



Adsorption of Reactive Blue 5G dye by activated carbon from babassu shells and pyrolyzed oil shale residue

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Abstract: This work aimed to study the adsorption mechanism of Reactive Blue 5G, usually found in wastewater from textile industries. The experiments were carried out in continuous systems, where the adsorption occurred in activated carbon from babassu shells and pyrolyzed oil shale residue in up flow fixed bed at 30°C. In order, to minimize the diffusional resistances it was investigated the flow rate influence in the breakthrough curves at feed concentration of 35 mg/l. Breakthrough curves for a flow range of 2-10 mL/min were carried out using a 15.5 cm of bed height to activated carbon and 9.5 cm to pyrolyzed oil shale residue, with an inlet diameter of 1.01 cm. Through the mass transfer parameters it was obtained the minimal resistance in the bed at 4 mL/min to the activated carbon and 2 mL/min to pyrolyzed oil shale residue. It was also concluded that the size of the pores has an important role in the adsorption mechanism.

Introduction

Dyes are the one of the major constituents of the wastewater produced from many industries related to textile, paint and varnishes, plastics, tannery, etc. Colored dye effluents pose a major threat to the surrounding ecosystem. Among various dyes, Reactive Blue 5G is a well-known reactive dye being used mainly in textile industries. As textile wastewater is characterized by deep blue color, which affects the nature of water by inhibiting sun light penetration and thus reducing photosynthetic action. Therefore, there is a considerable need to treat such effluents prior to discharge.

Adsorption has been shown to be a good method of color contaminant removal as it can be very simple and offers sludge free operation. According to Rozzi *et al.* (1999), the adsorption process in activated carbon is the best method for color removal from wastewater. On the other hand, it should be done from cost starting materials to provide economic benefit. As alternative is the use of activated carbon made from babassu shells, which are very abundant in the brazilian northeast (Jaguaribe *et al.*, 2005)

Another waste material that deserves attention are oil shale residues. Shale oil ash, for example, is an inorganic residue obtained after the direct combustion of the oil shale used as a source of energy. The total residual ash material that might be generated from oil shale reserves has been estimated, to about 3.2×10^{11} tons and such waste material may be applied as adsorbent (Al-Qodah, 2000). Another residue is the pyrolyzed oil shale residue generated in the pyrolysis of oil shale, known commercially as PETROSIX/PETROBRAS process. Such material has a diary production of about 6600 ton and has been investigated as adsorbent of organic substances (Stachiw, 2005).

Most of the studies of adsorption process of dyes have been conducted in batch system, but continuous processes are often applied in wastewater treatment. Unfortunately, the uptake process in continuous systems may not follow the batch mechanism (Barros *et al.*, 2004). Then, investigation about the best operational condition in fixed bed systems should be done to fulfill this lack of information. Therefore, this

work aimed to analyze the operational conditions that would minimize the mass transfer resistances faced by Reactive Blue 5G in the adsorption process using activated carbon from babassu shells and pyrolyzed oil shale residue.

Experimental

Materials

The synthetic effluent utilized for the runs was prepared using the dye (reactive blue 5G), which molecular structure is shown in Figure 1. The pH of the synthetic effluent was around 6.8. The measurement of concentration had been made in a Shimadzu UV – Visible Spectrophotometer UV-1601PC at 610 nm, as the procedures suggested from the manufacturer.

The babassu activated carbon (average particle diameter of 0.56 mm) was gently donated by Tobasa Bioindustrial. The sample was characterized by N₂ adsorption, zero point charge (ZPC), infrared spectroscopy and selective titration using Boehm titration method. The pyrolyzed oil shale residue (average particle diameter of 0.22 mm) was obtained from SIX/PETROBRAS and was characterized by N₂ adsorption and zero point charge (ZPC).

