotometer.

For the binary system, experiments were conducted, up to 8 h, at 25 °C and natural pH, with a bark dose of 5 g·L⁻¹ at various dyes concentrations. The influence of the initial dye concentration on their removal was evaluated by varying the concentration of one dye keeping the other constant. Thus, to determine the influence of MG on MB adsorption, MB concentration was fixed at 50 mg·L⁻¹ and MG concentration was varied (0 mg·L⁻¹- 5 mg·L⁻¹ - 25 mg·L⁻¹ - 50 mg·L⁻¹). The same procedure was used to analyze the effect of MB on MG adsorption. The remaining concentration of MG and MB in solution was determined according to the first-or-
Biosorption of methylene blue and malachite green..: Litefti et al.

The amount of dye adsorbed by pine bark, $q_t (\text{mg} \cdot \text{g}^{-1})$ and the percentage of dye adsorption were calculated, respectively, by Equation 1 and Equation 2:

$$q_t (\%) = \frac{(C_0 - C_t) V}{m}$$

$$\%\text{Adsorption} = \frac{(C_0 - C_t)}{C_0} \times 100$$

Where $C_0$ is the initial dye concentration (mg·L$^{-1}$), $C_t$ is the dye concentration at any time $t$, $V$ is the volume of solution (L) and $m$ is the mass of pine bark (g of oven dried (o.d.) bark).

Equilibrium experiments

To determine the adsorption equilibrium for single systems, experiments were conducted for 8 h at an initial dye concentration from 10 mg·L$^{-1}$ to 100 mg·L$^{-1}$ and an adsorbent dose of 5 g·L$^{-1}$ at three temperatures (25 ºC, 40 ºC and 60 ºC). After adsorption, the residual dye concentration in solution was measured as indicated before.

RESULTS AND DISCUSSION

Adsorbent characterization

Morphological characterization by SEM microscopy revealed that pine bark presented some honeycomb-like structures with a heterogeneous and porous surface with pores of different sizes and shapes (Litefti et al. 2019) before adsorption (Figure 1a). However, after adsorption, both methylene blue (Figure 1b) and malachite green (Figure 1c) covered the bark surface and filled the pores and free spaces, confirming the dyes adsorption.

On the other hand, shifts or changes in the intensity of some peaks in the FTIR spectra of the bark after adsorption (Figure 1d) and the appearance of new peaks evidenced that different functional groups participated in both dyes’ adsorption. Thus, as other authors found (Asfaram et al. 2017, Jiang et al. 2017), the intensities of the peaks of the mono-substituted and para-disubstituted benzene rings (between 500 cm$^{-1}$ and 1500 cm$^{-1}$) and of the C=C stretching of the benzene ring at 1619 cm$^{-1}$ increased after green malachite adsorption (Figure 1d). Additionally, intensity changes were detected in the peaks at 1166 cm$^{-1}$ and 2925 cm$^{-1}$ for the C-N stretching vibrations and C-H stretching of asymmetric CH$_3$ group, respectively.

Figure 1: (a) SEM images of cluster pine (Pinus pinaster Aiton) bark before and (b) after methylene blue (MB) and (c) malachite green (MG) adsorption, and (d) FTIR spectra of pine bark.
With respect to MB adsorption, the band of carboxyl groups (1448 cm$^{-1}$) diminished, whereas that of the C-O group (1056 cm$^{-1}$) increased slightly (Figure 1d), possibly because all were involved in dye adsorption (Zou et al. 2013). Band intensity changes and shifts of bonded C=O, aromatic nitro compound and C-C groups at 1618 cm$^{-1}$, 1334 cm$^{-1}$ and 831 cm$^{-1}$, respectively, were also detected as previously found for a citric acid modified sawdust (Zou et al. 2013) and carbonized watermelon rind (Jawad et al. 2019). Band shifting, corresponding to variations of energy of functional groups, indicated that MB was bonded on the surface of the cluster pine (*Pinus pinaster* Aiton) (Abdallah et al. 2016).

**Analysis of MB and MG in single and binary solutions**

Absorption spectra of single solutions of methylene blue and malachite green at 6 mg·L$^{-1}$ were recorded between 200 nm and 800 nm (Figure 2a). As can be seen, the wavelength for the maximum absorbance ($\lambda_{\text{max}}$), used to determine the calibration curves, were 663 nm and 616 nm, for MB and MG, respectively.

