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Research Article

FIXED BED ADSORPTION STUDIES OF RHODAMINE B DYE USING OIL PALM EMPTY FRUITS BUNCH ACTIVATED CARBON

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ABSTRACT

Global environmental pollution challenges can be alleviated if proper disposal and conversion of wastes is promoted. An attempt of converting waste to wealth was made in this study by converting oil palm empty fruits bunch to activated carbon through chemical activation with potassium hydroxide which was used for adsorption of Rhodamine B dye from waste water. Fixed-bed column adsorption system was implored in the dye removal studies. The effect of operating parameters such as influent concentration (50-200 mg/L), bed depth (5-10 cm) and solution flow rate (10-20 ml/min) on breakthrough curve was investigated. The maximum adsorption capacity of oil palm empty fruit bunch activated carbon for Rhodamine B dye adsorption (69.86 mg/g) was obtained at the highest influent initial dye concentration 200 mg/L, highest bed depth 10 cm, and solution flow rate of 15 ml/min. The experimental data was modeled using Thomas model to predict the column performance and breakthrough curves. The result of the model was found to be in good agreement with the experimental data. The result of the study revealed that oil palm empty fruits bunch activated carbon is a suitable adsorbent for removal of this harmful substance, Rhodamine B dye from waste waters.

KEY WORDS: Wastes, Adsorption, Breakthrough curve, Thomas model

INTRODUCTION

In many parts of the world fresh water is still a scarce commodity and its demand is on the rise due to increase in population and industrial activities. This challenge has prompted research into finding lasting solution to this menace by devising ways of improved purification technology, recycling and search for new water sources [1]. Water pollution has majorly been caused by human quest for industrialization which results in bye products that are often discharged into the environment. Dyes are among the commonest substances that are widely used by many industries such as textiles, printing, plastics, leather, food and paper to add value and beauty to their products. It is a common practice for such industries to discharge their impure chemical complex effluents into the environment thereby adding to other culprit pollutants and this is harmful to the entire ecosystem. Several thousands of dyes are available in the markets which are categorized into direct, reactive, acid and basic dyes [2]. In an attempt to solve dye pollution problems, methods like reverse osmosis, membrane separation, coagulation, chemical oxidation, biological treatments, photo-degradation and adsorption have been used; but the most efficient method has been through adsorption process [3,4]. Agricultural wastes materials and other cheaper and renewable substances have been proven to be useful alternative adsorbents sources to high-priced commercial activated carbon which has been the expedient ones used.

Rhodamine B (RhB) is one of the water soluble xanthenes class dyes, a basic red cationic dye which is a common water tracer fluorescent. It is often used textile and food industries. Several attempts have been made to alleviate its contamination by using cheaper and non conventional activated carbons produced from materials like scrap tires [5], banana bark [6], Rhizopus oryzae [7], *Azadirachta indica* bark [8] and so on. The limited available literatures on adsorption of RhB pollutant from effluents is the motivation to embark on this research to investigate other means of alleviating it. This study is aimed at using a real world environmental process column study which requires little operator attention, easy inspection and cleaning for regeneration of adsorbent [9]. Oil palm empty fruits bunch was converted to activated carbon through chemical activation with potassium hydroxide and used for adsorption of Rhodamine B dye from synthetic textile waste-water. Important design parameters such as influent concentration of RhB solution, flow rate of fluid and column height were investigated. The breakthrough curves were analyzed using Thomas model.

MATERIALS AND METHODS

Potassium hydroxide and Rhodamine B dye (RhB) of analytical grade were purchased from Merck's and Sigma-Aldrich Companies in South Africa. Oil palm empty fruits bunch waste was obtained from Enugu state in Nigeria. RhB has a chemical formula of $C_{28}H_{31}N_2O_3Cl$, maximum absorption wavelength 556 nm and its molecular structure is shown in Fig. 1.

Fig. 1 Molecular structure of RhB

Preparation of Oil palm empty fruits bunch activated carbon

The Oil palm empty fruits bunch was washed thoroughly with hot distilled water to remove some impurities until a pH 6.8-7 was attained and then dried. The dried oil palm empty fruits bunch was ground and sieved to 500 µm-1.00 mm particle sizes. It was mixed with potassium hydroxide in a ratio of 2:1 and then left overnight and dried in an oven. The mixture was placed in furnace under 150 ml/min nitrogen (99.99%) flow for 120 min to undergo activation. The activated sample was washed with distilled water until pH 6.8-7 was attained, and then dried in an oven for 6 h at 110 ^{o}C and packaged for in air tight container for further use.