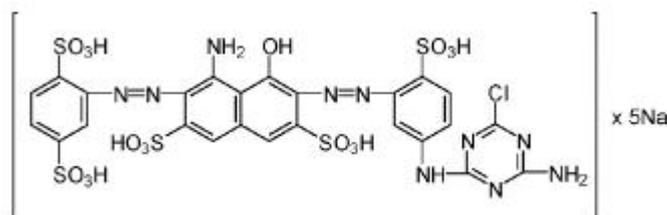


Figure 1 - The molecular structure of reactive blue 5G.

Activated carbon and pyrolyzed oil shale residue fixed beds

The adsorption process where the dynamic experiments were performed is shown in Figure 2. The adsorption column consisted of a clear glass tube 1.01 cm ID and 30 cm long and contained the adsorbent (granular activated carbon or pyrolyzed oil shale residue) supported by glass beads. The column was connected to heat exchange equipment that maintained all system at 30°C. Before starting the runs, activated carbon and pyrolyzed oil shale residue beds were rinsed by pumping deionized water up flow through the column to remove air bubbles. After bed accommodation at bed height of 15.5 cm to activated carbon (5.639 g) and bed height of 9.5 cm to pyrolyzed oil shale residue (7.264 g), the column was completed with glass beads and at this moment the adsorption started by pumping the dye solution also up flow. For the evaluation of the best operational condition the experimental data were obtained with a feed concentration of 35 mg/L with flow rates of 2, 4, 6, 8 and 10 mL/min. Samples at the column outlet were collected regularly. For the packed bed of the pyrolyzed oil shale residue it was also analyzed COD as it may contain some organics. In the packing step the column was washed with deionised water and when the adsorption process started such value was negligible (\cong 30 mg/L). All breakthrough curves were plotted taking into account the dye concentration in the outlet samples as a function of the running time (C/C_0 versus t) until the saturation of the column.

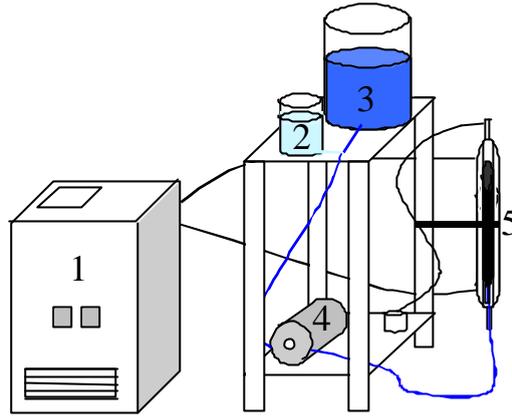


Figure 2 - Diagram for dynamic adsorption studies: 1- Heat exchanger equipment; 2- Deionized water tank; 3- Dye solution tank; 4- Pump; 5- Adsorption column.

Estimation of Mass Transfer Parameters

The dimensionless time of the breakthrough curves is defined as (McCabe et al., 2001):

$$t = \frac{1}{r_p(1-e)H(W_{sat} - W_o)} u_o C_o \left(t - H \frac{e}{u_o} \right) \quad (1)$$

where $H e/u_o$ is the time to displace fluid from the bed voids (normally negligible), $u_o C_o t$ is the total solute fed to a unit cross section of bed up to time t . This time t can be considered as the time equivalent to usable capacity of the bed (t_u) up to the break-point time (t_b) (Barros, 2002) that is defined as the time when the effluent concentration (C) reaches 1 mg/L. The term $r_p(1-e)H(W_{sat} - W_o)$ is the capacity of the bed, or the amount of the solute exchanged if the entire bed came to equilibrium with the feed, that is equal to the time equivalent to total stoichiometric capacity of the packed bed (t_t) (Geankoplis, 1993).

Therefore, Eq. 1 can be simplified to (Barros, 2002):

$$t = \frac{t_u}{t_t} \quad (2)$$

If the entire bed attains to equilibrium a mass balance in the column provide t_u and t_t (Geankoplis, 1993):

$$t_u = \int_0^{t_b} \left(1 - \frac{C}{C_o} \right) dt \quad \text{and} \quad t_t = \int_0^{\infty} \left(1 - \frac{C}{C_o} \right) dt \quad (3)$$

The dimensionless time t is the fraction of the total bed capacity or length utilized up to the breakpoint (Geankoplis, 1993). Hence, the length of unused bed is:

$$H_{UNB} = (1-t) \cdot H \quad (4)$$

The H_{UNB} represents the mass-transfer zone (MTZ). Small values of this parameter mean that the breakthrough curve is close to an ideal step with negligible mass-transfer resistance.