For analysis of binary solutions, a solution with 6 mg·L$^{-1}$ of each dye was prepared and the absorption spectra were obtained (Figure 2a). As shown, the spectra of MB and MG dyes in binary systems overlapped, and therefore, derivative spectrophotometric method had to be applied for the analysis of each dye in the presence of the other. From the first order derivative absorption spectra (Figure 2b), it can be concluded that MB can be determined at 300 nm in the presence of MG, and MG can be determined at 663 nm in the presence of MB. Thus, the calibration equations for dyes were obtained in the range of 1 mg·L$^{-1}$ - 12 mg·L$^{-1}$, at 300 nm and 663 nm, respectively (Figure 2f), with high correlation coefficients ($R^2 > 0.998$).

To establish the validity of the method used for the quantification of MB and MG in binary systems, a recovery study was performed according to Turabik (2008). For that, tests were done at different concentrations in 2 mg·L$^{-1}$ -12 mg·L$^{-1}$ range of MB and MG in binary solutions, as shown in Figure 2c, Figure 2d and Figure 2e, where it is observed that the changes in concentration did not affect the wavelengths of maximum absorbance previously selected. The statistical parameters used to validate the efficiency of the applied method were the recovery ($\%$), error ($\%$) and average percentage error $\epsilon$ ($\%$) between the theoretical concentration $C_t$ (mg·L$^{-1}$) and measured concentration $C_m$ (mg·L$^{-1}$), which were obtained using Equation 3, Equation 4, Equation 5. The results obtained are shown in Table 1.

\[
\text{Recovery} \ (\%) = \frac{C_m}{C_t} \times 100 \quad (3)
\]

\[
\text{Error} \ (\%) = \frac{C_m - C_t}{C_t} \times 100 \quad (4)
\]

\[
\epsilon \ (\%) = \frac{\sum_{i=1}^{N} \left( \frac{C_m - C_t}{C_t} \right)}{N} \times 100 \quad (5)
\]
Figure 2: (a) Absorption spectra of dyes in single and binary solutions, (b) First order derivative spectra of dyes in single and binary solutions (initial concentration, 6 mg·L⁻¹), First order derivative spectra of dyes in binary solutions at (c) MB concentration of 6 mg·L⁻¹ and MG concentration of 2 mg·L⁻¹ - 12 mg·L⁻¹, (d) First derivative spectra of dyes in binary solutions at MG concentration of 6 mg·L⁻¹ and MB concentration of 2 mg·L⁻¹ - 12 mg·L⁻¹, (e) First order derivative spectra of dyes in binary solutions (dye concentration of 2 mg·L⁻¹ - 12 mg·L⁻¹), (f) Calibration straight lines of the 1st order derivative spectra for both dyes in binary system.

Table 1: Recovery and error percentages for MB and MG in binary mixtures obtained by first order derivative spectroscopy.

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<th>Theoretical concentration MG (mg·L⁻¹)</th>
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The recovery percentages obtained for both dyes in binary mixtures were in the range from 90,3 % to 113,8 % for MB and from 76,6 % to 111,0 % for MG, and the average percentage errors were 2,77 % and 1,02 % for MB and MG, respectively (Table 1), values close to those reported by Turabik (2008) that proposed this method for the analysis of a mixture of Basic Red 46 and Basic Yellow 28 whose spectra also overlapped. Once the validity of the quantification method for the mixture was established, the effect of the main variables on the adsorption process was evaluated, and the corresponding results are described below.

**Single adsorption of dyes**

**Effect of initial pH**

MB and MG adsorption on cluster pine (Pinus pinaster Aiton) bark in single systems was studied as a function of pH, in the range from 2 to 6, at an initial dye concentration of 50 mg L\(^{-1}\), temperature of 25 °C, 5 g L\(^{-1}\) of adsorbent dosage and 0,5 mm -1 mm of particle size. It is known that changes in pH affect several functional groups such as amino, carbonyl, etc. on the surface of lignocellulosic materials wall which are responsible for binding of dye molecules (Boakye et al. 2022). As can be observed in Figure 3a and Figure 3b, the adsorption of both dyes was dependent on pH, increasing, in general, the adsorption capacity when the pH increased from 2 to 6.

