Removal of wood dyes from aqueous solutions by sorption on un-treated pine sawdust

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Abstract Synthetic dyes are extensively used in industry for various applications among which is the preparation of dyed wood veneers. The discharge of effluents containing dyes is of great concern due to their toxicity, mutagenicity and carcinogenicity and causes serious environmental problems. In this work, the possibility of using un-treated pine (*Pinus radiata*) sawdust, a waste product from the wood industry, as biosorbent for the removal of wood dyes from wastewaters was investigated. The BET surface area of the material was 0.36 ± 0.01 m^2/g and the point of zero charge 4.8. Batch adsorption experiments were performed at 25ºC, natural pH (5.1, 6.0, 6.2 for blue, black and red dyes, respectively), 100 rpm and initial dye concentration of 5 mg L^{-1} to analyze the effect of the adsorbent dose (5 or 10 g L^{-1}) and contact time (up to equilibrium) on the adsorption percentage for three dyes (blue, red and black). The highest adsorption percentage was attained at 10 g L^{-1} for an equilibrium time of 48 h: 67 ± 2.46% for blue, 34.46 ± 0.34% for black and 29.93 ± 0.27% for red. The maximum adsorption capacity decreased in this order: blue, 0.374 ± 0.032 mg g^{-1}; black, 0.183 ± 0.001 mg g^{-1} and red, 0.161 ± 0.002 mg g^{-1}. Kinetic data were best fitted to the pseudo-second order model, which suggests a chemisorption process.

Keywords: pine sawdust, wood dyes, biosorption, wastewaters

1. Introduction

Synthetic dyes are essential resources used in industries like wood, paper, cosmetic, textile, etc. to color their products. It was estimated that there are more than 100,000 commercial dyes and about 350,000 tons are useless and wasted every year (Şentürk & Yıldız, 2020). The discharge of these dyes in wastewater without treatment is of great concern for the environment and human health. There are a variety of techniques that have been studied for the removal of dyes from waters and wastewaters, such as chemical oxidation, adsorption, biodegradation, chemical coagulation, electrolysis, and flotation (Can, 2015, Al-Kadhi, 2020).

Adsorption has been revealed as one of the most effective processes for dyes removal, being cost-efficient and with a simple design and operation. A wide range of adsorbents have been used for dye removal from aqueous solutions. Activated carbons have been the most applied, however, their high cost and the difficulty of their regeneration have promoted the research on low-cost adsorbents. Numerous biowastes, have been pointed out as promising materials due to the lack of hazardous by-product formation, eco-friendliness, and flexibility under operating conditions, such as grapefruit peel, canola hull, pine cone, pine sawdust, peanut husk and rice hull. (Yagub et al., 2014). Pine sawdust from species like *Pinus duragensis*, *Pinus resinosa*, and *Pinus tabulaeformis* have been previously investigated for dyes removal (Salazar-Rabago et al., 2017, Can, 2015, Sahmoune and Yeddou, 2016) and revealed promising results.

In the present study, pine (*Pinus radiata)* sawdust, without any pretreatment, was analyzed as an alternative adsorbent for the removal of wood dyes from aqueous solutions. Batch experiments were performed to investigate the kinetics of the adsorption process and the influence of adsorbent dose on adsorption efficiency.

2. Materials and Methods

2.1. Adsorbent

Pine (*Pinus radiata*) sawdust was provided by a regional sawmill (Lugo, Spain). After drying in sun for 24 hours, the sawdust was sieved using a Ro-Tap type electrical sieve shaker (FTL-0200, Spain). The fraction between 0.5 and 1 mm was selected, stored in a plastic container, and used directly for adsorption experiments.

2.2. Adsorbent Characterization

The surface area of pine sawdust (PS) was calculated after drying at 50ºC for 72 h, by adsorption of N_2 at 77 K using an ASAP 2020 surface area analyzer (Micromeritics, USA).

The pH of the point of zero charge (pH_{PZC}) for the PS was evaluated as described in Şentürk & Yıldız (2020), although slightly modified. Thus, 0.2 g of PS were put in contact with 50 mL of NaCl 0.01 M solution at 200 rpm for 48 h to assure the equilibrium (Nordine et al., 2016).

2.3. Dyes

Acid wood dyes were used: Blue for wood AGN-270%, Red for wood GRA-200%, and Black Hispalan M-RN-140%. The solutions used in the experiments at the required concentration were prepared by dilution with distillated water from a stock aqueous solution of 500 mg L^{-1}.

2.4. Adsorption Experiments

Batch adsorption experiments were carried out by shaking 0.25 or 0.5 g of PS with 50 mL of a 5 mg L^{-1} dye solution at 100 rpm, natural pH (5.1, 6.0 and 6.2 for blue, black and red dyes, respectively) and 25ºC in an Unitronic orbital C shaker (Selecta, Spain). At predefined intervals of time, samples were removed and centrifuged 15 min at 4000 rpm. Dye concentration was determined by measuring the absorbance of the supernatant at the dye maximum wavelength, λ_{max}, using an UV/VIS spectrophotometer (V-630, Jasco, Japan). Dye removal efficiency was calculated as the percentage of dye adsorbed (equation 1). Adsorption capacity was calculated as the amount of dye adsorbed per mass unit of PS (equation 2).

$$\%\, Adsorption = (C_0 - C)/C_0 \times 100 \quad (1)$$

$$q\ (mg/g) = (C_0 - C)V/m \quad (2)$$

where C_0 and C are the initial and residual dye concentrations (mg L^{-1}), q is the adsorption capacity (mg g^{-1}), V is the volume of dye solution (L) and m is the dry mass of adsorbent used (g).

