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Adsorption modeling of alizarin yellow on untreated and treated charcoal

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Abstract

Adsorption studies of alizarin yellow from an aqueous solution were carried out on wood charcoal. Wood charcoal was subjected to various pretreatments. Various parameters such as pH, dosage amount, and contact time were studied to evaluate the adsorption behavior. Langmuir, Freundlich, Temkin, Harkin-Jura, and Halsey isotherm models were used to explain the experimental findings. The Freundlich model was best fitted, pointing out multilayer adsorption. Thermodynamic parameters such as ΔG°, ΔH°, and ΔS° were also calculated, which showed that a spontaneous and favorable reaction occurred for acid- and base-treated wood charcoal. The negative values of ΔH° for acid- and base-treated charcoal indicate that the adsorption mechanism was exothermic. From the Arrhenius equation, parameter E was equal to 5.36×10^{-4} kJ mol^{-1}, which corroborated the temperature dependency of the rate of adsorption.

Key Words: Adsorption, alizarin yellow, wood charcoal, Langmuir, Freundlich, Temkin, Harkin-Jura, Halsey

1. Introduction

Discharge of untreated or partially treated wastewaters and industrial effluents into natural ecosystems poses a serious problem to the environment (Bhole et al., 2004). Among effluents, dye-polluted water from textile and dyestuff industries is one of the most difficult waters to treat because of the synthetic and complex aromatic molecular structure of dyes, which makes them more stable and difficult to biodegrade (Fewson, 1998; Fu and Viraraghavan, 2001). It has been estimated that 10%-15% of dyes are lost in the effluent during the dyeing process (Al-Ghouti et al., 2003).

Physicochemical processes such as electrocoagulation, ozonation, photocatalysis, membrane filtration, and adsorption have been employed for the treatment of dye containing wastewaters (Alinsafi et al., 2005; Capar et al., 2006; Senthilkumaar et al., 2006; Shu et al., 2006; Silva et al., 2006). Among these technologies, adsorption is considered an efficient technology that involves phase transfer of dye molecules onto the adsorbent,

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leaving the clear effluent behind. Adsorption is a cheap method for removing dyes using low-cost adsorbents such as wood charcoal and biosorbents (Choy et al., 1999).

Several research groups treated dye-polluted water by employing the adsorption principle. Oladoja et al. (2008) used rubber seed shells to remove methylene blue from aqueous solutions. In addition, papaya seeds have been used as adsorbents for the adsorption of methylene blue (Hameed, 2009). Acid-treated activated carbon was another adsorbent for dyes (Wang and Zhu, 2007). Researchers have also looked at the surface chemistry of activated carbons in order to interpret dye adsorption (Al-Degs et al., 2000).

In the present work, alizarin yellow dye was removed by using wood charcoal. Alizarin yellow is a mordant dye, suitable for the dyeing of wool and nylon (Bahl et al., 2007). It usually exists as a sodium salt. In its pure form, it is a rust-colored solid (Lide, 2008). Its molecular formula is $C_{13}H_8N_3NaO_5$ (Na salt); its molecular mass is 309.21 g mol^{-1} and its λ_{max} is 370 nm. It is a slightly brown powder soluble in cold water. It causes irritation in the eyes, skin, digestive tract, and respiratory tract. This study also includes the calculation of equilibrium parameters and kinetics and a comparison of treated and untreated wood charcoal for adsorption of alizarin yellow. In addition, Langmuir, Freundlich, Temkin, Harkin-Jura, and Halsey isotherms were studied in detail.

2. Experimental work

2.1. Instrumentation

The pH was adjusted with a digital pH meter (Jenway Model 3320) using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). Alizarin was estimated with a UV/VIS spectrophotometer (Labomed UVD 3500) at $\lambda_{\max}$ 370 nm. An FTIR spectrometer (PerkinElmer FTIR-RX1) was used for adsorbent characterization.

2.2. Preparation of adsorbent

2.2.1. Untreated

Wood charcoal, collected from the local market, was crushed with laboratory-scale crushers, powdered with a disk pulverizer, and sieved to 60-80 mesh (ASTM). The powdered charcoal was washed, dried at 105 °C for 10 h in an oven, and stored in high-density polythene (HDPE) bags. The proximate analysis of the coal was carried out by using standard methods (ASTM D 5142-90). The powdered coal was also subjected to FTIR analysis for surface characterization.

