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Adsorption of Basic Red 46 by Granular Activated Carbon in a Fixed-bed Column

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Abstract. A continuous adsorption study in a fixed-bed column was carried out for the removal of Basic Red 46 (BR46) from synthetic waste water. In the present study, commercial grade granular activated carbon (GAC) was used as adsorbent. The effect of initial BR46 concentration in the range of 50-250 mg/L was investigated at pH 8.0. The experimental data were analyzed using Langmuir and Freundlich isotherm models. The equilibrium data indicate the best fit obtained with Freundlich isotherm model.

Keywords: Wastewater treatment, Adsorption, Activated carbon, Fixed-bed column

1. Introduction

In industrial waste streams, dyes are among the most common pollutants present. The dyes are discharged from sources such as textile, paper, leather, and plastic industries [1]. Dyes are compounds with complex aromatic structure that is widely used to bring color to other substances [2]. Synthetic dyes are preferred in the industry due to its ease of production and cost-effectiveness compared to natural dyes. The complex aromatic structures of dye makes them more resistant to light, heat and oxidizing agents and they are also usually non-biodegradable [3]. This is desirable in the industry as it attributes to color fastness, but it also makes it hard to treat wastewater effluents containing dye. Although effluents containing dyes into the environment only make up a small proportion of water pollution, but due to their brilliance, dyes are visible, even in small quantities. Moreover, some dyes are known to have carcinogenic and mutagenic properties.

Physical, chemical and biological processes are the principles used in treating dyes in effluent wastewater [4]. Methods used to treat wastewater containing dye include coagulation-flocculation[5], advanced oxidation process[5], adsorption[6] and reverse osmosis[6]. However, these methods are expensive and present operational problems such as development of toxic intermediates, lower removal efficiency, and higher specificity for a group of dyes, among others [7, 8]. Adsorption is the most versatile and widely used method of water treatment because of its low cost, ease of operation, and efficiency in treatment [9].

The continuous adsorption process more applicable in real water treatment industries due to its low operating cost and ability of columns to adapt to versatile processes [10]. With high volume of wastewater to be treated, as compared to batch treatment, continuous treatment is a lot more time efficient. However, most of the reported studies on the adsorption of dye by activated carbon were conducted in batch studies and only few of them evaluated performance of the adsorbent for continuous flow fixed bed adsorbers. The data obtained from batch studies are generally not applicable to treatment processes as the contact time in batch processes is not long enough to attain equilibrium in continuous flow processes [10]. Hence, in this work, the equilibrium data on continuous adsorption studies were carried out to evaluate the performance of continuous fixed-bed adsorbers.

2. Material and Methods

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2.1. Adsorbent Material and Dye

The commercially available activated carbon used in this research was Activated Charcoal Norit® purchased from a local supplier. The activated carbon was obtained in granular form. The particle size of the activated carbon used was 12-40 mesh size (0.425 – 1.70 mm).

The dye used in this study was Basic Red 46 (BR 46) or also known as Astrazon Red. BR 46 has a molecular formula of $C_{18}H_{23}BrN_6$ (MW: 403.3194 g/mol). The maximum absorbance wavelength (λ_{max}) of BR46 is at 530 nm.

2.2. Experimental Set Up

Adsorption tests were carried out in a continuous system using Basic Red 46 as the compound to be adsorbed by activated carbon. Figure 2.1 illustrates the schematic of apparatus for the study.

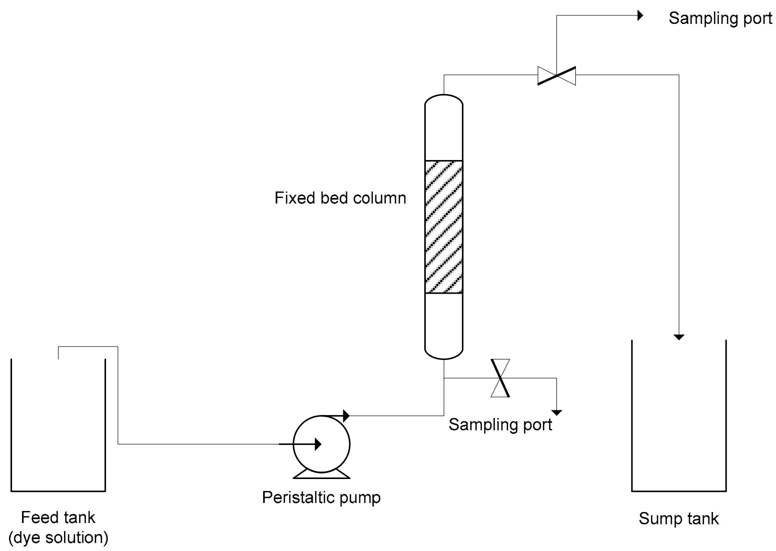

Figure 2.1: Schematic of continuous adsorption experimental rig.

