

"Research Note"

ADSORPTION OF REMAZOL BLACK RL AND REACTIVE YELLOW 145 FROM AQUEOUS SOLUTIONS BY PINE NEEDLES*

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Abstract– Adsorption of Reactive Yellow 145 (RY145) and Remazol Black RL (RBRL) onto pine needles (PN) was investigated with respect to initial dye concentrations, adsorbent dosage, and pH in a batch manner. The obtained data in the study were described according to the Langmuir and Freundlich isotherm models and the Langmuir model describes the experimental data very well with a q_{\max} value of 13.831 and 7.225 for RBRL and RY145 respectively. As the pH decreased, adsorption density increased gradually and the highest adsorption density was obtained at pH 2 for both adsorbents (91.57 and 64.77% for RBRL and RY145 respectively). Equilibrium adsorption rates of 70.15% with RY145 and 86.72% with RBRL onto PN were observed at 90 min. In order to better model the kinetics of adsorption, first order, pseudo second order and second order models were applied. Among these models, the pseudo-second order kinetic model provided a good correlation for the adsorption of RY145 and RBRL by PN with a $R^2 > 0.999$. Results showed that pine needles have great potential to remove Reactive Yellow 145 (RY145) and Remazol Black RL from aqueous solutions.

Keywords– Adsorption, reactive yellow 145, Remazol Black RL, pine needles

1. INTRODUCTION

The presence of dyes in textile industry wastewaters may be toxic, mutagenic and carcinogenic [1–3]. They may also resist light and heat, thereby reducing photosynthetic activity and negatively impacting the receiving environment.

There are numerous treatment methods for dye removal (e.g. membrane filtration [4], chemical oxidation [5], foam floatation [6], electrolysis [7, 8], biodegradation [9-11], adsorption [12], chemical coagulation [13, 14] and photocatalysis [15, 16]. Among them, the adsorption process provides an attractive alternative dye removal method, especially if the adsorbent is inexpensive or free and abundant in nature. This removal technique is a well-known separation process and is widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. Synthetic dyes represent one of the problematic groups. Adsorption, in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity, has been found to be superior to other techniques [12].

One widely used and effective adsorbent found in the literature is activated carbon, but its use is limited by the high costs associated with its regeneration or replacement [13, 17]. According to Bailey et al., an adsorbent can be considered as low-cost if it requires only a small process to prepare, is abundant in nature, or is a by-product or waste material from another industry [17]. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative adsorbents [18]. In the literature many similar agricultural adsorbents could be found. Ucar

*Received by the editors September 15, 2012; Accepted April 21, 2013.

and Armagan (2012) used cotton seed shell to remove Reactive Black 5 from aqueous solutions and maximum adsorption density was obtained as 12.19 mg.g^{-1} in the conditions of pH 2 and the contact time of 30 min [19]. In another adsorption study, where dehydrated beet pulp carbon and Chemazol Reactive Red 195 were used, maximum adsorption capacity was obtained as 58.0 mg.g^{-1} at temperature of $50 \text{ }^\circ\text{C}$. Similar to Ucar and Armagan's study, maximum adsorption density was again obtained in low pH (pH 1) [20]. Agricultural wastes can also be used to produce activated carbon. Cardoso et al. (2011) used Brazilian pine fruit shells to produce activated carbon and compared its adsorption efficiency with the natural form of pine shells. As activated carbon is an effective material, authors also reported favorable adsorption rates at pH values ranging from 2.0 – 7.0, whereas this value is 2.0 – 2.5 for natural form of pine shells. Contact time also varied between two materials (4 and 14 hours for activated carbon and natural form of pine shells respectively) [21]. Although processing Brazilian pine fruit shells to form activated carbon may be costly, it exhibits a great advantage in application. Different from agricultural originated adsorbents, methyl violet is successfully removed from aqueous solutions by adsorption onto halloysite nanotubes. The clay minerals of halloysite nanotubes exhibited rapid adsorption rate and high adsorption capacity of 113.64 mg.g^{-1} . Pseudo second order kinetic model is well fitted to kinetic experiment results with correlation coefficients greater than 0.999 [22]. Other than the studies summarized above, many workers have employed different materials such as perlite [23], biomaterial [24], recycled alum sludge [25], zeolites [26], agriculture waste residues [27] for removing the dyes from wastewater. For more studies upon the adsorption of textile dyes by low cost adsorbents, see the review of Crini [18].