2.2.2. Acid treatment

Powdered charcoal was soaked in HCl (0.1 mol L^{-1}) for 24 h, followed by filtering and washings with distilled water. Afterwards, it was dried in an oven at 105 °C for 10 h and stored in HDPE bags.

2.2.3. Base treatment

Powdered charcoal was soaked in a NaOH (0.1 mol L^{-1}) solution for 24 h, then filtered and washed with water, dried at 105 °C for 10 h, and stored in HDPE bags.

2.3. Study of process parameters

A series of experiments was carried out to study the effects of 3 parameters (adsorbent dose, pH, and contact time) on adsorption for the test solution (50 mg L^{-1}, 50 mL). While studying the effect of a parameter, that parameter was varied gradually while keeping the other 2 parameters constant.

To study the effect of adsorbent dose on the dye adsorption, different amounts of wood charcoal (0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, and 2.25 g) were added to different flasks. Flasks were agitated with an orbital shaker (top-loaded) at 125 rpm for 40 min and then filtered, and filtrates were subjected to a UV/VIS spectrophotometer to determine the dye concentration. Prior to the measurement, a calibration curve was plotted between standard alizarin yellow solutions and their respective absorbances.

Effect of contact time was studied by adding 2 g of untreated, 1.75 g of acid-treated, and 1.0 g of base-treated adsorbent to 50 mL of dye solution in separate experiments for different contact times (5-45 min). Agitation was done at a constant speed of 125 rpm using an orbital shaker. The dye concentrations were measured by a UV-VIS spectrophotometer at 370 nm.

Effect of pH on dye adsorption was studied by mixing 2 g of untreated, 1.75 g of acid-treated, and 1.0 g of base-treated wood charcoal to a dye solution of 50 mg L^{-1} in separate experiments at different pH levels (1-10). The pH was adjusted with HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}) solutions. Agitation was done for 5 min at a constant speed of 125 rpm. The dye concentrations were measured as stated earlier.

2.4. Isotherm studies

A series of experiments was carried out for isothermal and kinetic study of wood charcoal's adsorption of alizarin yellow dye. To 50 mL of dye solution, 2 g of untreated, 1.75 g of acid-treated, and 1.0 g of base-treated adsorbent was added, with initial concentrations in the range of 30-80 mg L^{-1} for untreated and base-treated and 100-225 mg L^{-1} for acid-treated wood charcoal.

Langmuir (Eq. 1), Freundlich (Eq. 2), Temkin (Eq. 3), Harkin-Jura (Eq. 4), and Halsey (Eq. 5) isotherms were plotted by using standard straight-line equations, and corresponding parameters for both metals were calculated from their respective graphs.

$$\frac{C_e}{X} = \frac{1}{K_1 K} + \frac{C_e}{K} \tag{1}$$

$$\log q = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

$$q = K_T \ln C_e + b_T \tag{3}$$

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e \tag{4}$$

$$\ln q_e = \frac{1}{n} \ln K - \frac{1}{n} \ln C_e \tag{5}$$

C_e is the equilibrium concentration of the adsorbate (mg L^{-1}) and X is the amount of adsorbate adsorbed (mg g^{-1}). K_1 indicates monolayer adsorption capacity (mg g^{-1}), K is the Langmuir equation constant (L mg^{-1}), K_F and 1/n are constants for a given adsorbate and adsorbent at a particular temperature, and b_T (kJ mol^{-1}) is the adsorption potential of the adsorbent. K_T is the Temkin isotherm constant and 1/A is the external surface area for the Harkin-Jura isotherm.

3. Results and discussion

3.1. Characterization of adsorbent

The charcoal analysis revealed that it had high moisture content and volatile matter. Ash content was also appreciable. Results are illustrated in Table 1. The FTIR spectrum affirmed the presence of hydroxyl and carboxylic acid groups in the coal sample. The reason for the presence of these groups was the incomplete conversion of wood to charcoal.

Table 1. Adsorbent characteristics.

