

Removal of Acid Orange 3 from Aqueous Solution by Activated Carbon Adsorption

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Removal of acid orange 3 from aqueous solution by activated carbon adsorption was studied. The optimal adsorption conditions for the removal of acid orange 3 aqueous solution were pH = 0.5, activated carbon 500 mg L⁻¹, initial concentrations of the dye 100 mg L⁻¹ and T = 35 °C, a removal efficiency of 98 % was achieved within 1 h. Kinetic data of adsorption were well fitted the pseudo-second-order kinetic model and the Langmuir isotherm. The approach may be applied to treat the industrial wastewater containing acid orange 3 if appropriate conditions are selected.

Key Words: Acid orange 3, Adsorption, Activated carbon, Langmuir model, Pseudo-second-order.

INTRODUCTION

Many industries use dyes and pigments, effluents from these industries such as dyeing, paper and pulp, textile, *etc.* contain many dyes which are toxic¹. Sulfur dyes can rapidly reduce oxygen content of the water and so, are harmful to aqueous organisms². Also, total dye consumption in the weaving world industries is more than 10⁷ kg/year and *ca.* 10 % of this amount 10⁶ kg/year is discharged to water streams³. Increasing limits imposed by environmental legislation on the concentrations of pollutants in aqueous effluents make treatment imperative. Adsorption is an attractive method for the removal of solutes from effluents since if the adsorption system is designed correctly, it will produce a high-quality treated effluent.

Adsorption in wastewater treatment process, gained prominence as a means of producing quality treated effluents from effluents, which contained low concentrations of dissolved organic compounds. Dissolved molecules are attracted to the surface of the adsorbent and this interaction may be expressed both in terms of adsorptive characteristics and physical properties. The most widely used adsorbent is activated carbon, which has been used in adsorption of pollutants from water and wastewater.

C.I. Acid orange 3 is used to a limited extent as a dye in semi-permanent hair colouring products and in the dyeing of textiles, which could cause renal toxicity in rats and mice. As far as we known, there is no report on using activated carbon for the removal of acid orange 3 from aqueous solution. Herein, the results for removal of acid orange 3 from aqueous solution in the presence of activated carbon is reported.

EXPERIMENTAL

Acid orange 3 is an acid non-azo dye has a neutral pH and is miscible in water, which is obtained from SINOCEM HEBEI, the Colour Index classification is C.I. 10385(CAS No: 6373-74-6; λ_{\max} (nm): 372; FW (g mol⁻¹): 452.37). The chemical structure is shown in Fig. 1. Activated carbon (200 mesh) was analytical grade reagent purchased from the Chemical Experimental Factory of Tianjin University, China.

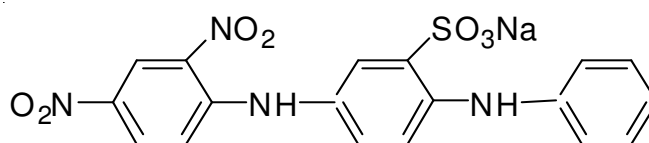


Fig. 1. Structure of acid orange 3

A pH meter (PHS-3C, Shanghai Hongyi Instrument Equipment Co., Ltd.) was employed for measuring pH values in the aqueous solutions. A TU-1901 double beam UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) was used to determine the dye concentrations.

Analysis: The concentrations of the supernatant solutions were measured at a wavelength of 372 nm, which corresponds to the maximum absorbance of acid orange 3 aqueous solution. Prior to the measurement, a calibration curve was obtained by using acid orange 3 solution at known concentrations. The calibration curve was linear in the range of 0-80 mg L⁻¹. The dye removal ratio was calculated as follows:

$$\text{Dye removal ratio (\%)} = (1 - C_t/C_0) \times 100 \quad (1)$$

where C_0 is the initial dye concentration, C_t is the dye concentration at measurable time t .

The amount of dye adsorbed at time t was calculated by the equation:

$$q_t = (C_0 - C_t) V/M \quad (2)$$

where q_t (mg mg⁻¹) is the amount of the absorbed dye at time t ; C_0 and C_t (mg L⁻¹) are the liquid phase concentration of the dye initially and at time t , respectively; V is the volume of solution (L) and M is the mass of adsorbent used (mg).