As mentioned before, the point of zero charge (pH\(_{PZC}\)) of the pine bark was 3,4, and, therefore, the adsorption of cationic dyes which can dissociate in aqueous solution as cationic dye ions is favored at pH > pH\(_{PZC}\). Probably, at these values of pH, the bark presents a negative surface charge due to the deprotonation of some functional groups as carboxylic and phenolic groups present, favoring the electrostatic attraction. At pH < 4 the bark surface is positively charged, which can explain the decrease in the dye’s adsorption efficiency, especially for MG, due to the electrostatic force of repulsion between surface and cationic dye ions. Similar results were found for these dyes by other authors (Zou et al. 2013, Bagheri et al. 2016, Adeyi et al. 2020).

The maximum adsorption percentages were 98,8 % and 97,0 % for MB and MG, respectively, at pH = 6. However, the natural pH (pH = 4) was selected for further experiments as at this pH the adsorption percentages were higher than 90 % for both dyes (11,3 and 9,8 mg·g\(^{-1}\) for MB and MG, respectively).

**Effect of adsorbent particle size**

The effect of bark particle size (0,1 mm – 0,5 mm, 0,5 mm – 1 mm and 1,6 mm -2 mm) on MB and MG adsorption was investigated at fixed initial dye concentration (50 mg L\(^{-1}\)), adsorbent dose (5 g L\(^{-1}\)), pH (4) and temperature (25 °C). The results are presented in Figure 3c and Figure 3d for MB and MG, respectively. For both dyes, a decrease in the particle size resulted in an increase in both the adsorption rate and the amount of adsorbed dye, because the smaller sizes facilitate the access of the dyes molecules to the pores (Bhatnagar and Jain 2005) and, probably, proportionate higher surface area with more active sites to interact with them (Dahri et al. 2015, Rápó and Tonk 2021). Anyway, as high adsorption percentages were also obtained for the particle size of 0,5 mm -1 mm, 98 % (11,2 mg·g\(^{-1}\)) for MB and 91,7 % (9,5 mg·g\(^{-1}\)) for MG, and, moreover, the adsorbent-solution separation was significantly improved, this size was selected to continue experimentation.

**Effect of adsorbent dose**

Bark dose is other parameter influencing the dye adsorption efficiency. Thus, different amounts of adsorbent in the range from 2,5 g·L\(^{-1}\) to 10 g·L\(^{-1}\) were assayed at fixed initial dye concentration (50 mg·L\(^{-1}\)), pH (4), particle size (0,5 mm - 1 mm) and temperature (25 °C) (Figure 3e and Figure 3f). As expected, adsorption capacity decreased and adsorption percentage increased (Chikri et al. 2020), from 18,6 mg·g\(^{-1}\) (86,7 %) for MB to 11,2 mg·g\(^{-1}\) (98,0 %) (Figure 3e) and from 16,8 mg·g\(^{-1}\) (84,9 %) to 9,5 mg·g\(^{-1}\) (91,7 %) for MG with increasing the adsorbent dose from 2,5 g·L\(^{-1}\) to 5 g·L\(^{-1}\). When the adsorbent dose increases, greater number of adsorption sites on the bark surface are available, favoring the dye removal (Rápó and Tonk 2021). A further increase up to 10 g·L\(^{-1}\) did not improve significantly neither MB removal (98,6 % and 5,4 mg·g\(^{-1}\)) nor MG removal (97,5 % and 5,2 mg·g\(^{-1}\)). Considering these results, a bark dose of 5 g·L\(^{-1}\) was selected to study the influence of temperature.

**Effect of temperature**

Methylene blue and malachite green adsorption at three different temperatures (25 °C, 40 °C and 60 °C) were also studied at the conditions previously selected (i.e., initial dye concentration of 50 mg·L\(^{-1}\), pH = 4, 0,5 mm -1 mm of particle size and 5 g·L\(^{-1}\) of bark dosage) as shown in Figure 3g and Figure 3h. It is observed that as the temperature increases, the adsorption rate increases evidencing that the dye adsorption is possibly...
of endothermic character (Litefti et al. 2019), but practically does not affect the equilibrium conditions and high adsorption percentages (> 91 %) were obtained for all temperatures essayed. Consequently, the lowest temperature was selected for the following experiments.