2.3. Column Studies

A 100 mm of granular activated carbon (GAC) was placed inside a fixed-bed column. The column dimension was 12 mm I.D. and 210 mm height. Prior to each experiment, distilled water was passed through the column to rid the column impurities and air bubbles. The dye solution of known concentration at pH 8.0 was pumped upwards through the column at 50 ml/min. Effluent samples were collected from the top of the column at different intervals and the concentration of BR46 was analyzed by measuring the absorbance at 530 nm with a UV/VIS spectrophotometer. All tests were carried out at room temperature, 25^{o}C.

3. Results and Discussion

3.1 Effect of initial dye concentration

The effect of initial dye concentration on the performance of the activated carbon has been studied by testing at various concentrations between 50 to 250 mg/L with keeping the bed height at 100 mm, pH 8.0 and the flow rate at 50 ml/min constant. The breakpoint time, equilibrium time, equilibrium BR46 uptake, and percentage dye removal are shown in Table 3.1.

Table 3.1: Column data and parameters obtained at different initial dye concentration.

Initial concentration, C_0 (mg/L)	Mass of adsorbent, m_{ad} (g)	Breakpoint time, t_b (min)	Equilibrium time, t_{eq} (min)	Equilibrium BR46 uptake (q_e) (mg/g)	Dye removal (%)
50	5.33	6	34.38	65.71	31.02
100	5.36	4.5	89.36	42.83	10.63
150	5.42	4	139.27	41.53	7.14

200	5.29	2	189.68	39.38	5.15
250	5.23	2	240.42	36.06	3.82

Table 3.1 shows the breakpoint time decreases with increasing of the initial dye concentration from 50 mg/L to 250 mg/L. The breakthrough time of the initial dye concentration of 50 mg/L and 250 mg/L reduced from 6 to 2 minutes, respectively. The time required for the process to reach equilibrium decreases as the initial dye concentration increase. This is expected as a higher concentration of solute occupies the available binding sites faster, causing the remaining solutes unable to bind onto the adsorbent.

The amount of BR46 adsorbed decreases from 65.71 to 36.06 mg/g, as the initial concentration of dye increases from 50 mg/L to 250 mg/L. The percentage of dye removal is the highest at the lowest initial dye concentration. This is due to the slower transport caused by decreased diffusion coefficient or decreased mass transfer coefficient, effect of a low concentration gradient [11]. The slower transport gives the dye molecules more time to bind to the adsorption sites thus increasing the removal efficiency. Besides that, the high concentration of dye causes saturation of adsorption sites resulting in dye molecules to be emitted in the effluent.

3.2 Isotherm studies

The adsorption isotherm indicates the relationship between the adsorption capacity at equilibrium and the equilibrium concentration at constant temperature. In the investigation, the pH, flow rate, and bed height was kept constant while the initial dye concentration were varied. The experiments were all carried out at room temperature to maintain a constant temperature and to closely imitate real-life industrial application conditions. Results obtained for adsorbate adsorption, q_e (mg adsorbate/g adsorbent) starting at different initial dye concentrations against the residual adsorbate concentration, C_e (mg adsorbate/L solution) in equilibrium are fitted into two of the most common isotherm models for determining adsorption efficiency, Langmuir and Freundlich.

The most widely used isotherm equation for modeling equilibrium data is the Langmuir model. The Langmuir equation may be presented as:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad \text{Eq. (3.1)}$$

Eq. (3.1) can be rearranged to a linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad \text{Eq. (3.2)}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_m the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), C_e the concentration of adsorbate at equilibrium (mg/L) and b is a constant related to the affinity of the binding sites (L/mg).

The Freundlich expression is an empirical equation based on the sorption of a heterogeneous surface. The Freundlich's equation is given by:

$$q_e = K_f C_e^{1/n} \qquad \text{Eq. (3.3)}$$

A linear form of Freundlich expression can be obtained by taking logarithm of Eq. (3.3);

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \qquad \text{Eq. (3.4)}$$

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_f and n are Freundlich constants with n giving an indication of how favorable the adsorption process. K_f is the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon for a unit equilibrium concentration. The value of n in the range between 1 and 10 denotes favorable adsorption.