Procedure: The pH value of the dye aqueous solution was adjusted with 0.1 N NaOH and HCl solution by using a pH meter. To a dye solutions different quantities of adsorbents were added. The mixture was stirred for a period of time at designated temperature. Samples were taken from the conical flask periodically using a pipette and were analyzed after centrifugation. In the presence of activated carbon, blanks containing no acid orange 3 were used for each series of experiments. Each experiment was replicated twice.

RESULTS AND DISCUSSION

Effect of amount of activated carbon: Adsorbent dosage is an important factor because it determines the capacity of an adsorbent for a given adsorbate at the operating conditions. The effect of adsorbent dosage (adsorbent used in each batch) on dye removal was studied, keeping all other experimental conditions constant in a range of 500-2500 mg L⁻¹ activated carbon with respect to 100 mg L⁻¹ acid orange 3. As shown in Fig. 2, the removal of acid orange 3 increased with the activated carbon dosage in a non-linear mode. With increasing adsorbent more surface area is available for adsorption due to increase in active sites on the adsorbent⁴. There is no significant increase in removal when the amount of activated carbon is exceeded 2500 mg L⁻¹, because the removal ratio is approach to 100 %. The amount of dye adsorbed per unit weight of adsorbent decreased with increase in adsorbent mass. The amount of dye adsorbed decreased from 0.088 to 0.040 mg mg⁻¹ for an increase in adsorbent dosage from 500 mg L⁻¹ to 2500 mg L⁻¹, whereas the dye removal increased from 44.0 to 99.4 %. The results show that as the adsorbent mass increases, the overall percentage of dye adsorbed also increases, but the amount adsorbed per unit mass of the adsorbent decreases considerably. The decrease in unit adsorption with increase in the dose of adsorbent is basically due to adsorption sites remaining unsaturated during the adsorption process⁵. In this condition 1000 mg L⁻¹ activated carbon is most suitable.

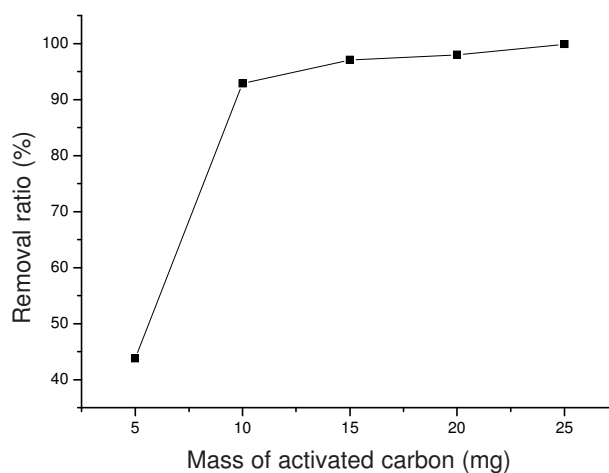


Fig. 2. Effect of amount of activated carbon; $C_0 = 100 \text{ mg L}^{-1}$, $V = 0.05 \text{ L}$, $T = 35 \text{ }^\circ\text{C}$, contact time = 50 min, pH = 3

Effect of dye initial concentration: Dye removal is highly concentration dependent. The increase in loading capacity of the adsorbent with relation to dye adsorption concentration, it is probably due to a high driving force for mass transfer. In fact, the more concentrated the solution, the better is the adsorption.

The data shows that using 1000 mg L⁻¹ activated carbon with respect to 50-250 mg L⁻¹ initial concentration of the dye from each 0.05 L aqueous solution at room temperature, within 50 min the removal of acid orange 3 is decreased from 99.0 to 34.0 %. The removal efficiency decreased as is seen in Fig. 3.

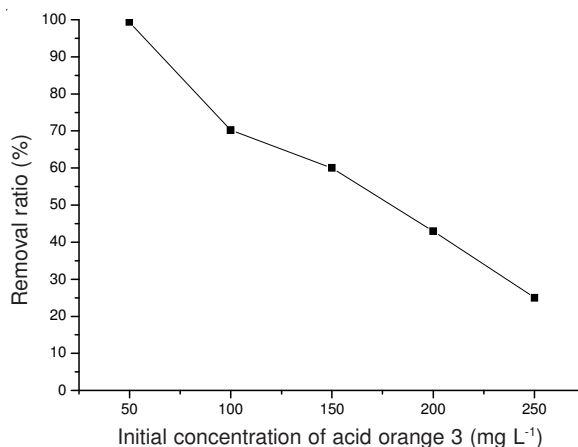


Fig. 3. Effect of initial concentration activated carbon 1000 mg L⁻¹, C₀ = 50-250 mg L⁻¹, V = 0.05L, T = 20 °C, contact time 50 min, nature pH