Many organic wastes are used directly or indirectly (in the form of activated carbon) to treat textile industries wastewaters [20, 21]. Since the cost is one of the most important parameters in wastewater treatment systems, it is necessary to find suitable materials free of charge. Pine needles (PN), found in forests all over the world, represent a huge renewable and low cost bioresource similar to Brazilian pine fruit shell [20] and beet pulp [21]. Although this abundant forest waste is used for the adsorption of some anions and cations [28], PN is not put to any use of dye removal. Reactive Yellow 145 (RY145) and Remazol Black RL (RBRL) are extensively used in the studies found in the literature and also in textile industry (i.e. in Moroccan industry) [29]. Therefore, these dyes are selected to compare the results with the literature. So the aim of this study is to investigate the adsorption of Reactive Yellow 145 (RY145) and Remazol Black RL (RBRL) by the leaves of *Pinus sp.* The experiments were conducted in a batch system in order to evaluate the adsorption capacity of PN.

2. MATERIALS AND METHODS

a) Adsorbents

In this work, the potential removal of RY145 and RBRL by PN was investigated. Prior to use, PN were washed thoroughly with distilled water to remove dust, and were subsequently dried overnight in a heater at $60 \text{ }^\circ\text{C}$. The PN were then rendered into small pieces by a home type coffee grinder. Only the PN with 1-2 mm dimensions were selected for use, and were stored in glass bottles. This material was used directly in the adsorption experiments without further treatment. Similar adsorbent preparation procedure was also reported [20, 22]

b) Chemicals

RY145 and RBRL (Fig. 1) were used as received without further purification. The test solutions containing required dye concentrations were prepared by diluting 1000 mg.L^{-1} dye stock solution. The range of dye concentrations used for the experiments ranged between $50 - 1000 \text{ mg.L}^{-1}$. The pH of each solution was adjusted to the required value with 0.1 M HCl and NaOH solutions before coming into

contact with the adsorbent. For each dye, some properties are shown in Table 1.

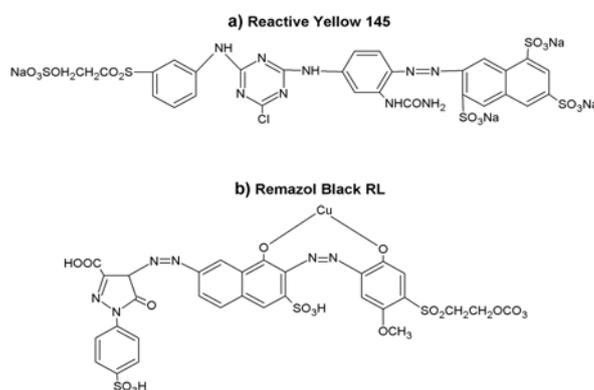


Fig. 1. Chemical structure of (a) RY145 and (b) RBRL

Table 1. Properties of RBRL and RY145

Dye	λ (nm)	MW (g.mol ⁻¹)
RBRL	575	1006.25
RY145	420	1026.2

c) Adsorption studies and analytical techniques

Adsorption studies were conducted in a routine manner using the batch technique as followed by many researchers [1-3, 19-21]. A certain volume (45 ml in each case) of RY145 and RBRL dye solutions and a predetermined amount of adsorbent were added to batch bottles. The batch reactors were then placed in a rotary shaker. The adsorbent was separated from the aqueous phase by filtering supernatant through 0.45 μ m polyethersulfone membrane syringe filters. The adsorbed amount was measured as the difference between the initial and final dye concentrations in the supernatant.