Parameters	Moisture	Volatile Matter	Ash	Fixed C	% S	Heating Value (kJ kg^{-1})	FTIR Spectrum (cm^{-1})
Values	4.5%	22.13%	10.5%	59.7%	1.4%	35.96	3784, 2934, 2361, 1688, 1564, 1460, 1289

3.2. Effect of adsorbent dosage

The effect of adsorbent dosage on adsorption of alizarin yellow dye was studied using different dosages in the range of 0.25-2.25 g 50 mL^{-1} (Figure 2). It was found that the adsorption efficiency was highly dependent on the quantity of adsorbent added. Maximum removal was 96.96%, 99.12%, and 75.44% for doses of 2.0 g 50 mL^{-1}, 1.75 g 50 mL^{-1}, and 1.0 g 50 mL^{-1} of untreated, acid-treated, and base-treated adsorbents, respectively. This was expected, as with the increasing concentration of the adsorbent, more surfaces, or in other words, more active sites, become available for metal ions. The decrease in efficiency at the higher adsorbent concentrations could be because of a partial aggregation of adsorbent, which results in a decrease in effective surface area for metal uptake.

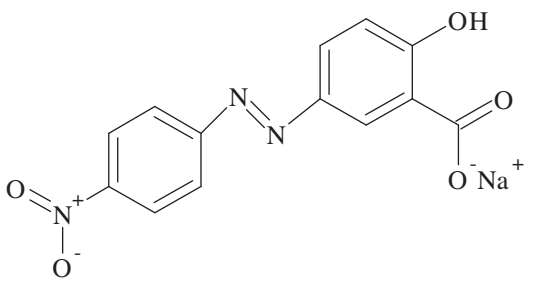

Figure 1. Structure of alizarin yellow (Na salt).

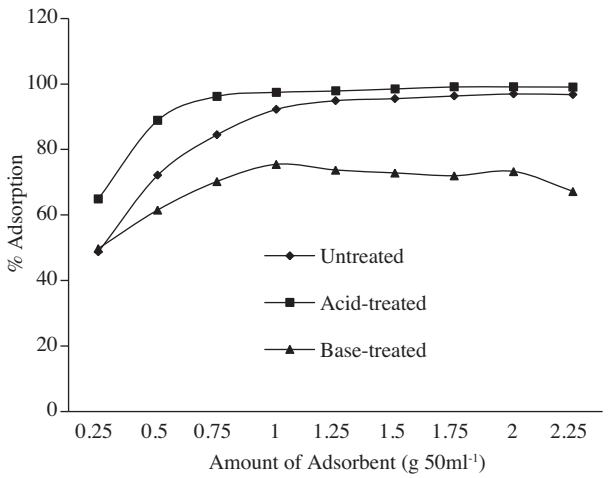

Figure 2. Effect of adsorbent dosage.

3.3. Effect of contact time

The effect of the contact time on dye adsorption was studied by varying the time of contact from 5 to 50 min. The results are shown in Figure 3. Increase in removal efficiency with an increase in time of contact is due to the fact that more time becomes available for the adsorbate to coordinate with the adsorbent. Initial removal occurs immediately, as soon as the dye and charcoal come into contact. However, after that, when some of the easily available active sites become unavailable, the dye needs time to find more active sites for binding. It is concluded that alizarin yellow and charcoal (untreated, acid-treated, and base-treated) should be in contact for at least 15-20 min for good adsorption.

3.4. Effect of pH

Effect of pH was studied in the range of 1-9. As shown in Figure 4, maximum adsorption took place at pH 1 in each case, i.e. for untreated, acid-treated, and base-treated adsorbents. Above the optimum pH, adsorption decreased. This trend can be understood by considering the structure of the dye. Alizarin yellow is an azo dye having carboxylate and nitro groups, as shown in its structure (Figure 1). Due to the acidic treatment of charcoal, it becomes protonated, having a positive charge on its surface, which provides effective sites for the dye adsorption. Figure 4 also explains that acid-treated charcoal becomes more effective in adsorption for the above reason. At low pH levels, acid-treated, base-treated, and untreated charcoal have almost equal adsorption capacity, and afterwards, the following trend was obtained in decreasing adsorption capacity.

