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Removal of Rhodamine B from Aqueous Solution Using Natural Clay by Fixed Bed Column Method

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***Abstract*—**The discharge of dye in industrial effluents is of great concern because their presence and accumulation have a toxic or carcinogenic effect on living species. The removal of such compounds at such low levels is a difficult problem. The adsorption process is an effective and attractive proposition for the treatment of dye contaminated wastewater. Activated carbon adsorption in fixed beds is a very common technology in the treatment of water and especially in processes of decolouration. However, it is expensive and the powdered one is difficult to be separated from aquatic system when it becomes exhausted or the effluent reaches the maximum allowable discharge level. The regeneration of exhausted activated carbon by chemical and thermal procedure is also expensive and results in loss of the sorbent. The focus of this research was to evaluate the adsorption potential of the raw clay in removing rhodamine B from aqueous solutions using a laboratory fixed-bed column. The continuous sorption process was conducted in this study in order to simulate industrial conditions. The effect of process parameters, such as inlet flow rate, adsorbent bed height, and initial adsorbate concentration on the shape of breakthrough curves was investigated. A glass column with an internal diameter of 1.5 cm and height of 30 cm was used as a fixed-bed column. The pH of feed solution was set at 8.5. Experiments were carried out at different bed heights (5 - 20 cm), influent flow rates (1.6- 8 mL/min) and influent rhodamine B concentrations (20 - 80 mg/L). The obtained results showed that the adsorption capacity increases with the bed depth and the initial concentration and it decreases at higher flow rate. The column regeneration was possible for four adsorption–desorption cycles. The clay column study states the value of the excellent adsorption capacity for the removal of rhodamine B from aqueous solution. Uptake of rhodamine B through a fixed-bed column was dependent on the bed depth, influent rhodamine B concentration, and flow rate.

***Keywords*—**Adsorption, Breakthrough curve, Clay, Fixed bed column, Rhodamine B, Regeneration.

I. Introduction

MOST environmental problems have their solutions from the environment which are identified through research [1]. The release of toxic and hazardous dyes from the textile industry has created a global concern due to their considerable toxicity.

Color is an effluent characteristic, which is easily detected and readily traced back to its source. Physicochemical techniques such as coagulation, flocculation, ozonation, reverse osmosis and adsorption on activated carbon, manganese oxide, silicagel and clays are among the methods employed [2]–[8]. Catonic dye molecules also have very high affinity for clay surfaces and are readily adsorbed when added to clay. The elimination of the organic dye by clay was studied by several researchers [9]-[11]. The continuous fixed bed adsorption process approximates the practical application of RB adsorption, which provides a better understanding of the adsorption mechanism. For the column system, the application is practical and economic as the operation is conducted continuously and the process is controllable [12]. Moreover, in practical industrial water treatment processes, adsorption in fixed-bed columns are preferable, and the experimental data obtained from the laboratory scale fixed-bed columns are helpful for industrial application [13]. The aim of this study is to determine the raw clay ability in removing RB ion by varying bed height, flow rate and initial concentration. The column regeneration was possible for four adsorption desorption cycles.

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II. Materials and Methods

A. The Adsorbent

In this study, the adsorbent used as raw material is a raw clay. The chemical analysis of the raw material was carried out by X-ray fluorescence, and the result given in mass percentage is presented in Table I.

TABLE I
CHEMICAL COMPOSITION OF NATURAL CLAY

Chemical compound	% Mass
CaO	9.74
SiO_2	45.84
Al_2O_3	14.64
Fe_2O_3	9.63
SO_3	0.04
K_2O	0.89
MgO	2.22
Na_2O	0.52
ZnO	0.02
TiO_2	0.03
Cl	17.5

B. The Adsorbate

The dye used during our work is the Rhodamine B (CI no. 45170). It is an organic compound whose physicochemical properties are grouped in Table II.

C. Column Experiments

The column tests were carried out in a glass column with inside diameter of 1.5 cm and high of 20 cm. The clay was put in the column and the average temperature during the experiments was maintained at 25°C. In an adsorption column test, an aqueous dye solution was fed to the top of the column by a pump, flowed through clay bed, and exited from the bottom of the column. Before carrying out discoloration, the clay bed was percolated by the distilled water during 2h to ensure the damping and the swelling of clay. The influence of bed height, initial dye concentration, and volumetric flow rate on the breakthrough curves was determined, and the experimental conditions are presented in Table III.