In order to determine the effect of the pH, RY145 and RBRL solutions were adjusted to different pH values as explained above. The amount of adsorbent added to the batch bottles was kept constant at 1 g, except while determining the optimum adsorbent amount, and only dye concentrations were changed in the isotherm experiments. The flasks were agitated at 180 rpm for 4 hours to ensure equilibrium conditions. All measurements were made at an ambient temperature (22.5 ± 1 °C).

The concentration of the RY145 and RBRL in the adsorption medium was measured by using a spectrophotometer (Shimadzu UV01) where the maximum absorbance peak was observed at 420 nm and 575 nm for RY145 and RBRL, respectively. The results are given as the units of adsorbed RY145 and RBRL quantity per gram of adsorbent (adsorbent density) at any time (q , mg.g⁻¹). Adsorbent density was calculated by Eq. (1) below.

$$\Gamma = \frac{a(C_i - C_e)}{k} \quad (1)$$

where, Γ is adsorption density (mg.g⁻¹); C_i is initial dye concentration (mg.L⁻¹); C_e is dye concentration at equilibrium (mg.L⁻¹); k is amount of adsorbent (g); and a is volume of synthetic wastewater (L).

For the adsorption isotherm studies, 1 g of PN and 45 mL of RY145 and RBRL solution containing different concentrations of dye (50 – 1000 mg.L⁻¹) were shaken continually at 180 rpm until adsorption equilibration was attained. Final concentrations were measured as described above in order to determine equilibrium concentrations.

3. RESULTS AND CONCLUSIONS

a) Kinetics of adsorption

The adsorption kinetic curve was studied at a dye concentration of 50 mg.L^{-1} . Pseudo first order, pseudo second order and second order models, which control the process, were tested in order to evaluate the kinetic mechanism. As shown in Fig. 2, the time necessary to reach this equilibrium is about 90 minutes. Such a rapid uptake of RY145 and RBRL may indicate that the PN have an affinity for the dyes pointing towards physical adsorption where electrons did not exchange between adsorbent and adsorbate. In addition, desorption studies were performed to explain the interaction of dyes on PN. To do this, 1 g RY145 – PN and RBRL – PN combinations (obtained from the reaction of 1 g PN with 100 mg.L^{-1} RY145 and RBRL) was added to distilled water and shaken for 90 minutes. At the end of the experiment, in the supernatant, 17.30 mg.L^{-1} RY145 and 14.28 mg.L^{-1} RBRL were measured. This experiment shows that interactions between PN and dyes were relatively weak, and therefore likely to be physical.

At the equilibrium, removal of RBRL was higher than that of RY145 (70.15% and 86.72% for RY145 and RBRL, respectively). In physical adsorption, most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Therefore, adsorption mechanism in this study indicates the physical adsorption.

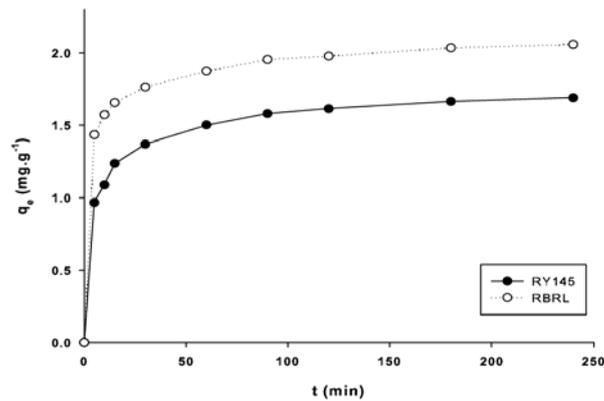


Fig. 2. Kinetics of RY145 and RBRL adsorption by PN (t = Time as minutes; q_t = adsorption density at that time)