Another parameter that should be considered for a column evaluation is the average residence time (\bar{t}). From the principles of probability the average residence time of a fluid element is given as follows:

$$\bar{t} = \int_0^{\infty} t dF(t) \quad (5)$$

For breakthrough curves, F(t) is equivalent to C/Co.

According to Barros (2002), an indirect measure of how far from the optimum operating condition the column operates is described as the operational ratio as:

$$R_0 = \frac{1}{t_u} |\bar{t} - t_u| \quad (6)$$

Values of operational ratio close to zero indicate that the residence time of the fluid in the packed-bed (\bar{t}) is similar to the desirable time in the column (t_u). In such case, the column operates close to the optimal region of operation (Barros, 2002).

With the average residence time it is also possible to evaluate the dimensionless variance of the breakthrough curve (Fogler, 1999), which is given by:

$$s_q^2 = \frac{1}{\bar{t}^2} \left[\int_0^{\infty} t^2 \left(\frac{dF(t)}{dt} \right) dt - \bar{t}^2 \right] \quad (7)$$

This parameter, initially applied for non-ideal reactors, has now being applied also in adsorption process to estimate the dispersion in the packed bed. Values of $s_q^2 \approx 0$ mean that the packed bed behaves close to an ideal plug flow with negligible axial dispersion and small mass-transfer resistance (Fogler, 1999). In adsorption processes the dimensionless variance could reach values higher than one, as a consequence of the degree of dispersion in the sorption column.

The bed performance for reactive blue 5G dye uptake is well evidenced through the breakthrough capacity of the column. $U_{dye}^{t_u}$ is defined as the amount of dye adsorbed prior to the break point ($C = 1$ mg/L). The integration of areas under the breakthrough curve gives the amount of dye not recovered by the adsorbent; based upon the difference of the quantity of dye fed to the column, this value permits the determination of the amount retained by the adsorbent (Valdman *et al.*, 2001).

Results and discussion

From the N₂ adsorption it was obtained a BET area of 816 m²/g and the t-method micropore surface area of 663 m²/g, which indicates the existence of some meso or macropores. Moreover, the BJH method indicates that the micro and mesopore volumes were 0.33 cm³/g and 0.06 cm³/g, respectively. The BET area for the pyrolyzed oil shale residue was obtained as 6.12 m²/g with negligible contribution of micropores. The mesopore volume was 0.006 cm³/g. The ZPC method of the carbon was obtained at pH \approx 9.5 and for the pyrolyzed oil shale residue was obtained at pH \approx 9. As all solution had pH around 6 - 7, the carbon surface preferentially retain anions, as it is the case of the dye. Boehm titration method showed the presence of carboxylic, lactonic and phenolic groups, 0.2, 0.3 and 0.35 μ mol/g, respectively. The infrared spectroscopy can be seen in Figure 3.