TABLE II
CHARACTERISTICS OF RHODAMINE B

Chemical compound	% Mass
Chemical formula	$C_{28}H_{31}N_2O_3Cl$
Mass molar	479.02g mol-1
Maximum absorbance	554 nm
Ionisation	Basic
Fusion temperature	210°C

TABLE III
EXPERIMENTAL CONDITIONS OF FIXED BED COLUMN TEST

Run	Height (cm)	Initial concentration (mg L^{-1})	Flow rate (L min^{-1})
1	10	80	8
2	10	80	6
3	10	80	4
4	10	80	1.6
5	5	80	4
6	15	80	4
7	20	80	4
8	10	60	4
9	10	40	4
10	10	20	4

D. Column Data Analysis

The column performances were evaluated through the break-through curve of the continuous fixed bed system. Commonly, the breakthrough curve was described by C_t/C_0, in which C_t and C_0 represent the effluent and influent concentrations, respectively. The curve was expressed as C_t/C_0 against the contact time. The effluent volume, V_{eff} (mL), can be calculated from (1) [14]:

$$V_{eff} = Ft_{total} \quad (1)$$

where F is the volumetric flow rate (mL/min), t_{total} is the total flow time (min).

The value of the total mass of dye adsorbed, q_{total} (mg), can be calculated from the area under the breakthrough curve (2) [15]:

$$q_{total} = \frac{F}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\,dt \quad (2)$$

where C_{ad} is the concentration of dye removal (mg/L).

Equilibrium dye uptake or maximum capacity of the column, q_{eq} (mg/g), in the column is calculated as:

$$q_{\exp} = \frac{q_{total}}{m} \quad (3)$$

where m is the dry weight of adsorbent in the column (g).

Total amount of dye ion entering column (m_{total}) is calculated from [16]:

$$m_{total} = \frac{C_0 F t_{toal}}{1000} \quad (4)$$

The removal percentage of RB ions can be obtained from:

$$R(\%) = \frac{q_{total}}{m_{total}} \times 100 \quad (5)$$

III. RESULTS AND DISCUSSION

A. Effect of Bed Height

Clay bed depth strongly affects the volume of solution treated or throughput volume. The effect of the bed depth on the breakthrough curves for the investigated system in presented in Fig. 1. The results indicate that the profile of the breakthrough curves varies largely with bed depth which is proportional to the weight of clay in column. Curves in the inlet section of the bed have a concave profile and follow the characteristics "S" shaped profile. The research on the adsorption of dyes [17]-[21] shows similar profiles. Higher beds contain more adsorbent; therefore, more contact time and more binding sites will be available for RB to attach, which will lead to higher bed capacity [14], The RB molecules will diffuse deeper into adsorbent and subsequently the percentage of dye removal increased proportionally to the bed depth.

B. Effect of Flow Rate

The breakthrough curves at various flow rates are shown in Fig. 2. Breakthrough time reaching saturation was increased significantly with a decreased in the flow rate. On the basis of mass transfer fundamentals, the variation in the slope of the breakthrough curve and adsorption capacity may be explained. At a higher flow rate, the adsorption capacity was lower due to the insufficient residence time of the RB in the bed and low internal diffusion of the solute (in the pore of clay), and therefore, the solute leaves the column before equilibrium reached. At higher flow rates, film surrounding the particle breaks thereby reducing the adhesion of solute to the sorbent particle.

C. Effect of Influent Initial Concentration

The adsorption column was operated with different flow rates until no further RB removal was detected. The experiments of different initial concentrations are given in Fig. 3. It is illustrated that the breakthrough time decreased with increasing influent RB concentration: the binding sites became more quickly saturated in the column. As influent concentration increased, sharper breakthrough curves were obtained. In addition, the adsorption capacity of the bed increased with the increasing initial RB concentration. This can be explained by the fact that a high concentration difference provides a high driving force for adsorption.