The kinetics of dye adsorption, important for determining kinetic parameters in designing adsorption systems, which can be modeled by the first order rate equation [30], the pseudo-second order rate equation [31] and the second order equation [2] are given below, respectively.

$$\frac{\log(q_e - q_t)}{q_e} = \frac{-K_v t}{2.3} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{2.K.q_e^2} + \frac{t}{q_e} \quad (3)$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k.t \quad (4)$$

Where K_v is the rate constant for the first-order (min^{-1}); K is the pseudo second-order rate constant of adsorption ($\text{min}^{-1}.\text{g}/\text{mg}$) and k is the rate constant of the second-order ($\text{min}^{-1}.\text{g}/\text{mg}$); q_e and q_t are the amounts of dye adsorbed per mass unit of adsorbent (mg.g^{-1}) at equilibrium and at time t , respectively.

The results showed that the correlation coefficients for the first order and the second order kinetic models were very low. However, the pseudo-second order kinetic model produced a very high correlation

coefficient ($R^2 > 0.999$) and theoretical q_e values were very close to the experimental q_e values (Table 2). The plots of the linearized form of the pseudo-second order equation are shown in Fig. 3. Thus, it could be noted that the pseudo-second order kinetic model provides a good correlation for the adsorption of RY145 and RBRL by PN. This complies with the literature [2, 31, 32].

Table 2. First order, Pseudo second order and second order model constants.

Dyes / Kinetic Models	First order rate		Second order rate			Second Order Model		
	K_v (min^{-1})	R^2	K ($\text{min}^{-1} \cdot \text{g}/\text{mg}$)	q_e ($\text{mg} \cdot \text{g}^{-1}$)	R^2	K ($\text{min}^{-1} \cdot \text{g}/\text{mg}$)	q_e ($\text{mg} \cdot \text{g}^{-1}$)	R^2
RBRL	0.065	0.404	0.1977	2.012	0.983	0.053	2.08	0.999
RY145	0.057	0.707	0.1968	6.075	0.971	0.043	1.72	0.999

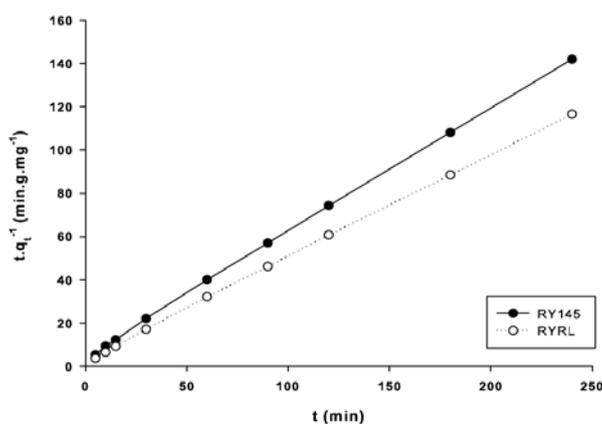


Fig. 3. Linearization of dye adsorption kinetics by PN for the pseudo-second order kinetic model (t = Time as minutes; q_t = Adsorption density at that time)

b) Effects of pH on adsorption

Adsorption tests as a function of pH were carried out to determine the optimum pH value for the adsorption of RY145 and RBRL by PN. Although no decolourization of RY145 was observed at pH 3 – 10, adsorption efficiency of 64.77% was shown at pH 2. On the other hand, poor decolourization efficiency ($< 25\%$) for RBRL was shown at pH 3 – 10 while maximum efficiency (91.51%) was observed again at pH 2 (Fig 4). Therefore, all other experiments were carried out at pH 2. Similar observations have been reported by other workers [32, 33]. These observations may be explained by the low solubility rates of both dyes at acidic pH values.

