

Adsorption of Acid Orange-7 Dye onto Activated Carbon Produced from Bentonite - A Study of Equilibrium Adsorption Isotherm†

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Abstract: The adsorption behaviour of acid orange-7 from aqueous solution onto activated carbon prepared from bentonite was investigated under various experimental conditions. To evaluate the adsorption capacity, initial dye concentration, contact time, effect of solution pH and adsorbent dosage were investigated in the batch mode. Experimental isotherm data was represented with Langmuir and Freundlich adsorption isotherms models. The adsorption data were found to follow the Langmuir model better than the Freundlich model. The result showed that this novel adsorbent had a high adsorption capacity ($Q_0=238.0952$ mg/g) making it suitable for use in the treatment of Acid orange-7 enriched wastewater.

Keywords: Activated bentonite, Bentonite, Acid orange-7, Adsorption isotherm

Introduction

Dye waste water discharged from textile and dye stuff industries have to be treated due to their impact on water bodies and growing public concern over their toxicity and carcinogenicity in particular¹. Dyes and pigments represent one of the problematic groups, they are discharged into wastewaters from various industrial branches, mainly from the dye manufacturing, food coloring, cosmetic, paper, textile and carpet industries². The complex aromatic structures of dyes make them more stable and more difficult to biodegrade³. About 6,34,900 metric tons of dyes are produced worldwide each year and nearly 10-15% of them are discharged as effluent⁴. Some of the dyes, especially benzidine based dyes, are toxic, carcinogenic⁵ and also causes rapid depletion of dissolved oxygen affecting aquatic life adversely⁶. Therefore, decolourisation of dyes is an important aspect of wastewater before discharge. Removing color from waste water can be done via several methods namely chemical, biological and physical methods. Chemical methods use coagulation, filtration, precipitation and ozonisation to remove color. Biological treatment utilizes fungi, bacteria

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or biomass and is widely accepted due to its economical advantages. Physical methods often applied are membrane filtration and adsorption techniques⁷. Among these methods, adsorption is a widely used for removal of dyes from wastewater⁸. The most commonly used adsorbent for colour removal is activated carbon, because of its capability for efficiently adsorbing a broad range of different types of adsorbate⁹. At present, there is a growing interest in using low-cost and non conventional alternative materials instead of traditional adsorbent¹⁰. In this investigation, bentonite (BN) and acid activated bentonite (ABN) were applied for the removal of acid orange-7 dye from aqueous solution.

Experimental

The adsorbent used in the present study are bentonite (BN) and acid activated bentonite (ABN). The collected material was crushed well and activated by heating for 2 h at 80 °C. This activated adsorbent was used in the adsorption process. 15 g of natural bentonite was activated by refluxing with 200 mL 50/50(v/v) H₂SO₄ at 60 °C for 2 h in a round-bottom flask. The suspension was cooled in air and filtered off and then washed several times with double-distilled water and dried in an air oven at 120 °C for 2 h prior to use¹¹.

Methods of analysis

Concentration of dye was determined by finding the absorbance at the characteristic wave length using UV-Vis spectrophotometer (Systronics 2201). A standard solution of the dye was taken and the absorbance was determined at 490 nm. This wave length was used for preparing the calibration curves between absorbance and the different concentration of the dye solution. The calibration plot of absorbance *versus* concentration with the help of the linear portion of the calibration curve¹². The percentage of dye removal was calculated using the following formula;

Percentage removal of dye = $\left[\frac{C_0 - C_e}{C_0} \right] \times 100$, where C₀ is the initial concentration of dye

solution and C_e is the final concentration of dye solution.

Batch adsorption experiments

In present work, the experiments were carried out by batch adsorption process. The reaction parameters such as initial concentration, contact time, dose of adsorbent and pH of the dye solution were studied. Initially the experiments were carried by treating 50 mL of dye solution with the required amount of adsorbent. The reaction mixture was shaken vigorously for the contact time period of 30 minutes. Then the solution was subjected to filter and the filtrate were analyzed. To find out the percentage of removal of dye solution. Percentage removal = $(C_i - C_e) 100 / C_i$ and amount adsorbed = $(C_i - C_e) V/m$ where C_i and C_e are the initial and final concentration in mgL⁻¹ of dye solution respectively, m is the mass of a adsorbent (gL⁻¹) and V is the volume of dye solution in mL.