Acid-treated charcoal > untreated charcoal > base-treated charcoal.

The decrease in sorption capacity at high pH values is attributed to the accumulation of a negative charge at the adsorbent surface, providing relatively fewer effective sites for dye adsorption due to an increase in repulsive forces. Thus, it was concluded that the lowest possible pH should be maintained for efficient removal of alizarin yellow from aqueous solutions.

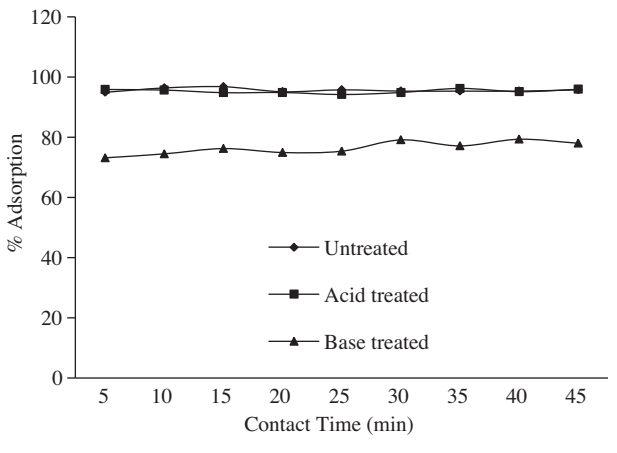

Figure 3. Effect of contact time.

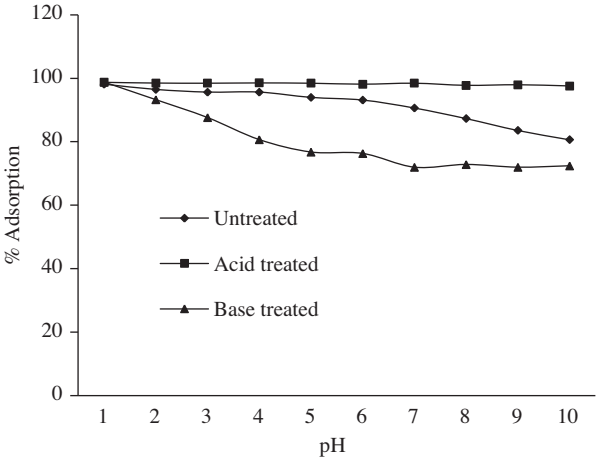

Figure 4. Effect of pH.

3.5. Adsorption isotherm

Isotherm parameters, evaluated from the linear plots of Eqs. (1-5) (Langmuir, Freundlich, Temkin, Harkin-Jura, and Halsey), are illustrated in Table 2. The K_1 value for the Langmuir isotherm, i.e. 14.93 mg g^{-1}, indicated the high adsorption capacity of charcoal toward alizarin adsorption. The R^2 (correlation coefficient) value of 0.905 indicated that the Langmuir isotherm is good for explaining the alizarin adsorption.

Table 2. Isotherm parameters.

Isotherm	Parameters		
Langmuir	k_1 (mg g^{-1}) = 14.93	k (cm^3 g^{-1}) = 0.127	R^2 = 0.905
Freundlich	K_f = 0.024	n = 0.399	R^2 = 0.976
Temkin	K_T = 2.898	b_T (kJ mol^{-1}) = 3.242	R^2 = 0.962
Harkin-Jura	A = 0.092	B = 0.762	R^2 = 0.962
Halsey	n = 0.395	K = 0.226	R^2 = 0.962

The R^2 value for the Freundlich isotherm was found to be 0.97, indicating that the experimental data can be better explained by the Freundlich isotherm than the Langmuir. The K_f (ultimate adsorption capacity) value as calculated from the Freundlich isotherm was 0.024. The Temkin equation was also good to explain the experimental data, with an R^2 value of 0.96. b_T (heat of sorption) was calculated from the Temkin plot as 3.242 kJ mol^{-1}, indicating moderately strong cohesive forces between alizarin yellow and charcoal. A value less than 8 indicates a weak interaction between the adsorbent and adsorbate (Anwar et al., 2010).