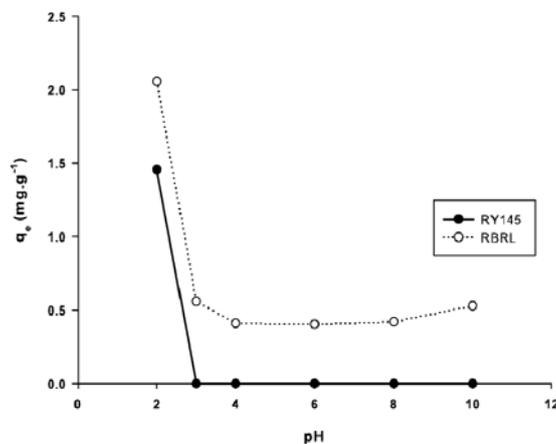


Fig. 4. Adsorption of RY145 and RBRL by PN at different pH values (q_e = Adsorption density at equilibrium)

c) Adsorption isotherms

In order to design an adsorption system, equilibrium data, commonly known as adsorption isotherms, are a basic requirement. The most widely used isotherm equations for the modeling of adsorption data are the Langmuir and Freundlich equations. The equilibrium studies were carried out at pH 2 with the contact time required to reach adsorption equilibrium.

For adsorption data interpretation, both the Langmuir and Freundlich isotherm models were used. Langmuir isotherm model [32, 34, 35] was used due to the homogeneous surface of the adsorbent, since the Freundlich isotherm [36] is applied in the case of heterogeneous surfaces. The Langmuir isotherm considers the adsorbent surface as homogeneous, with identical sites in terms of energy.

Results showed that the Langmuir isotherm model best fits the adsorption data to explain the adsorption isotherm and results shown in Table 3. The higher determined coefficient of 0.990 and 0.987 for the Langmuir isotherm that predicted the active sites of the PN for the adsorption of RY145 and RBRL are identical and homogeneous in terms of energy and similar results can be found in the literature for similar organic dyes [37]. According to the Langmuir isotherm model, maximum adsorption capacity and the Langmuir constant can be determined. Plots of the linearized form of the Langmuir isotherm model with the correlation coefficient of 0.990 and 0.987 for RY145 and RBRL, respectively, are given in Fig. 5.

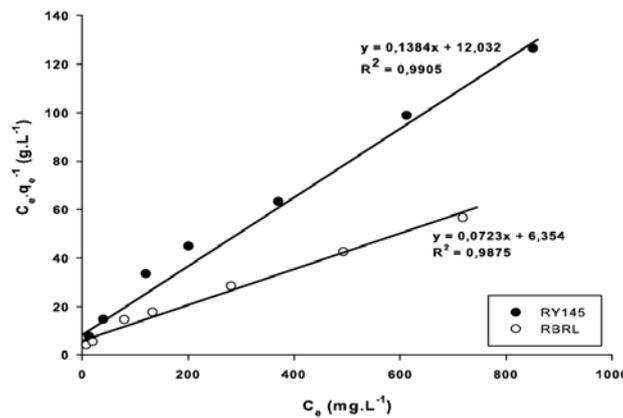


Fig. 5. The Linearized Langmuir adsorption isotherm of RY145 and RBRL by PN (C_e = Dye concentrations at equilibrium; q_e = Adsorption density at equilibrium)

Table 3. Parameters of Langmuir and Freundlich isotherm models

Dyes / Isotherm Models	Langmuir isotherm model			Freundlich isotherm model		
	K_L	q_{max}	R^2	K_F	n	R^2
RBRL	0.010	13,831	0.987	0.926	2.435	0.971
RY145	0.012	7.225	0.990	0.747	2.998	968

The value determined for maximum saturation capacity of the adsorbent monolayer was 7.225 and 13.831 mg of dye per gram of adsorbent. The Langmuir constant was 0.012 and 0.010 L.mg⁻¹ for RY145 and RBRL, respectively.

d) Effect of the adsorbent dosage

While initial RY145 and RBRL concentrations were kept constant at 50 mg.L⁻¹, varied amount of PN (from 0.1 to 1 g) was applied in order to investigate the effect of adsorbent amount on the adsorption of both dyes. As shown in Fig. 6, the removal of RY145 and RBRL increased from 23.774% to 78.024%,

and from 53.004% to 99.008%, respectively. Increase in the removal efficiency at high adsorbent dose can be explained by the availability of more adsorption sites. Although the percentage removal for both dyes increased as PN dosage increased, the adsorption density decreased due to its reverse ratio with the adsorbent amount.