Fixed-bed adsorption column experiment

The fixed bed column was made of Pyrex glass tube of 1.2 cm inner diameter and 19.5 cm height. In an upward flow of the influent solution with the aid of peristaltic pump, adsorption of RhB on oil palm empty fruit bunch activated carbon (OPBC) was carried out and samples were analysed at intervals of time with the aid of UV-Vis spectrophotometer (Shimadzu UV/Vis 1600, Japan) at maximum wavelength, λ_{max}=556 nm. The column performance of RhB adsorption on OPBC was studied at different RhB influent concentration (50-200 mg/L), bed depth of (5-10 cm) and flow rate of (10-20 mL/min). The amount of the dye adsorbed at time t, at equilibrium Q_e (mg/g) was calculated using the following equation:

$$Q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentration of the dye at the initial and equilibrium respectively; V (L) is the volume of the solution; and W (g) is the mass of the dry adsorbent used.

Effect of initial concentration

Influent concentrations of 50, 100 and 200 mg/L were used with bed height of 10 cm and flow rate of 15 mL/min kept constant throughout the study of effect of variation of concentration on the column parameters.

Effect of bed depth

Different bed heights (5, 7.5, and 10 cm equivalent to 4.4, 5.9, 9.4 g of OPBC) were used to determine their effect on column parameters of the adsorption study. Other parameters kept constant were initial concentration of 100 mg/L and flow rate of 10 mL/min.

Effect of solution flow rate

The effect of solution flow rate on the column performance was studied by varying flow rates as 10, 15 and 20 mL/min. Bed height and dye concentration of 7.5 cm and 50 mg/L respectively were maintained throughout the study.

Analysis of column data for RhB adsorption on OPBC

The shape of a breakthrough curve which aid in determining the performance of column study was obtained through analysis of pollutant removal from the solution by plotting of the curves. This was done by plotting C_t or C_t/C_o (mg/L) against V_t (mL) or t (min) ; where C_t is the effluent concentration, C_o influent concentration, V_t is treated volume and t is the service time. The treated effluent volume, V_t is determined as:

$$V_t = Qt_e \quad (2)$$

where Q is the volumetric flow rate (mL/min) and t_e is the time at exhaustion (min). The exhaustion and breakthrough points were set at 90% and 10% of the influent concentration respectively.

The maximum column capacity, q_{total} (mg), for a given feed concentration and flow rate is equal to the area under the plot of the adsorbed dye concentration. This can be expressed as, C_d (C_{ad}=C_o-C_t) mg/L, against effluent time t (min) and is gotten from equation (3):

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\,dt \quad (3)$$

Where t_{total}, Q and A are the total flow time (min), volumetric flow rate (mL/min) and the area under the breakthrough curve, respectively. Equilibrium uptake ($q_{eq(exp)}$) (mg/g) is calculated from equation (4):

$$q_{eq(exp)} = \frac{q_{total}}{m} \quad (4)$$

Where m is the total amount of OPBC (g) in the column. The total amount of dye sent to the column (W_{total}) is calculated from equation (5):

$$W_{total} = \frac{C_o Q t_{total}}{1000} \quad (5)$$

The total amount of dye in percentage removed is the ratio of the maximum capacity of the column (q_{total}) to the total amount of dye sent to the column (W_{total}) expressed as eqn. (6):

$$R = \frac{q_{total}}{W_{total}} \times 100 \quad (6)$$

Breakthrough curve Kinetic models

The breakthrough curves for the effluent parameters were predicted to enhance absolute design of the fixed bed adsorption process by using Thomas model. The model was used to predict the dynamic behavior of the column.