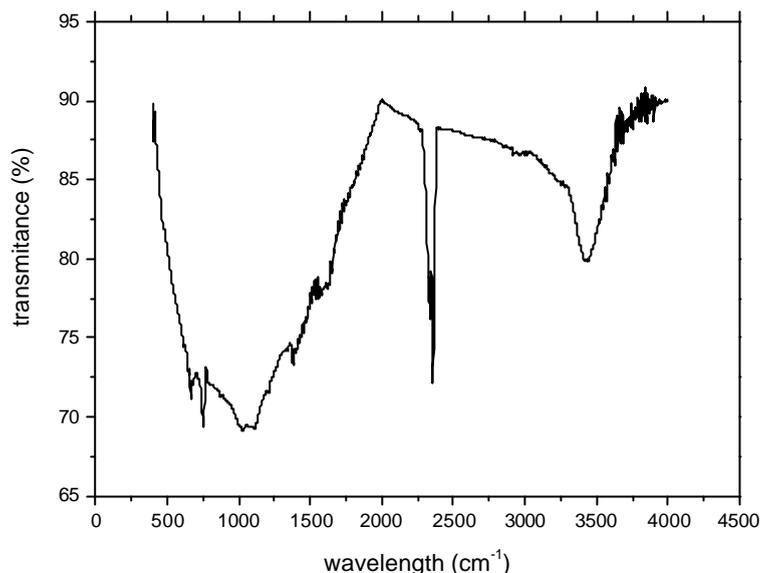


Figure 3 - FTIR spectrum of activated carbon sample

The presence of peaks in the band wavelength around 3200-3600 cm^{-1} indicates the existence of carboxylic groups. In the band wavelength around 1000-1200 cm^{-1} indicates the existence of phenolic, lactonic and ether groups. There are some peaks related to C=O bonds that may be seen in the band wavelength around 2250-2400 cm^{-1} (Prahdan and Sandle, 1999). These data are in accordance with the results found for the method of Boehm. Therefore, it may be supposed that the dye can be adsorbed in these superficial sites besides the physisorption process (Attia *et al.*, 2006).

Figure 4 shows the breakthrough results for a flow rate of 2 up to 10 mL/min and a feed concentration of 35 mg/L on the activated carbon bed. In the same way, Figure 5 shows the breakthrough results for the bed of pyrolyzed oil shale residue. The effect of changing flow rate from 2 up to 10 mL/min promoted a faster saturation of the bed and a lower breakpoint time, considered as 1 mg/L.

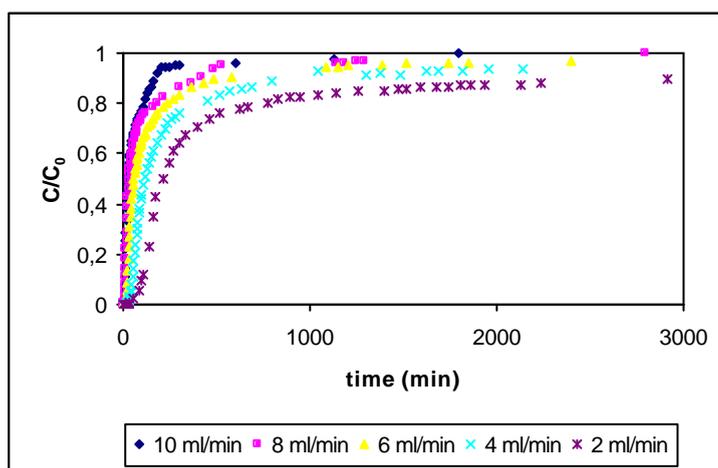


Figure 4 - Breakthrough curves for activated carbon and $C_o = 35$ mg/L.

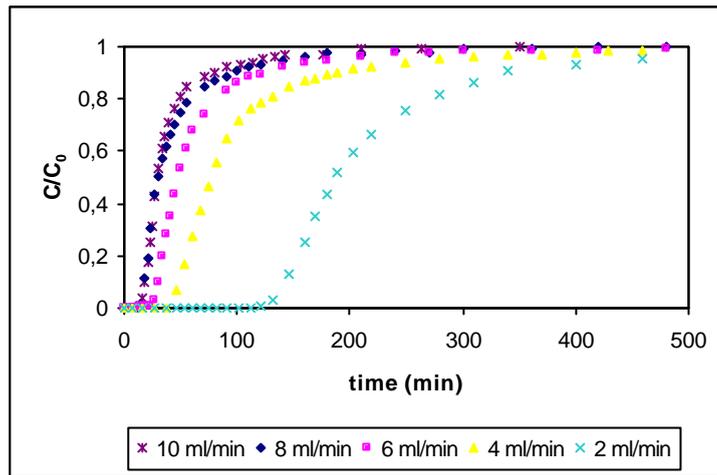


Figure 5 - Breakthrough curves for pyrolyzed oil shale residue and $C_o = 35$ mg/L.