D. Regeneration Studies

Regeneration of the adsorbent and recovery of the adsorbed dye was obtained by elution using HCl solution 0.1 mol L^{-1} at 25°C. At the column top, samples were collected at regular time intervals, and the concentration was determined by spectrophotometry. The desorbed dye mass (md) was determined from the area below the elution curve. The tests of regenerability for the RB show that the desorbed percentage was 88.7%, 85.6% and 82.7% for the four respective adsorption –elution cycles.

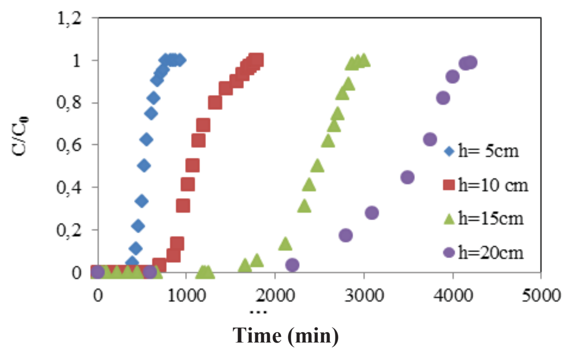

Fig. 1 Breakthrough curves: the effect of different bed depths on RB adsorption (C_0 = 80 mg/L, F = 4 ml/min)

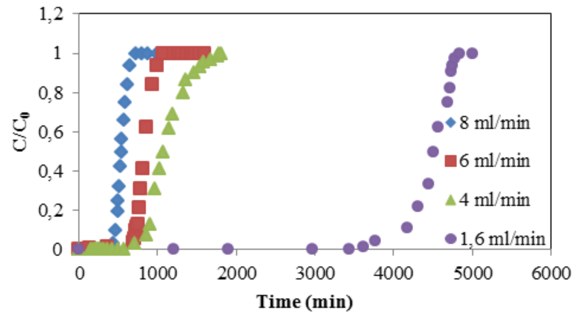

Fig. 2 Breakthrough curves: the effect of flow rate on RB adsorption (C_0= 80 mg/L, h = 10 cm)

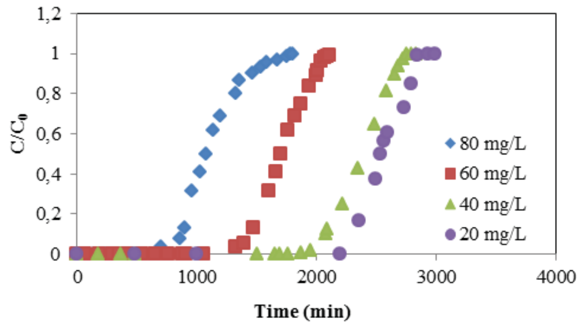

Fig. 3 Breakthrough curves: the effect of influent concentration on RB adsorption (F= 4 mL/min, h = 10 cm)

TABLE IV
OPERATION CONDITIONS AND RESULTS FOR THE FIXED BED COLUMN EXPERIMENTS

C_0(mg/L)	F(ml/min)	Z (cm)	t_{total} (min)	V_{effl} (ml)	m_{total}(mg)	qe (mg/g)	qtotal (mg)	Total Removal of RB (%)
80	8	10	792	6336	506.88	47.6	456.96	90.15
80	6	10	1073	6438	515.04	51.2	491.52	95.43
80	4	10	1754	7016	561.28	57.6	552.96	98.52
80	1.6	10	5000	8000	640	66.13	634.85	99.2
80	4	5	702	2808	224.64	46.8	221.83	98.75
80	4	15	2897	11588	927.04	64.5	922.35	99.49
80	4	20	4125	16500	1320	68.4	1299.6	98.45
60	4	10	2081	8324	499.44	51.8	497.28	99.56
40	4	10	2738	10953	438.11	45.4	435.84	99.48
20	4	10	2804	11216	224.32	24.8	238.08	94.22

IV. CONCLUSION

Clay is a suitable adsorbent for the removal of RB from water. The adsorption of RB in a fixed bed with continuous feed was depended on the flow rate, the inlet RB concentration and bed depth. The increase in the bed depth was followed by increase in the quantity of treated water, with a reduction in adsorption quantity. At lower flow rates, the quantity of treated water and adsorption capacity were found increasing. The column regeneration was possible for four adsorption-desorption cycles.

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