Figure 6 and 7 indicate that, in terms of percentage removal of both dyes, the optimum adsorbent amount is 1 g. However, 0.1 g adsorbent is the optimum amount for obtaining maximum adsorption density.

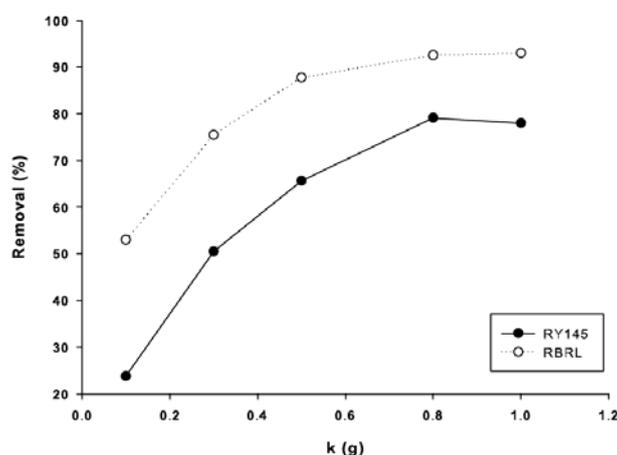


Fig. 6. Effect of adsorbent dosage on the % removal of dyes (k = Amount of adsorbent; q_e = Adsorption density at equilibrium)

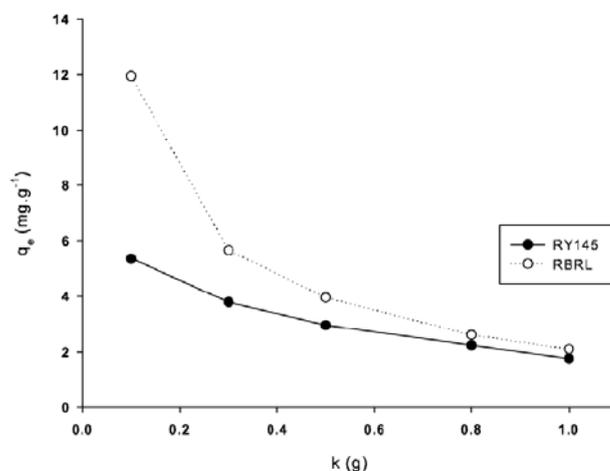


Fig. 7. Effect of adsorbent dosage on the adsorption density of PN (k = Amount of adsorbent)

4. CONCLUSION

In this study, the ability of PN to bind RY145 and RBRL was investigated by means of optimum pH, adsorbent dosage, kinetics and equilibrium. The results indicated that the adsorption process is pH dependent and that maximum adsorption density is obtained at pH 2 for both dyes. The kinetics of RY145 and RBRL adsorption onto PN was studied using the pseudo-first and pseudo-second order and second order kinetic models. The results indicated that the pseudo-second order equation provided the best correlation for the adsorption data. According to pseudo second order model, equilibrium adsorption densities were 2.012 and 6.075 mg.g^{-1} . Optimum contact time was 90 minutes for both dyes. In the adsorption equilibrium studies, the Langmuir equation was used to fit the experimental data obtained. According to experimental data, the Langmuir model provided the 7.225 and 13.831 mg.g^{-1} maximum

adsorption density for RY145 and RBRL, respectively. It is also reported that the percentage removal of RY145 and RBRL increased with increasing PN amount. However, the optimum adsorbent concentration obtained was 2.22 g.L^{-1} . It may be concluded that PN, a free and abundant natural resource, are an efficient adsorbent for the removal of RY145 and RBRL from aqueous solution.

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