The model constants corresponding to experimental data were determined by using the least squares fitting method. The linearized Freundlich and Langmuir isotherms of BR46 obtained are shown in Figures 3.1 and 3.2 with the correlation coefficients. Considering the values of the linear regression coefficients, the Freundlich model is more suitably fitted to the sorption data in the studied concentration range with an R^2 value of 0.988 compared to the Freundlich model with only 0.748.

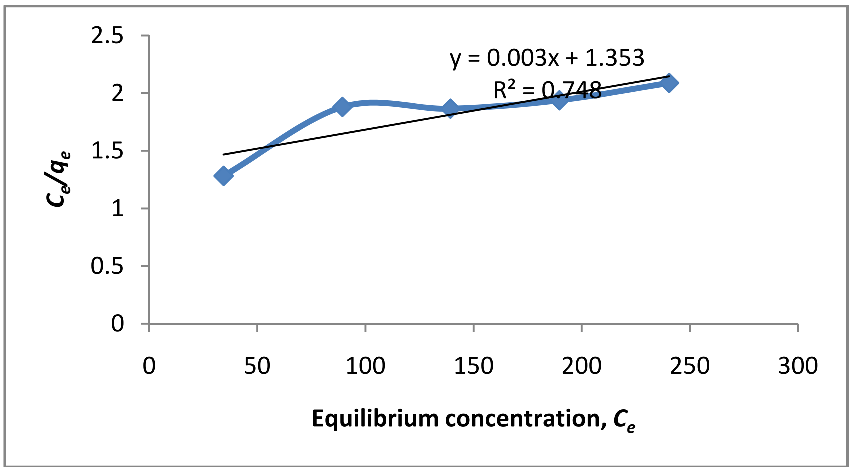

Figure 3.1: The linearized Langmuir adsorption isotherm for BR46 adsorption to activated carbon

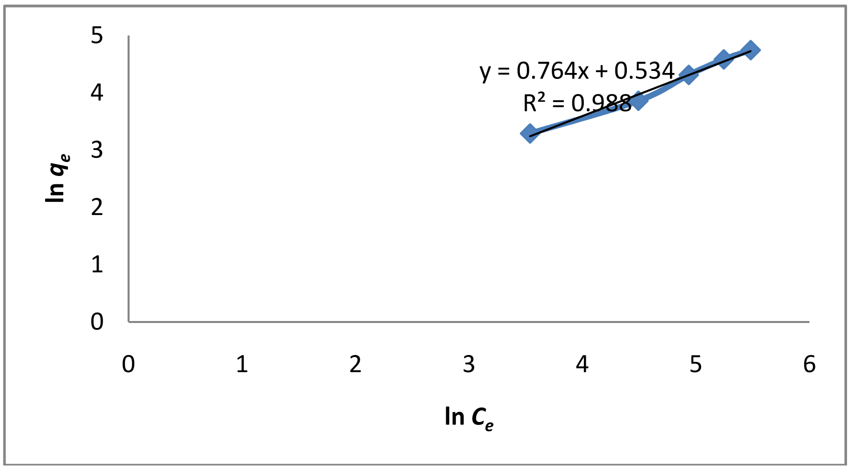

Figure 3.2: The linearized Freundlich adsorption isotherm for BR46 adsorption to activated carbon.

Table 3.2 shows the calculated constants for Langmuir and Freundlich isotherm based on the data collected. The Langmuir constants q_m and b were determined from the plot of C_e/q_e versus C_e. The q_m which represents the total capacity of adsorption for dye is found to be 333.33 mg/g while b is 0.0022. For Freundlich isotherm, the constants K_f and n are used to represent adsorption capacity and adsorption intensity, respectively. The closer the n value is to zero, the more heterogeneous is the system [12]. As the n value is calculated to be 1.31, it is assumed that the system is heterogeneous, which makes it more suitable for Freundlich isotherm. The Langmuir isotherm assumes monolayer coverage while Freundlich model is more suited for heterogeneous surface adsorption.

Table 3.2: Equilibrium constants for BR 46 adsorption on activated carbon.

Langmuir			Freundlich		
q_m (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n (L/mg)	R^2
333.33	0.0022	0.748	1.71	1.31	0.988

4. Conclusion

The continuous adsorption of BR46 has been studied in a fixed-bed column using granular activated carbon as adsorbent. The investigation on the effect of initial dye concentration showed that the adsorption was effective at low initial dye concentration. The equilibrium data indicate the best fit obtained with Freundlich isotherm model.

5. Acknowledgements

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