Effect of contact time: To find out the optimum contact time, the experiments were performed using 0.05 L aqueous solutions of acid orange 3 with 500 mg L⁻¹ activated carbon for different durations ranging from 0.5 to 3.0 h at 20 °C (Fig. 4). The removal of acid orange 3 increased with increase of the contact time and reached a plateau when equilibrium was established. The optimum contact time was found to be 1 h. This was caused by strong attractive forces between the dye molecules and the adsorbent; fast diffusion onto the external surface was followed by fast pore diffusion into the activated carbon, lead intraparticle matrix to attain rapid equilibrium.

Effect of initial pH value: The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity⁶. The effect of pH on the amount of dye removal was analyzed range from 0.5 to 13.0. In this study, 0.05 L of dye solution of 100 mg L⁻¹ with 500 or 1000 mg L⁻¹ activated carbon was taken and stirred for 1 h at 20 °C to reach equilibrium. As shown in Fig. 5, when pH value was 0.5, the removal ratio was 92.0 % (500 mg L⁻¹ activated carbon) and 99.6 % (1000 mg L⁻¹ activated carbon), respectively. When pH value exceeded 3.0, the removal ratio decreased to 73.0 and 97.0 %, respectively. The adsorption of this charged dye group onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is in turn influenced by the solution pH. At low pH values, the surface of the adsorbent solids is positively charged and easily adsorbs the acid orange 3 ion having a negative charge but at high pH values, the surface charge on the activated carbon may get negatively charged, which does not

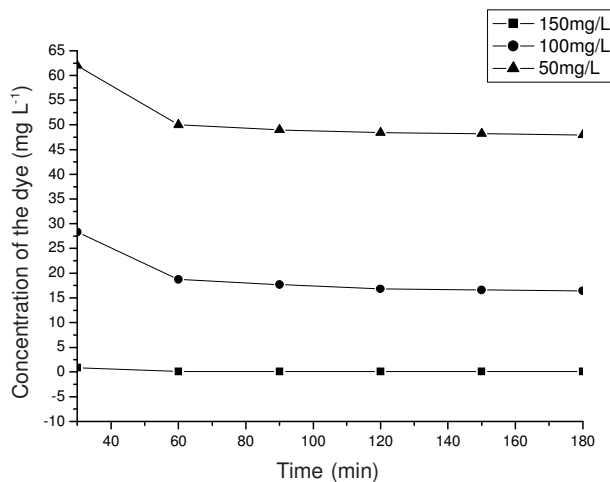


Fig. 4. Effect of contact time; pH = 1, 500 mg L⁻¹ activated carbon, V = 0.05 L, T = 35 °C

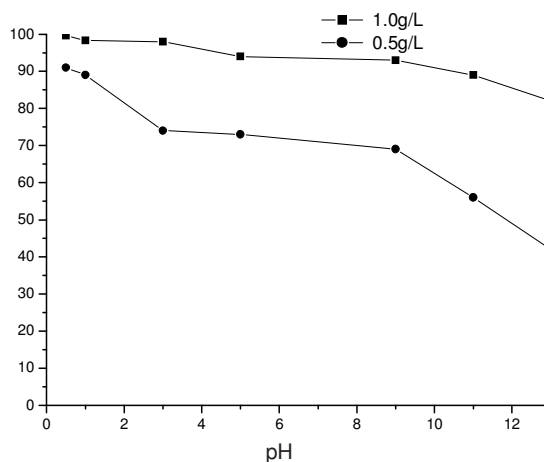
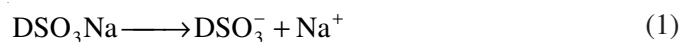


Fig. 5. Effect of initial pH value; C₀ = 100 mg L⁻¹, V = 0.05 L, T = 35 °C, contact time = 1 h

favour the adsorption of negatively charged dye anions (eqn. 1)⁷. It is known that the anions of the dye upon dissolution release coloured dye anions into solution (eqn. 1):



The surface of activated carbon may contain a large number of active sites and the solute (dye ions) uptake can be related to the active sites and also to the chemistry of the solute in the solution.