2.5. Adsorption Kinetics

Kinetic models were applied to explain the adsorption process and examine the mechanism of the interactions:

- Pseudo-First Order

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (3)$$

where q_t and q_e are the amounts of dye adsorbed (mg g^{-1}) at time t (min) and at equilibrium, respectively, and k_1 represents the first-order rate constant (min^{-1}).

- Pseudo-Second Order

$$t/q_t = (1/k_2 q_e^2) + t/q_e \quad (4)$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant (Ho and McKay, 1999).

- Intra-particle diffusion

$$q_t = k_{id} t^{1/2} + I \quad (5)$$

where I is the intercept and k_{id} is the rate constant of intra-particle diffusion (mg g^{-1} $min^{-1/2}$) (Weber and Morris, 1963).

3. Results and Discussion

3.1. Adsorbent Characterization

The surface area of PS was 0.36 ± 0.01 m^2/g. Similar values have been reported for pine sawdust from *Pinus duragenesis* and for durian wood (*Durio zibethinus)* sawdust (Salazar-Rabago et al., 2017, Chowdhury et al., 2016).

The relationship between pH and pH_{PZC} plays a key role to understand the adsorption process since pH affects the surface charge of the adsorbent, the degree of ionization, and in turn, the binding specificity of the adsorbate. As can be observed in Figure 1, the point of zero charge of PS is 4.8, indicating that when the pH is lower than pH_{PZC} the PS surface is positively charged and negatively charged when is higher than pH_{PZC}. When pH is less than pH_{PZC} the sawdust will adsorb anionic dyes and when pH is higher than pH_{PZC} the adsorbent will adsorb cationic dyes (Ratnamala et al., 2016). Acid wood dyes are negatively charged, so it is probable that a positively charged PS surface leads to increased adsorption of acid dye anions.

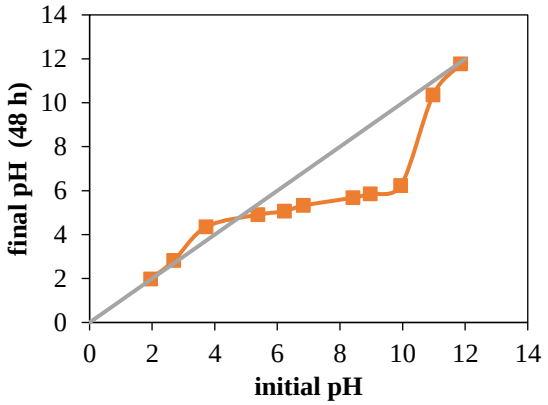

Figure 1. Determination of point of zero charge for pine sawdust.

3.2. Batch Adsorption Studies

Effect of contact time

Figure 2 presents the adsorption efficiency versus time for the blue, red, and black dyes at two adsorbent doses for PS.

As can be seen in Figure 2, the adsorption proceeds in two stages. A fast first stage followed by a slower one until equilibrium is reached. At the initial phase, the sawdust presents a more available and porous surface which favors the rapid adsorption of the dye. As the adsorption progresses the surface becomes progressively saturated with the consequent decrease in the number of sorption sites on the PS and the adsorption becomes slower (Al-Kadhi, 2020).

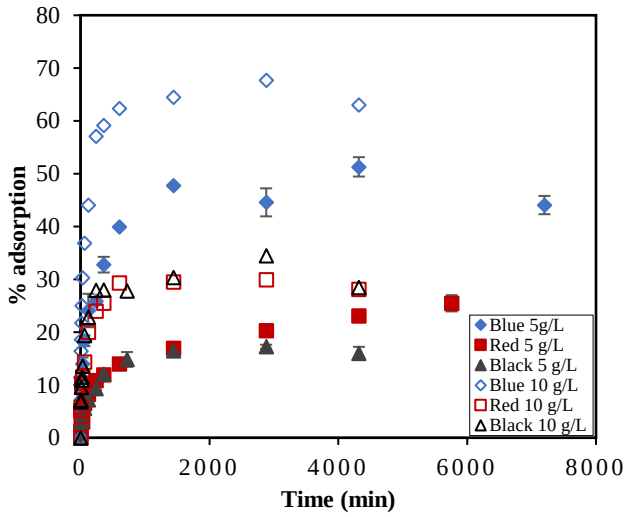

Figure 2. Adsorption efficiency versus time for blue, red and black dyes (adsorbent dose: 5 and 10 g/L; dye initial concentration: 5 mg L^{-1} 25 °C).

