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Sorption kinetic study on the removal of Basic Blue–9 dye using activated carbon produced from water spinach

Timi TARAWOU [1*], D. WANKASI [2] and M. HORSFALL Jnr [3]

[1,3]Department of Pure and Industrial Chemistry, University of Port Harcourt, PMB 5323, Choba, Port Harcourt, Nigeria.
[2]Department of Chemical Sciences, Faculty of Science, Niger Delta University, Wilberforce Island, PMB 71, Yenagoa, Bayelsa State.
[*] Corresponding author, E- mail: ttarawoufgc@yahoo.com

ABSTRACT

Batch adsorption experiments were performed to study the removal kinetics of Basic Blue-9 dye from aqueous solution using activated carbon produced from water spinach. The percent removal of dye increased with time and attained equilibrium in 3 hrs and 20 mins for an initial dye concentration of 250 mg/l. Optimum removal of 96% dye was achieved at the equilibrium time of 200 mins. The equilibrium sorption capacity (q_{e1}) obtained from the pseudo-first order linear plot was 2.75 mg/g with a rate constant, K_1 of 0.0115 g/ (mg/min. The experimental data was most suitably analyzed by the pseudo- second order model with a regression coefficient (R^2) value of 0.9949. The initial sorption rate, h_o was found to be 0.095 mg/g min with an equilibrium sorption capacity (q_{e2}) of 4.80 mg/g. The correlation coefficients R^2_1 and R_2^2, for the first – and second – order equations were all high (>0.97), suggesting the suitability of both models for the experimental data.

Keywords: Activated carbon, Basic Blue-9, kinetics, sorption, water spinach.

INTRODUCTION

Wastewater from textile and dyeing industries contain residual dyes, which are not readily biodegradable and are major contributors to water pollution and posses' serious threat to the environment (Kumar et al., 2005). Adsorption processes using activated carbon have been efficiently used for the effective treatment of dye contaminated wastewater. There have been an increasing interest in the use of lignocellulosic materials for the production of activated carbon such as beech sawdust (Batzias and Sidiras, 2004), pine (Tseng et al., 2003; Munoz et al., 2003), Indian rose wood (Garg et al., 2004; Garg et al., 2003), mahogany (Malik, 2004; Malik, 2003) and wood char (Mathew and David, 2003). The study of sorption kinetics in wastewater treatment is significant as it provides valuable insight into the reaction pathways and mechanism of sorption reactions. Kinetics describe the solute uptake rate that controls the residence time of sorbate uptake at the solid-solution interface, and are important to design appropriate sorption treatment plans, and to predict the rate at which any pollutant is removed.

The pseudo-first order rate equation of Lagergren has been widely used since 1898. The use of the pseudo-first order kinetics for the sorption of methylene blue on water hyacinth roots has been reported by Low et al. (1995). A pseudo-second order kinetic expression for the sorption system of divalent metal ions with sphagnum Moss Peat was developed by Ho et al. (1995). It has also been applied to the sorption system of lead ions (Ho and Mckay, 1998a). The pseudo-second order rate equation of Ho has also been successfully applied to sorption systems such as those of basic and acid dyes with peat (Ho and Mckay, 1998b) and pith (Ho and Mckay, 1999).

Earlier studies have shown that chemical activation using phosphoric acid at moderate temperatures produce, in certain lignocellulosic materials, a high surface area and a high degree of microporosity (Toles et al., 1997). The objective of this study is to produce activated carbon from water spinach using phosphoric acid as the activating reagent and to carry out an investigation on the kinetics of Basic Blue-9 dye sorption using the activated carbon as sorbent. Some physicochemical characteristics of the activated carbon were also determined to know the suitability of the carbon as a sorbent. This study also tested the suitability of pseudo-first order and pseudo-second order rate equations for the removal of Basic Blue-9 dye from solution by the activated carbon sample.

MATERIALS AND METHODS

The fresh water weed, viz; water spinach (Ipomoea aquatica) was collected from the Epie River in Yenagoa of Bayelsa State of Nigeria. The sample collected was washed thoroughly with water and then rinsed with deionized water and air-dried. The air-dried weed was then cut into small pieces and carbonized.