Effect of reaction temperature: The removal of acid orange 3 on activated carbon was studied at 20, 28 and 35 °C, respectively. As seen in Fig. 6, the higher temperature, the more removal ratio is. This type of adsorption is likely classified as irreversible. In this case, temperature dependence on adsorption would be comparatively stronger than desorption.

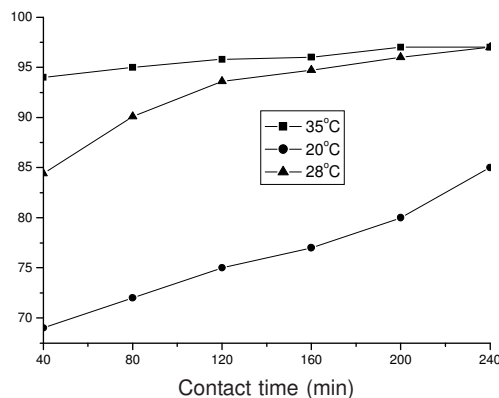


Fig. 6. Effect of temperature pH = 3, activated carbon 500 mg L⁻¹, V = 0.05 L, C₀ = 100 mg L⁻¹

Adsorption kinetics: Adsorption is a process that involves the mass transfer of a solute (adsorbate) from the fluid phase to the adsorbent surface⁸. A study of kinetics of adsorption desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. The transient behaviour of the dye adsorption process was analyzed by using pseudo-second-order.

The kinetic data were analyzed by using Ho's pseudo-second-order kinetics⁹, which is represented by following eqn. 2:

$$t/q_t = 1/k_{ps}q_{eq}^2 + t/q_{eq} \quad (2)$$

where k_{ps} is the rate constant of second-order adsorption (mg mg⁻¹ min⁻¹). If second-order kinetics is applicable, then the plot of t/q_t vs. t should show a linear relationship (Fig. 7). The calculated k_{ps} and the corresponding linear regression correlation coefficient r^2 values are summarized in Table-1. The correlation coefficients for the second-order kinetics model r^2 were from 0.985 to 0.998, so the adsorption kinetics of the dye could be described by the pseudo-second-order reaction model.

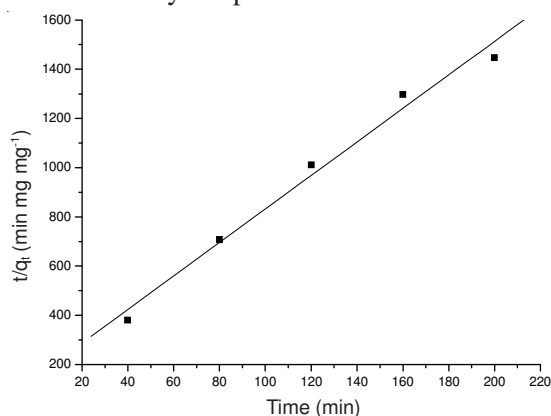


Fig. 7. Pseudo-second-order plots for dye onto activated carbon; T = 20 °C, activated carbon 500 mg L⁻¹, C₀ = 100 mg L⁻¹, pH = 9

TABLE-1
 ADSORPTION KINETIC OF DYE ONTO ACTIVATED CARBON*

K_{sp} (mg mg ⁻¹ min ⁻¹)	r^2
0.07	0.993
0.09	0.998
0.06	0.985

*pH = 9, T = 20 °C, activated carbon 500 mg L⁻¹, C₀ = 100 mg L⁻¹

At other pH values the trend was alike.

Adsorption isotherm: The analysis and design of the adsorption process requires the relevant adsorption equilibrium, which is the most important piece of information to understand the adsorption process. Adsorption equilibria provide fundamental data for evaluating the applicability of the adsorption process as a unit operation. The two most commonly used equilibrium relations are Langmuir and Freundlich isotherm equations.