Results and Discussion

Effect of initial concentration

The uptake of acid orange-7 over various adsorbents such as BN and ABN were investigated at different range of initial concentration, keeping contact time (30 min), initial pH of solution (7-7.5), dose (2 gL⁻¹) and adsorbents fixed. Figure 1 shows that the amount of dye adsorbed increases with increase in concentration and also the extent of percentage removal decreases exponentially with increase in concentration. It is also noted that the rate of

removal is faster at lower concentration and decreases with increasing concentration. This indicates that there exists a reduction in immediate solute adsorption owing to the lack of available active sites required for high initial concentration of dye¹³.

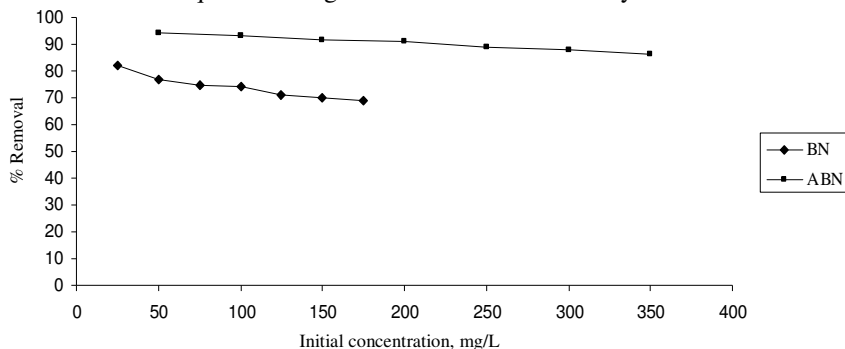


Figure 1. Effect of the initial concentration on the percentage removal of acid orange-7 by BN and ABN (dose 2 g/L, time 30 min, pH 7-7.5)

Effect of contact time

The time dependent behaviour of dye adsorption was examined by varying the contact time between adsorbate and adsorbent in the range of 10-60 min. Figure 2 shows that the percentage removal for dye by the adsorbent is rapid and thereafter it proceeds at a slower rate and finally attains saturation. The higher concentration solution of dyes employed, the longer equilibrium time was needed. The rate of removal of the adsorbate is higher in the beginning due to the large surface area of the adsorbent available for the adsorption observed because there are few active sites on the surface of sorbent. The optimum time duration required color removal was 40 minutes for BN and ABN.

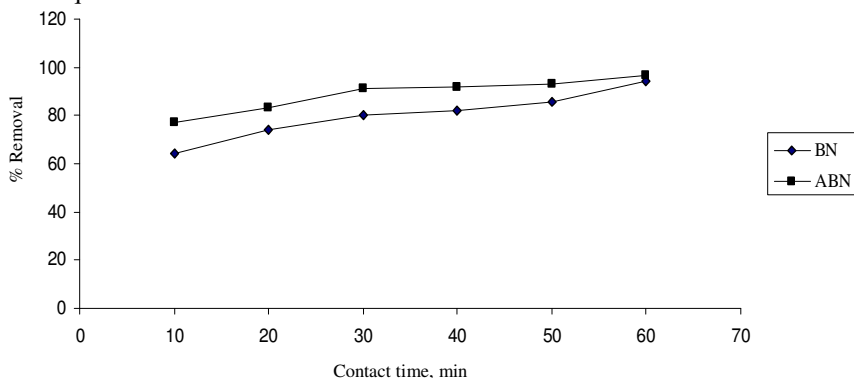


Figure 2. Effect of the contact time on the percentage removal of acid orange-7 by BN and ABN (Concentration 25 mg/L for BN and 50 mg/L for ABN, dose 2 g/L, pH 7-7.5)

Effect of initial pH of dye solution

The most important parameter influencing sorption capacity is pH of the adsorption medium. Adsorption capacity for all the adsorbents in the dye was analyzed in the pH range 2-9. The plots are shown in Figure 3. It was apparent from the results that adsorption of Acid orange-7 are pH dependent. In case of acid orange-7, at lower pH range 2-4, increased percentage removal was observed (98-88%) and at higher pH percentage removal decreased.