**Figure 3:** Time dependence of methylene blue (MB) and malachite green (MG) removal by pine bark in single systems (50 mg·L⁻¹) as a function of pH (25 °C, bark dose = 5 g·L⁻¹, particle size = 0.5 mm -1 mm) (a) MB and (b) MG; Particle size (25 °C, bark dose = 5 g·L⁻¹, pH = 4) (c) MB and (d) MG; Bark dose (25 °C, pH = 4, particle size = 0.5 mm - 1 mm) (e) MB and (f) MG and temperature (pH = 4, bark dose = 5 g·L⁻¹, particle size = 0.5 mm -1 mm) (g) MB and (h) MG.
Binary adsorption of dyes: Effect of initial dye concentration

Generally, more than a single pollutant is present in industrial wastewaters. Hence, the binary adsorption of the dyes was also investigated, and the effect of the initial concentration of each dye on the simultaneous removal of the mixture was studied. For that, the concentration of each dye was varied between 0 and 50 mg·L⁻¹, maintaining the other at 50 mg·L⁻¹.

As it can be observed (Figure 4a and Figure 4b), methylene blue or malachite green removal efficiency was greatly diminished in presence of MG or MB, respectively. Thus, the maximum adsorption capacities obtained, previously, for the mono-component systems at the equilibrium time, 8 h (i.e., 9.5 mg·g⁻¹ for MG and 11.2 mg·g⁻¹ for MB) were reduced by 4.2, 6.3 and 30.5 % for MG and 6.3, 9.8 and 21.4 % for MB, when the MB or MG concentration, respectively, was increased from 5 mg·L⁻¹ to 50 mg·L⁻¹. These results indicated the existence of an antagonistic adsorption between MB and MG as other authors found for the same dyes (Adeyi et al. 2019), and which is favored at higher concentrations. This behaviour can be due to saturation of the active sites in the bark surface and competition for these sites since both dyes have the same cationic nature (Ghaedi et al. 2013). Again, the pine bark showed more affinity towards the methylene blue than the malachite green, independently on MG concentration added, although was slightly more significant at 50 mg·L⁻¹.

Figure 4: (a) Time dependence of methylene blue (MB) and (b) malachite green (MG) removal by pine bark in binary systems (50 mg·L⁻¹) in function of MG concentration (5 mg·L⁻¹ – 50 mg·L⁻¹) and MB concentration (5 mg·L⁻¹ - 50 mg·L⁻¹), respectively (25 ºC, particle size = 0.5 mm - 1 mm, bark dose = 5 g·L⁻¹, pH = 4).

Kinetic studies for single and binary adsorption

Figure 3 and Figure 4 show the effect of time on dyes adsorption for all conditions studied. As it can be seen, at the beginning of the process, the adsorption rate increases quickly, and then it decreased gradually till equilibrium was attained. In general, removal percentages higher than 70 % are obtained for both dyes in less than 1 h, and almost of 100 % at the equilibrium.

To identify the kinetic mechanism, the pseudo-first order (Lagergren 1907) and pseudo-second order kinetic models (Ho and McKay 1999) were used (Equation 6 and Equation 7, respectively):

\[
\log \left( q_e - q_t \right) = \log \left( q_e \right) - \frac{k_1}{2.303} t
\]  

(6)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]

(7)

Where \(q_t\) and \(q_e\) are the adsorption capacity (mg·g⁻¹) at t and equilibrium time (h), respectively, and \(k_1\) (h⁻¹) and \(k_2\) (g·mg⁻¹·h⁻¹) are the pseudo-first and the pseudo-second-order rate constants, respectively.

The experimental data were better fitted by the Ho’s model than by the Lagergren one (results not shown) for both dyes and all experimental conditions essayed. Thus, high correlation coefficients (\(R^2 > 0.99\)) (Table
and, in general, a good agreement between calculated and experimental values of $q_e$ were found (Figure 3 and Figure 4). This confirms the good fit of the pseudo-second order kinetic model for the adsorption of MB and MG in both single and binary systems and, therefore, that a chemical sorption can be involved during the process (Ho and McKay 1999).