The time necessary to reach equilibrium was 72 h at 5 g/L and 48 h at 10 g/L for the blue dye, 96 h at 5 g/L and 48 h at 10 g/L for the red one, and 48 h for the black one at both adsorbent doses. The maximum efficiency of adsorption was attained for the blue dye at both adsorbent doses (see Table 1) which can be related with the lower pH of this dye (5.1) in comparison with the black (6.0) and the red ones (6.2). At pHs far above the pH_{PZC} the surface might be more negatively charged, and this could lead to electrostatic repulsion and, consequently, to a lower amount of dye adsorbed. Previous studies with pine sawdust also demonstrated that for acid dyes, adsorption improved at lower pH. (Özacar & Şengil, 2005, Can, 2015, Akhouairi et al., 2019).

Effect of adsorbent dose

Table 1 shows the influence of the adsorbent dose on the equilibrium adsorption efficiency. The adsorption efficiency increased when increasing the adsorbent dose from 5 to 10 g/L, but more remarkably for the blue and black dyes.

This can be explained by the increase in the number of available adsorption sites and enhanced surface area due to the increase of adsorbent dose. Regarding the equilibrium adsorption capacity (q_{max}), it decreases with increasing adsorbent dose, except for the black dye (see Table 2).

Table 1. Maximum removal efficiency for blue, red and black wood dyes onto pine sawdust.

Adsorbent dose	Blue AGN270%	Red GRA200%	Black M-RN-140%
(g/L)	Maximum dye adsorption (%)		
5	51.30 ± 1.83	25.47 ± 1.54	17.25 ± 0.37
10	67.67 ± 2.46	29.93 ± 0.27	34.46 ± 0.34

3.2.1. Adsorption kinetics

In order to explain the kinetics of dye removal using un-treated pine sawdust, the experimental data were fitted to the pseudo-first order (eq. 3), second order (eq. 4), and intraparticle diffusion (eq. 5) kinetic models. The kinetic parameters obtained are listed in Table 2. In view of the results, the second order model is the one that best fits the experimental data with correlation coefficients higher than 0.975 for all dyes. Additionally, a good agreement between the experimental maximum adsorption capacity (q_{max}) and that predicted by the model (q_e) was obtained.

Regarding the intraparticle diffusion kinetic model, the kinetics of the adsorption process was divided into two linear regions (1) lower contact times and rapid uptake and (2) higher contact times and slow uptake until reaching equilibrium. High correlation coefficients (>0.9) were obtained for the first region which suggests the possibility of intraparticle diffusion of the dye from the outer surface into the pores of the sawdust at the initial phase of the adsorption process. However, the low correlation coefficients for the second region indicates a change in the adsorption mechanism.

Table 2. Pseudo-first order, pseudo-second order and intraparticle diffusion kinetic model parameters.

		Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
Dye (S/L)	**q_{max} (mg/g)**	**k_1 (min^{-1})**	**q_e (mg/g)**	**R^2**	**k_2 (g $mg^{-1}min^{-1}$)**	**q_e (mg/g)**	**R^2**	**k_i**	**C**	**R^2**
Blue 5 g/L	0.509	0.001	0.338	0.644	0.042	0.461	**0.995**	0.0169	0.024	**0.963**
								0.0002	0.450	0.030
Blue 10 g/L	0.374	0.002	0.216	0.783	0.141	0.353	**0.998**	0.0214	0.031	**0.951**
								0.0007	0.317	0.448
Red 5 g/L	0.276	0.0005	0.225	0.920	0.015	0.260	**0.975**	0.0072	0.002	**0.965**
								0.0026	0.074	0.989
Red 10 g/L	0.161	0.003	0.110	0.955	0.324	0.149	**0.995**	0.0078	0.013	**0.931**
								0.0003	0.137	0.149
Black 5 g/L	0.182	0.003	0.148	0.969	0.066	0.172	**0.994**	0.0060	0.006	**0.970**
								0.0004	0.144	0.289
Black 10 g/L	0.183	0.001	0.108	0.578	0.167	0.168	**0.995**	0.0091	0.018	**0.957**
								0.0006	0.132	0.510

In summary, the pseudo-second order kinetic model can describe the whole adsorption processes through a chemical sorption mechanism involving valence forces due to the interchange of electrons. Simultaneously, the intraparticle diffusion kinetic model also explains the adsorption process at the initial stage with the transfer of the dye from the outer surface into the pores of the material (Semerjian, 2018, Şentürk & Yıldız, 2020).

4. Conclusion

Pine sawdust was used as an adsorbent for the removal of wood dyes for wastewater treatment. At both adsorbent doses essayed, the maximum equilibrium sorption efficiency was attained for the blue dye followed by the black and the red ones, which could be related with dye natural pH. The increase of the adsorbent dose increased the removal efficiency for all dyes, but more remarkably for the blue and black ones. The kinetics of dye adsorption was better explained by the pseudo-second order kinetic model. Also, the first stage of the adsorption process could be characterized by intraparticle diffusion model.

The obtained results showed that pine sawdust has the potential to remove dyes from aqueous solutions, however, factors such as pH, initial dye concentration, and temperature might influence dye sorption and removal efficiency and will be studied in the near future.

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6. References

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