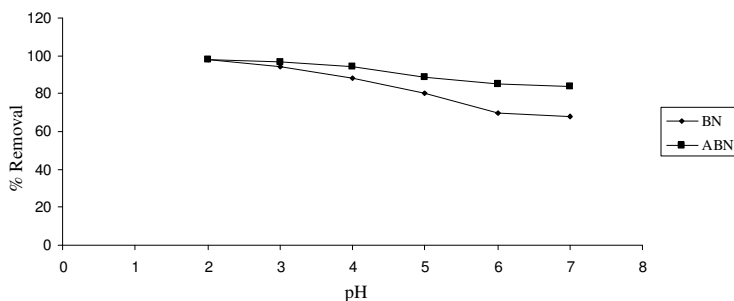


Figure 3. Effect of the pH on the percentage removal of acid orange-7 by BN and ABN (Concentration 25 mg/L for BN and 50 mg/L for ABN, dose 2 g/L, time 40 min)

The acidic medium is favorable for the adsorption process of acid orange-7. High adsorption of dye at low pH indicates that, the surface of active carbons seems to be acidic which increase the protonation at their surfaces due to neutralization of negative charges, resulting in easier diffusion. This provides more active surface of the adsorbents and result into more adsorption at their surfaces. On increasing pH, deprotonation takes place, which decreases the diffusion and adsorption^{14,15}.

Effect of dose variation of adsorbents

The effect of dose variation of adsorbent was studied at optimum initial concentration of dyes, contact time and fixed initial pH. Figure 4 shows that the percentage removal of the acid orange-7, increased with increase in the dose of adsorbent. This may be due to the availability of surface activities resulting from the increased dose and conglomeration of the adsorbent. The increase in the extent of removal of acid orange-7 is found to be insignificant after a dose of 2 gL⁻¹ for BN and ABN. So which, they are fixed as optimum dose of adsorbent for further studies.

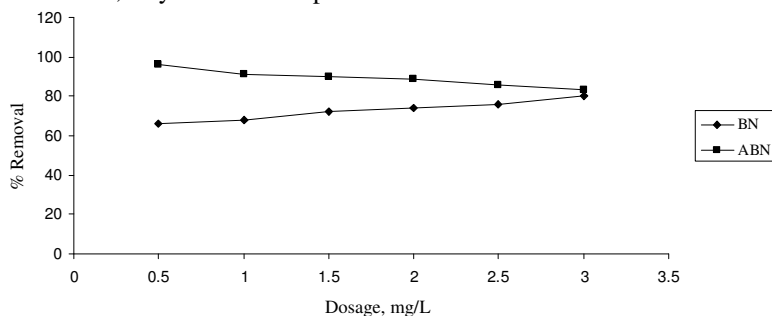


Figure 4. Effect of the dosage on the percentage removal of acid orange-7 by BN and ABN (Concentration 25 mg/L for BN and 50 mg/L for ABN, time 40 min, pH 7-7.5)

Adsorption isotherm

The adsorption isotherms indicate how the adsorption molecules distribute between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose⁹. Adsorption isotherm study is carried out on two well-known isotherms, Freundlich and Langmuir. The adsorption data for the dyes was fitted to the linear form of Freundlich isotherm: $\log q_e = \log K_f + 1/n \log C_e$. The graph is plotted between $\log C_e$ against $\log q_e$. It is shown in Figure 6.

The linearity of the graph indicates the applicability of Freundlich isotherm to the experimental data. The values of K_f and n are calculated from intercept and slope of the straight line. The Langmuir model assumes that uptake of adsorbate ions occurs on the homogenous surface by monolayer adsorption¹⁶⁻¹⁸. The Langmuir equation is expressed as follows $C_e/q_e = (1/Q_0 b + C_e/Q_0)$. The graph is plotted between C_e/q_e against C_e . It is shown in Figure 5. Langmuir constants Q_0 (mgg^{-1}) and b (Lmg^{-1}), related to the adsorption capacity and energy of adsorption are obtained from slope and intercept of the straight line.