Langmuir¹⁰ proposed a theory to describe the adsorption of gas molecules onto metal surfaces. It is assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. Therefore, a saturation value is reached beyond which no further sorption can take place. The saturated or monolayer (as $C_t \rightarrow \infty$) capacity can be represented by the expression: (eqn. 3)

$$Q_e = K_L C_e / (1 + a_L C_e) \quad (3)$$

where Q_e is solid phase adsorbate concentration at equilibrium (mg mg⁻¹), C_e is aqueous phase sorbate concentration at equilibrium (mg L⁻¹), Langmuir isotherm constant K_L and a_L are listed in Table-2.

TABLE-2
 LANGMUIR ISOTHERM CONSTANTS FOR
 ADSORPTION OF DYE ONTO ACTIVATED CARBON

K_L	0.07	0.02	0.06
a_L	0.48	0.12	0.38

From the Table-2, k_L is between 0 and 1, the Langmuir isotherm model is favour to describe the process of the adsorption. Langmuir isotherm data for adsorption of acid orange 3 are listed in Table-3.

TABLE-3
 LANGMUIR ISOTHERM DATA FOR ADSORPTION OF ACID ORANGE 3*

C_0 (mg L ⁻¹)	C_e (mg L ⁻¹)	q_e (mg mg ⁻¹)	R (%)
50	0.03	0.100	99.94
100	2.09	0.196	97.90
150	7.24	0.286	95.20
200	18.4	0.367	91.80
250	30.5	0.439	87.80

*Activated carbon 500 mg L⁻¹, initial concentrations of the dye 50-250 mg L⁻¹, V = 0.05 L, initial pH = 0.5, T = 35 °C

The linearized equation of Langmuir is represented as follows:

$$C_{\text{eq}}/q_{\text{eq}} = 1/bQ_m + C_{\text{eq}}/Q_m \quad (4)$$

b and Q_m are from the slopes and intercepts of the straight lines of plot of $C_{\text{eq}}/q_{\text{eq}}$ vs. C_{eq} (Fig. 8).

The values obtained from the error function showed that contradicting results from linearization were obtained, in which, the Langmuir isotherm had the low error values and $R^2 = 0.98$, $R^2 > 0.9$ and thus fit the experimental.

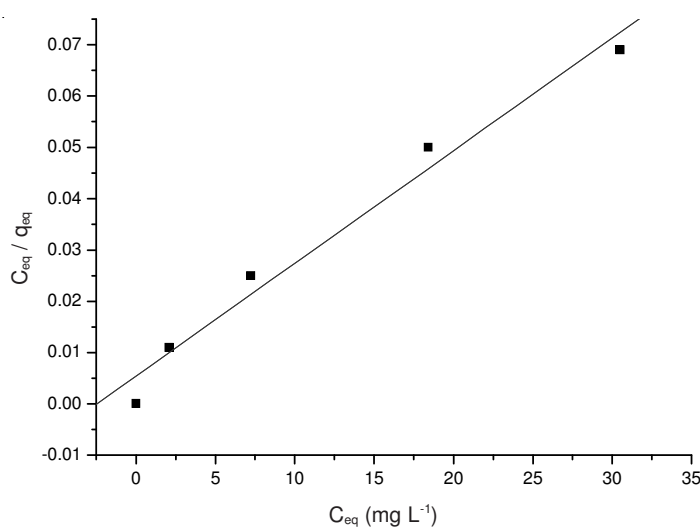


Fig. 8. Langmuir isotherms for adsorption of acid orange 3; activated carbon 500 mg L^{-1} , $V = 0.05 \text{ L}$, initial $\text{pH} = 0.5$, $T = 35 \text{ }^\circ\text{C}$, $C_0 = 50\text{-}250 \text{ mg L}^{-1}$

Conclusion

The maximum adsorption capacity of activated carbon towards the dye was found to be 0.196 mg mg^{-1} ($\text{pH} = 0.5$, $T = 35 \text{ }^\circ\text{C}$, 500 mg L^{-1} activated carbon, contact time = 1 h). The optimal adsorption conditions for the removal of acid orange 3 aqueous solution were $\text{pH} = 0.5$, activated carbon 500 mg L^{-1} , initial concentrations of the dye 100 mg L^{-1} at $35 \text{ }^\circ\text{C}$, a removal efficiency of 98 % was achieved within 1 h. The kinetic data of adsorption were well fitted the pseudo-second-order kinetic model and the Langmuir isotherm. The simplicity of the procedure may be a significant advantage for adsorption in the treatment of dye wastewaters that are difficult to deal with using biological methods.

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