Carbonization of water spinach

The dried plant based biomaterial was carbonized according to the method described by Tarawou and Horsfall (2007).

Chemical activation of carbon

The activation followed the method described by Toles et al. (1997).

Adsorbate

Basic Blue –9 (a cationic dye) was used for the adsorption studies. Basic Blue-9 (C. I. 52015, λmax = 664 nm) was manufactured by Gurr, BDH Chemicals Ltd, Poole England. The molecular formula of Basic Blue- 9 dye is $C_{16}H_{18}CIN_3S$ with a molecular weight of 319.86. A stock solution of the dye with a concentration of 1000 mg per liter was prepared. This was done by weighing 1.0 g (1000 mg) of dye and transferring it into a 1000 ml volumetric flask. The dye was then dissolved in de-ionized water and the solution made up to the 1000 ml mark in the flask. Serial dilutions of the stock solution were made to obtain specific concentrations required for the adsorption study.

Data analysis

The percent adsorption was determined using the expression;

$$\%\ adsorption = \frac{C_o - C_e}{C_o} \times 100 \qquad \ldots..(1)$$

Where C_o is the initial concentration of sorbate in solution (mg/l), Ce is the concentration of the sorbate at equilibrium (mg/l).

The mass transfer properties of the adsorption of Basic Blue-9 dye by activated carbon from water spinach was evaluated using different kinetic models namely; the Lagergren pseudo-first order and the pseudo-second order kinetic models (Ho and Mckay, 1998a).

The linearized form of the pseudo-first order equation is generally expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad \text{….(2)}$$

Where q_e and q_t are the sorption capacities at equilibrium and at time, t respectively (mg/g), k_1 is the rate constant of pseudo-first order adsorption (g/ (mg/min). The plot of log (q_e-q_t) versus t, after linearization gave a relationship from which k_1 and q_e can be calculated from the slope and intercept respectively.

The linear form of the kinetic rate-expression model for a pseudo-second-order reaction developed by Ho and Mckay (1998a) was applied to the experimental data (equation 3).

$$\frac{t}{q_t} = \frac{1}{h_O} + \left(\frac{1}{q_e}\right)t \quad \text{……………….(3)}$$

Where q_t is the amount of dye molecules on the activated carbon surface (mg/g) at time t, q_e is the amount (mg/g) of dye molecules adsorbed at equilibrium and the initial sorption rate, h_o (mg/ g min) is given as:

$$h_O = k_2 q_e^2 \quad \text{………………… … (4)}$$

Where k_2 is the pseudo-second order rate constant (g/ (mg/min). The parameters h_o and K_2 are determined experimentally from the slope and intercept of a plot of t/q_t against t.

Determination of equilibrium time

4.0 g activated carbon of water spinach of 200 µm particle size was weighed and introduced into several 100 ml conical flasks. 50 ml of 250 mg/l solution of dye was added to each conical flask containing the activated carbon. The flasks were then labeled for time intervals of 40, 80, 120, 160, 200, and 280 minutes. The pH of the suspensions was adjusted to 7.5. The flasks were tightly covered with cellophane and agitated at 150 rpm for the appropriate time interval. The suspension was filtered through fiber glass filters and then centrifuged for 5 minutes. The supernatants were analyzed using a Unicam UV-visible spectrophotometer vision software V3.40. This experiment was run in triplicates.

RESULTS

The data for proximate analysis, physical properties of the activated carbon are presented in Table 1.

Determination of equilibrium time

The effect of contact time on the percent removal of Basic Blue-9 dye from solution was studied by contacting 50 ml of 250 mg/l dye solution with pH 7.5 using optimum carbon dosage (4 g) and kept in a mechanical shaker and equilibrated for the period ranging from 40 to 280 min.

The adsorption rate curve for Basic Blue-9 dye by the activated carbon sample is shown in Figure 1. It was observed that the percent removal of dye increased with time and attained equilibrium in 250 mins for an initial dye concentration of 250 mg/l.

Sorption kinetic studies

The rate at which sorption takes place in a batch sorption process is very important in designing batch sorption systems. Consequently, it was important to establish the time dependence of such systems under various process conditions. In an attempt to understand the sorption process, the pseudo-first and pseudo-second order kinetic rate-expression models have been applied to our experimental data in this study.