Thomas model

It is also used to describe column performance and predict breakthrough curves. It follows the Langmuir kinetics of adsorption and desorption. The model assumes negligible axial dispersion in the column adsorption since the rate driving force obeys the second order reversible reaction kinetics [10]. The expression of Thomas model for an adsorption column is given as:

$$\frac{C_t}{C_o} = \frac{1}{1+\exp[(K_{Th}/Q)(Q_o M - C_o V_t)]} \quad (7)$$

where Q is the flow rate (mg/L); M is the mass of adsorbent (g); V_t is the volume of effluent treated (mL); Q_o is the maximum solid phase concentration of dye per unit mass of OPBC (mg/g); and K_{Th} is the Thomas rate constant (mL/(mg min)). The equation (8) can be linearized as follows:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{K_{Th} Q_o M}{Q} - \frac{K_{Th} C_o}{Q} V_t \quad (8)$$

Thomas constants Q_o and K_{Th} can be determined from plots of In[(C_o/C_t)-1] against t.

RESULTS AND DISCUSSION

Effect of concentration

The breakthrough curves for studies of effect of initial concentration variations from 50-200 mg/L at constant bed depth of 10 cm and flow rate of 15 mL/min are presented in Fig. 2 Spontaneous (<3 h) exhaustion of the OPBC bed by highest initial RhB concentration of 200 mg/L was observed yielding the earliest breakthrough. Subsequently, other breakthroughs were formed as the concentration decreases. This was probably due to higher concentration gradient at higher inlet concentrations due to larger mass transfer coefficient. The presence of more molecules at higher concentrations gave room for competition for the fewer binding sites of the adsorbent used. The structural breakthrough curves revealed that steeper slopes were formed at higher inlet concentrations curves as compared with those of lower concentrations. Similar trend has been reported in literature for lead removal from effluents using Pinus sylvestris saw dust [11] and removal of nickel (II) from aqueous solution [12]. Adsorption capacity of 29.47 and 69.86 mg/g were obtained for 50 and 200 mg/L concentrations respectively as shown in Table 1. This further confirmed that concentration variation has great impact on the column adsorption of RhB on OPBC.

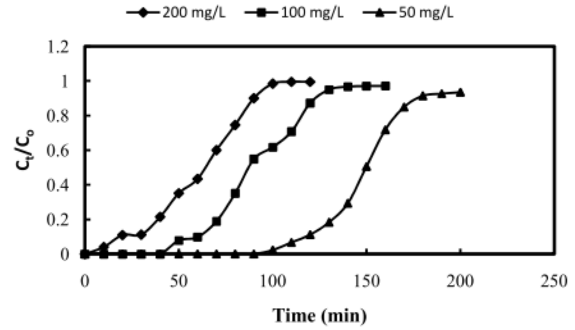

Fig. 2 Breakthrough curves at different influent concentrations with fixed flow rate of 15 mL/min, bed depth of 10 cm, 30 °C for RhB adsorption on OPBC

Effect of bed depth

The result breakthrough curves and parameters of studies of effect of bed depth are presented in Fig. 3 and Table 1, respectively. At fixed initial influent concentration of 100 mg/L and 10 mL/min flow rate conditions, bed depths of 5, 7.5 and 10 cm corresponding to 4.4, 5.9 and 9.4 g respectively were varied to study the variation effect. It has been reported that axial dispersion phenomena, reduced solute diffusion and insufficient residence time of solute with adsorbent were activities observed at lower bed depths during fixed bed adsorption of lead (II) ions [11]. The variation in mass of adsorbent for different bed height was proportional to the surface area available per each bed depth. At higher bed depth of 10 cm, adsorbent mass was more residing in the column thereby providing larger service area for binding, fixation, diffusion and permeation of the solute to the adsorbent. Longer bed depth also provided more reaction area and larger volume of influent treatment which translated to higher adsorption capacity. Lower bed depth of OPBC had lower adsorption effects since the residence time between the solute and adsorbent was limited. Similar observation has reported on this phenomenon [13,14]

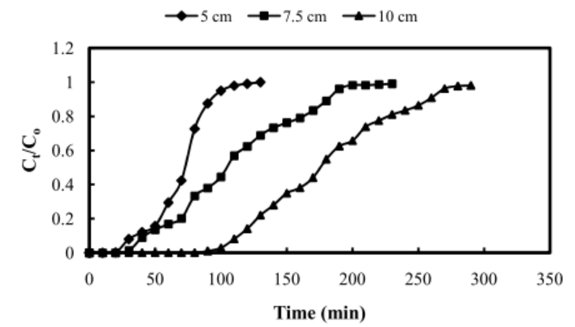

Fig. 3 Breakthrough curves at different depth depths with fixed influent concentration of 100 mg/L, flow