Table 1 presents the quantitative results of the breakthrough curves for the activated carbon related to the breakthrough curves presented in Figure 4. It can be seen that 4 mL/min provided a minimum MTZ and R_o and the maximum amount of $U_{dye}^{t_u}$. The parameter s_q^2 is the maximum, indicating that, in this case, the more disperse is the bed, better it will be the adsorption, due to, maybe, the large size of the dye molecule that interacts with the micropores of the carbon. Therefore, 4 mL/min is the best operational condition over the flow rates investigated.

Table 1 – Mass transfer and reactive blue 5G dye uptake parameters for fixed bed adsorption onto activated carbon.

Flow rate (mL/min)	MTZ (cm)	R_o	s_q^2	$U_{dye}^{t_u}$ (mg/g)
10.0	14.07	0.94	6.4	0.39
8.0	14.43	0.96	2.0	0.31
6.0	14.21	0.95	7.6	0.57
4.0	13.94	0.92	8.6	0.88
2.0	14.35	0.96	6.4	0.77

Table 2 presents the quantitative results of the breakthrough curves for the pyrolyzed oil shale residue. It can be seen that 2mL/min provided a minimum MTZ , R_o and s_q^2 and the maximum amount of $U_{dye}^{t_u}$. Therefore, 2 mL/min is the best operational condition over the flow rate investigated.

Table 2 – Mass transfer and reactive blue 5G dye uptake parameters for fixed bed adsorption onto pyrolyzed oil shale residue.

Flow rate (mL/min)	MTZ (cm)	R_o	s_q^2	$U_{dye}^{t_u}$ (mg/g)
10.0	7.038	0.747	0.890	0.54
8.0	6.534	0.700	1.227	0.58
6.0	5.873	0.623	1.011	0.75
4.0	5.909	0.622	0.792	0.77
2.0	4.268	0.463	0.511	1.23

In this case, the dimensionless variance is much lower than in the case of adsorption in babassu activated carbon, which means that a large amount of mesopores facilitates the diffusion of the dye molecule. Moreover, the aggregation of dyes in aqueous solutions (Dakyki and Nemcova, 1999) may

hardly influence the adsorption process. As the superficial groups, responsible for the chemisorption process in the activated carbons, are located in the micropores, the dye molecule is electrostatically attracted but inhibited to be adsorbed successfully due to steric problems. Then, the contribution of chemisorption process may be more important in the external area of the activated carbon. This fact explains, besides the lower amount of dye retained, the higher values of dimensionless variance obtained for the fixed bed of activated carbon.

Conclusions

Analyzing the results of this work, the main conclusions are:

- The activated carbon has a pronounced microporosity with some superficial groups while the pyrolyzed oil shale residue is basically a mesoporous material. Such differences influence in the adsorption process of a large molecule such as the dye Reactive Blue 5G;
- Probably in the activated carbon, both processes of physisorption and chemisorption are involved in the dye uptake. Contribution of chemisorption may be more important in the external area due to steric problems involved in the diffusion of the dye molecules;
- The uptake mechanism in both adsorbents may occur with dimensionless variance higher than one due to the steric problems faced by the large molecule of the dye in order to diffuse and to adsorb in the sites. Moreover, higher pore size decreases the dimensionless variance;
- The optimized conditions for an up-flow activated carbon fixed bed could be accepted as 4 mL/min and for fixed bed of the pyrolyzed oil shale residue, could be accepted as 2 mL/min for the adsorption column of ID 1.01 cm operated at 30°C. In such flow rates it was observed for both cases a small length of unused bed and operation ratio and high breakthrough capacity of the column;
- Comparing the efficiency of both adsorbents, it may be concluded that pyrolyzed oil shale residue is more efficient for the dye uptake in a dynamic adsorption operation, due to the presence of mesoporosity, where the dye has less diffusional problems, comparing with the activated carbon, that is basically microporous.

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