Pseudo-first order model

The time dependent experimental data was analyzed using the pseudo-first order rate equation of Lagergren. In order to determine the rate constants, the straight line plot of log (q_e-q_t) against time was taken as presented in Figure 2.

The rate constant k_1 and the equilibrium adsorption capacity, q_{e1} were calculated from the slope and intercept of the plot in Figure 2. The pseudo-first order rate constant, equilibrium sorption capacity and the regression coefficient are given in Table 2.

Pseudo-second order sorption model

The time based equilibrium experimental data was also analyzed using the pseudo-second order kinetic model. The pseudo-second order kinetic model considers the rate-limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent. And that pseudo-second order kinetics predicts the behaviour over the whole range of studies supporting a pseudo-second order equation. A plot of t/q_t against time was taken and is shown in Figure 3.

The pseudo-second order rate constant (K_2), the initial sorption rate (h_o) and the equilibrium sorption capacity (q_{e2}) were evaluated from the slope and intercept of the plot in Figure 3 and with the correlation coefficient (R_2^2) are presented in Table 3

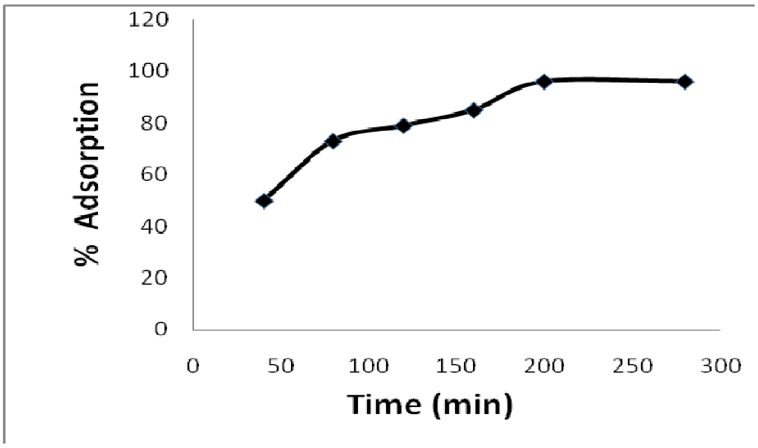

Figure 1: Effect of contact time on the percent removal of Basic Blue -9 dye from aqueous solution by the activated carbon sample.

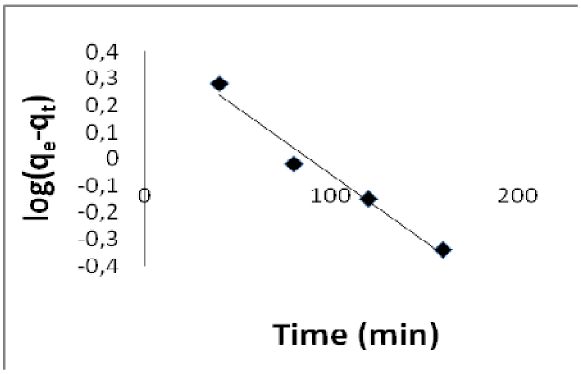

Figure 2: Plot of pseudo-first order sorption kinetics of Basic Blue -9 dye onto the activated carbon sample.

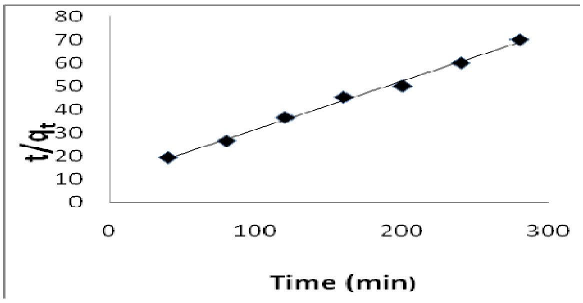

Figure 3: Plots of pseudo - second order sorption kinetics of Basic Blue -9 dye onto the activated carbon sample.

Table 1: Physicochemical characterization of activated carbon from water spinach.