**Equilibrium studies for single systems**

Adsorption equilibrium experiments were performed in a range of dye initial concentrations ($C_0$) from 10 to 100 mg L$^{-1}$ and at the three temperatures essayed (25, 40 and 60 °C) under the previous conditions selected (bark dose = 5 g L$^{-1}$, particle size = 0.5-1 mm and pH = 4). The data were fitted to the linear Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) isotherms models (Equation 8 and Equation 9) and the isotherm parameters and the correlation coefficients, $R^2$, are presented in Table 2.

\[
\frac{C_e}{q_e} = \left(\frac{1}{K_a q_m}\right) + \frac{C_e}{q_m} \quad (8)
\]

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (9)
\]

With $q_m$ and $K_a$ being the Langmuir isotherm constants, the maximum adsorption capacity (mg g$^{-1}$) and the constant related to the energy of adsorption (L·mg$^{-1}$), respectively, and $K_f$ (mg$^{\frac{1}{n}}$·L$^{\frac{1}{n}}$·g$^{-1}$) and $n$ are the Freundlich constants, indicating the adsorption capacity and intensity, respectively.

The correlation coefficients ($R^2$) for the Langmuir isotherm are higher than for Freundlich ones, therefore, MB and MG adsorption by cluster pine (*Pinus pinaster* Aiton) bark occurred by a monolayer adsorption with homogeneous active centers. The highest values of $q_m$ were obtained at 40 °C, 50,0 mg·g$^{-1}$ and 41,7 mg·g$^{-1}$ for MB and MG, respectively. In addition, $K_a$ values did not differ remarkably which means that there are not substantial changes between the binding capacity of the dyes with the bark surface. In fact, the value of the separation factor, $R_L$ (Equation 10), a characteristic of this isotherm (Vázquez *et al.* 2009), indicated a favorable adsorption for both dyes for all initial concentration essayed (0 < $R_L$ < 1):

\[
R_L = \frac{1}{1 + K_a C_0} \quad (10)
\]
Table 2: Pseudo-second order kinetic model and isotherm parameters for MB and MG removal by pine bark.

<table>
<thead>
<tr>
<th>Adsorbent dose (g·L⁻¹)</th>
<th>pH</th>
<th>Methylene Blue (MB)</th>
<th>Malachite green (MG)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kₑ (g·mg⁻¹·h⁻¹)</td>
<td>qₑ (mg·g⁻¹)</td>
<td>R²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.13</td>
<td>10.4</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>4 (Natural)</td>
<td>0.21</td>
<td>11.9</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.40</td>
<td>11.3</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.08</td>
<td>20.4</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.27</td>
<td>11.8</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.64</td>
<td>5.5</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>0.1-0.5</td>
<td>2.29</td>
<td>12.0</td>
<td>0.99</td>
</tr>
<tr>
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<td>0.5-1</td>
<td>0.27</td>
<td>11.8</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>1.6-2</td>
<td>0.22</td>
<td>10.9</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.21</td>
<td>11.9</td>
<td>0.99</td>
</tr>
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<td></td>
<td>40</td>
<td>0.70</td>
<td>9.7</td>
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</tr>
<tr>
<td></td>
<td>60</td>
<td>4.51</td>
<td>10.5</td>
<td>0.99</td>
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<tr>
<td></td>
<td>MG or MB (mg·L⁻¹)</td>
<td>0.0048</td>
<td>11.6</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>MB (50 mg·L⁻¹)</td>
<td>5</td>
<td>0.0054</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>MG (50 mg·L⁻¹)</td>
<td>25</td>
<td>0.0051</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0078</td>
<td>8.8</td>
<td>1.00</td>
</tr>
</tbody>
</table>

CONCLUSIONS

In this work, Pinus pinaster bark was used as an efficient adsorbent for the elimination of malachite green (MG) and methylene blue (MB) from aqueous systems. Pseudo-second-order kinetic model satisfactorily explained dye adsorption in both single and binary systems. On the other hand, the Langmuir isotherm described well equilibrium data for single systems. Adsorbent particle size, initial solution pH and adsorbent dosage were found to affect MG and MB adsorption by pine bark, whereas temperature hardly influenced dyes adsorption process. In general, pine bark showed more affinity for MB than for MG with slightly higher adsorption capacities for the former. The removal efficiency was lower in binary systems which might be due to a competitive effect between dyes.
Authorship contributions

K. L.: Investigation, validation, visualization, writing—original draft. M.S.F.: Conceptualization, methodology, resources, supervision, writing — review and editing. M.S.: Conceptualization, methodology, writing — review. J.G-A.: Conceptualization, methodology, resources, supervision, project administration, writing — review and editing.

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REFERENCES