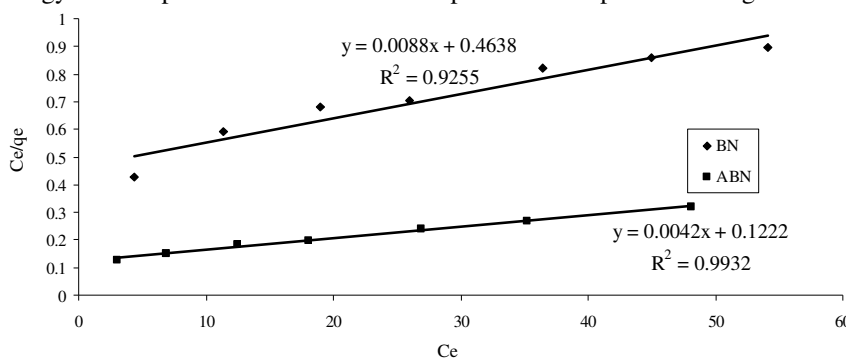


Figure 5. Langmuir adsorption isotherm for BN and ABN

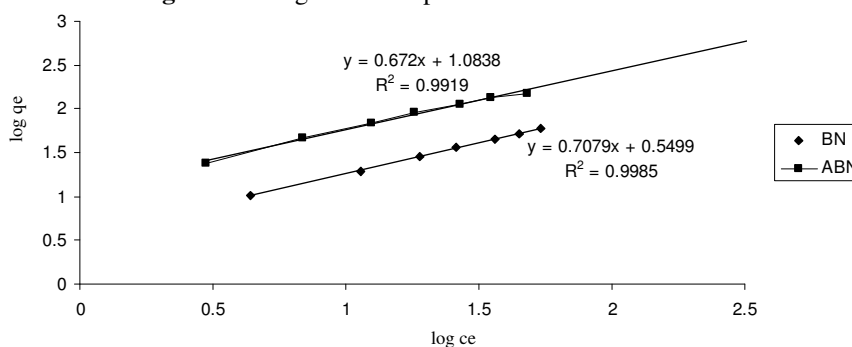


Figure 6. Freundlich adsorption isotherm for BN and ABN

The correlation analysis of Freundlich and Langmuir data isotherm are presented in Table 1. The applicability of the isotherm data was best explained by Langmuir model. The results conclude that Langmuir isotherm is best fitted compared to Freundlich, confirming the monolayer adsorption. Further, the Langmuir constants are used to find the favorable or unfavorable adsorption by a dimensionless parameter R_L . $R_L = 1 / (1 + bC_0)$, ($R_L=1$, $0 < R_L < 1$, $R_L=0$ and $R_L > 1$ means unfavorable, linear, favorable and irreversible respectively). In all these case, R_L value found to be less than 1. Hence, the nature of adsorption process is favorable and the monolayer adsorption capacities (Q_0) of adsorbent in acid orange-7 are in the order $ABN > BN$.

Table 1. Adsorption isotherms of acid orange-7 dye

Adsorbent	Freundlich isotherm			Langmuir isotherm			
	$1/n$	K_f	r	$Q_0, \text{mg/g}$	$b, \text{g.L}^{-1}$	$R_L, \text{L/mg}$	r
BN	0.71	0.5499	0.9992	113.6364	0.01897	0.607	0.9620
ABN	0.99	1.0838	0.9959	238.0952	0.03437	0.428	0.9965

Conclusion

The present investigation is dealt with the adsorption of acid orange-7 dye on BN and ABN. The following conclusion is obtained in the research work. The percentage removal decreases with increase in the concentration and particle size. With increase in contact time and amount of dose, the percentage removal was increases. The acid orange-7 dye has maximum percentage removal at lower pH (acidic medium). The linearity of the curve and correlation coefficient value of isotherms such as Freundlich and Langmuir shows that the system covered monolayer adsorption. The adsorption capacity value Q_0 (mg/g) is in the order:

ABN (238.0952) >BN(113.6364). The optimum dose of adsorbent was 2 gL^{-1} for BN and ABN. From the above results we conclude that, the adsorbent ABN was effective in removing anionic dye from aqueous solution in the range of concentration investigated, because this type of clays are plentiful and inexpensive adsorbent.

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