Property	**Activated carbon**
Moisture (%)	19.80 ± 0.01
Porosity	0.893 ± 0.015
Iodine number (mg/g)	152.39 ± 0.10
Ash content (%)	27.60 ± 0.92
Volatile matter (%)	37.36 ± 0.15
Density (g/cm^3)	0.256 ± 0.052
pH	6.92 ± 0.08
Surface area (m^2/g)	106.14 ± 0.20

Table 2: Pseudo-first order rate parameters for the sorption of Basic Blue- 9 dye on to the activated carbon sample.

Sorption capacity at equilibrium q_{e1} (mg/g)	**Pseudo first order rate constant K_1 (g/(mg/min)**	**Regression coefficient (R_1^2)**
2.75	0.0115	0.9722

Table 3: Pseudo- second order rate parameters and equilibrium sorption capacity for the sorption of Basic Blue-9 dye onto the activated carbon sample.

Equilibrium sorption capacity, q_{e2} (mg/g)	**Initial sorption rate, h_o (mg/g min)**	**Pseudo second order rate constant K_2 (mg/g min^{½})**	**Regression coefficient (R_2^2)**
4.80	0.095	4.12 x10^{-}3	0.9949

DISCUSSION

The analysis (Table 1) showed a low amount of moisture, ash and volatile matter, indicating that the particle density is relatively small and that the carbon should be an excellent material for use in column or fixed bed reactors. The porosity, iodine number, surface area and pH are comparable to other materials used for batch analysis (Horsfall et al., 2003; Tarawou et al., 2007).

The percent removal was constant after the equilibrium time, probably due to surface saturation. No significant change in dye removal was observed after about 3 hrs 20 mins (200 mins). The figure further shows that the uptake of dye molecules was fast at the initial stages of the contact period, and thereafter, it became slower near the equilibrium. This may be due to the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the dye molecules on the adsorbent and bulk phases. Similar results were obtained by Kumar et al. (2005) and Rengaraj et al. (2002). It was also observed that at the end of equilibrium time, the activated carbon sample was able to remove about 96% dye from solution.

Table 2 shows that the equilibrium sorption capacity (q_{e1}) obtained from the pseudo-first order linear plot was 2.75 mg/g. It was also observed that the pseudo-first order rate constant, K_1 was 0.0115 g/(mg/min). The regression coefficient (R_1^2) value was high (0.9722). This indicates that the pseudo-first order model was suitable for the adsorption of Basic Blue-9 dye on to the activated carbon in the present study.

The results presented in Table 3 showed that the pseudo-second order rate constant, K_2 was 4.12×10^{-3} mg/g $min^{1/2}$ while the equilibrium sorption capacity (q_{e2}) was 4.80 mg/g. Table 3 further reveals that the initial sorption rate, h_o was 0.095 mg/g min and the pseudo-second order correlation coefficient (R_2^2) for the sorption of Basic Blue-9 dye from solution was very high 0.9949, showing that the kinetic sorption experimental data was suitably described by the pseudo-second order rate model. Similar results were obtained when caladium bicolor (wild cocoyam) biomass was used for the sorption of lead and cadmium ions from aqueous solution (Horsfall and Spiff, 2005).

It was observed from Tables 2 and 3 that the values of the correlation coefficients R_1^2 and R_2^2, were all very high (>0.97). This shows that the results fitted both the pseudo-first and the pseudo-second order models. However, the pseudo-second order correlation coefficient value (R_2^2=0.9949) was found to be slightly higher than that of the pseudo- first order value (R_1^2 =0.9722). It was also observed that, the equilibrium sorption capacity for pseudo-second order (q_{e2}) was found to be higher than the sorption capacity for pseudo-first order (q_{e1}). These results suggest that the sorption of Basic Blue- 9 dye onto the activated carbon follows better the pseudo-second order model.

Conclusion

This study demonstrates that water spinach could be used as a novel raw material for the production of activated carbon. The activated carbon produced in this study was effective for the removal of Basic Blue-9 dye from aqueous solution. The equilibrium between the adsorbate in solution and on the adsorbent surface was practically achieved in 200 minutes. Adsorption kinetics was found to follow both the pseudo- first and pseudo-second order rate expressions with high regression coefficient (R^2) values >0.97. The initial sorption rate, h_o, is 0.095 mg/g min.

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