Effect of flow rate

At initial influent dye concentration of 50 mg/L and bed depth of 7.5 cm maintained, the flow rate of the dye solution was varied as 10, 15 and 20 mL/min to study its variation effect on the breakthrough. The result of the flow rate effect variation parameters determined and breakthrough curves are presented in Table 1 and Fig. 4, respectively. The insufficient contact or residence time experienced by the adsorbents at higher flow rates of dye solution, thereby depriving solute ample privilege of diffusing into the adsorbent pores resulted in lower adsorption capacity. The high flow rate did not allow for equilibrium condition attainment before the exit of the solute from the column. This lead to faster formation of breakthrough at higher flow rates due to increase in diffusion or mass transfer coefficient. Similar trend of results has been reported in the literature [15,16].

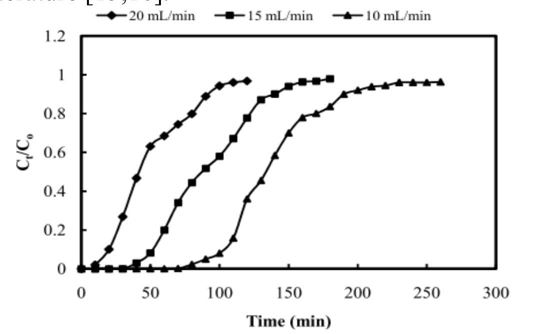

Fig. 4 Breakthrough curves at different flow rates with fixed influent concentration of 50 mg/L, bed depth of 7.5 cm, 30 °C for RhB adsorption on OPBC

Table 1 Column data parameters obtained at different inlet dye concentration, bed depths and flow rates

C_o (mg/L)	H (cm)	Q (mL/min)	q_{total} (mg)	q_e (mg/g)
50	7.5	20	105.62	17.90
50	7.5	15	108.28	18.35
50	7.5	10	115.20	19.53
50	10	15	276.99	29.47
100	10	15	475.16	50.55
200	10	15	656.69	69.86
100	5	15	148.33	33.71
100	7.5	15	294.66	44.95

Thomas model parameters at different operating conditions

The model rate constant K_{TH} and maximum solid-phase concentration Q_o parameters were determined from the slope and intercept of plots (Fig. not shown) as presented in Table 2. The suitability of this model for adsorption process occurs where the external and internal diffusions will not be the limiting step [11]. The values of Q_o decreased while K_{TH} increased with increasing flow rate while at increasing initial concentration, Q_o increased with K_{TH} decreasing. The limited resident time experienced by the adsorbent bed at higher flow rates affected their solid-phase concentration leading to decrease of Q_o as the flow rate increases. The higher flow rates further promoted faster saturation of the adsorbents as more mass transfer of solute was experienced. This result is similar to those on the study of removal of Cu (II) from aqueous solutions using rice husk based activated carbon [17]. The relatively high values of correlation coefficients R^2 obtained indicated that Thomas model can be used to describe the breakthrough curves behavior for the adsorption of RhB on OPBC.

Table 2 Parameters of Thomas model obtained at different bed depths, influent concentration and flow rates

H (cm)	Q (mL/min)	C_o (mg/L)	Q_o (mg/g)	K_{TH} ((mL/(mg min))	R^2
7.5	10	50	132.90	0.0088	0.983
7.5	15	50	85.56	0.0168	0.994
7.5	20	50	45.63	0.0236	0.935
5	15	100	37.13	0.0193	0.957
7.5	15	100	49.45	0.0273	0.966
10	15	50	80.33	0.0321	0.902
10	15	100	96.26	0.0108	0.979
10	15	200	118.62	0.0059	0.956

CONCLUSION

This study showed that adsorption of RhB from waste waters is feasible with activated carbon produced from empty palm oil fruit bunch (OPBC) in fixed bed column adsorption system. Thomas model was found adequate to describe breakthrough behavior of the adsorption process which had optimum conditions at high bed depth (OPBC), low influent concentration (RhB) and flow rates.

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