The Harkin-Jura expression of the value of the correlation coefficient was 0.887, providing less suitability for the experimental data of alizarin yellow on wood charcoal. Halsey's expression of the value of correlation coefficients was 0.9770, providing a better fit for the experimental data of alizarin yellow on wood charcoal. The Harkin-Jura and Halsey equations were more suitable to explain the multilayer adsorption of the adsorbate on the adsorbent (Oladoja et al., 2008).

3.6. Thermodynamics parameters

Thermodynamic parameters such as standards Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also calculated using Eqs. (6) and (7), and the results obtained are illustrated in Table 3.

$$\Delta G^\circ = -RT \ln K \tag{6}$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

Here, k denotes the distribution coefficient for the adsorption. R is the universal gas constant and T is the absolute temperature in Kelvin. The negative value of ΔG° at the studied temperature range indicated that the sorption of alizarin yellow on charcoal was thermodynamically feasible and spontaneous. The increase in the value of ΔG° with temperature further showed the increase in feasibility of sorption at the elevated temperatures for untreated, acid-treated, and base-treated charcoal. In other words, sorption is endothermic in nature. The positive value of ΔH° for untreated charcoal showed that adsorption was endothermic, and the negative value of ΔH° for acid-treated and base-treated charcoal showed that adsorption was exothermic. The positive value of ΔS° showed an increased randomness at the solid alizarin yellow solution interface during the adsorption of alizarin yellow, reflecting the affinity of wood charcoal for alizarin yellow.

Table 3. Thermodynamic parameters.

Charcoal Type	Temperature K	ΔG° kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° kJ mol^{-1} K^{-1}
Untreated	298	-5.76	4.99×10^{-4}	0.0204
Acid-Treated	298	-8.58	-2.09×10^{-3}	0.0252
Base-Treated	298	-3.90	-3.82×10^{-4}	0.0121

3.7. Arrhenius equation

Activation energies for adsorption of alizarin on charcoal were calculated using the Arrhenius equation (Eq. 8), plotted in Figure 5 and tabulated in Table 4. The activation energies obtained in each case, i.e. acid-treated, base-treated, and untreated adsorbents, indicate that physical forces are involved in the sorption mechanism and sorption feasibility.

$$LogK = LogA - \frac{E_A}{2.303RT} \tag{8}$$

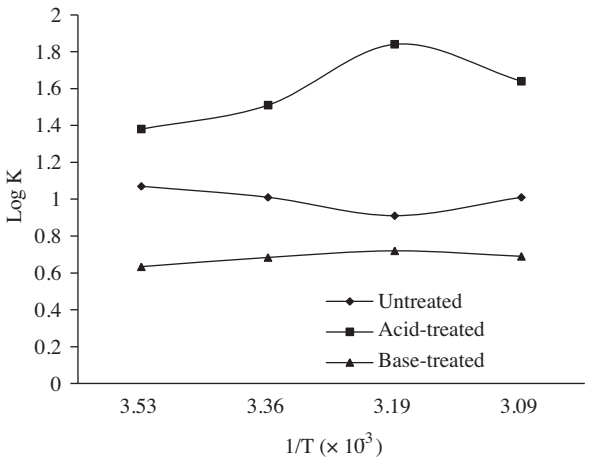

Figure 5. Arrhenius parameters.

Table 4. Arrhenius parameters.

Charcoal Type	log A	E_a (kJ mol^{-1})
Untreated	11.75	5.36×10^{-4}
Acid-Treated	20.65	-2.13×10^{-3}
Base-Treated	4.280	-3.83×10^{-4}

4. Conclusion

Wood charcoal proved to be an effective adsorbent for alizarin removal from aqueous media. Study of process parameters indicated the comparative efficiency of treated and untreated adsorbents. Acid-treated charcoal adsorption proved to be the most efficient due to the increase in efficiency of active sites. The Freundlich isotherm model was found to be the most suitable model for explanation of observed sorption because of the high value of its correlation coefficients. Thermodynamic study showed that spontaneous and favorable adsorption of alizarin yellow was well achieved with untreated and base-treated wood charcoal. Activation

energy values affirmed the physiosorption. Hence, it can be concluded that charcoal can be effectively used for alizarin removal from aqueous media, especially in developing countries like Pakistan. Acid treatment of charcoal enhances its efficiency.

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