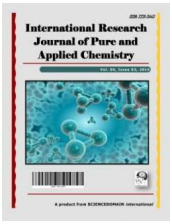

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Removal of Acid Alizarin Black Dye from Aqueous Solution by Adsorption Using Zinc Oxide

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Authors' contributions

This work was carried out in collaboration between all authors. Author HAMS designed the study and wrote the protocol. Authors SAMS and RAR performed the experimental, while author HAMS preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The adsorption of Acid Alizarin Black (AAB) dye (C.I. 21725) on zinc oxide was investigated in this study. The adsorption was carried out under different operating conditions. The operating conditions were contact time, adsorbent dosage (10, 30, 50, 70 and 100 mg), initial dye concentration (10, 20, 30, 40, 50, 60 and 70 mg/L), the pH of the solution (2, 4, 6, 7, 8, 10 and 12) and temperature (20, 30, 40, 50 and 60℃). The remo val percentage of dye on ZnO decreases from 67% to 54% with increase in initial dye concentration from 10 to 70 mg/L, respectively. It was found that the increasing of ZnO dosage enhanced the dye removal. The increasing of temperature insignificantly enhanced the removal of dye. The study reports that the best pH of solution for the adsorption of AAB on ZnO were 7 and 8. The adsorption data have been analysed using Langmuir, Freundlich and Temkin. It is indicated that the adsorption of dye onto ZnO was endothermic. The uptake process of AAB obeyed the pseudo second order kinetic expression.

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Keywords: Alizarin black dye; zinc oxide; adsorption isotherms; kinetic.

1. INTRODUCTION

Aquatic environmental pollution is primarily caused by the effluent disposal from the industries. Many industries such as rubber, paper, plastics, textile, leather, food processing, printing and paints industries, discharge a huge quantity of dyes into the water, which cause pollution of water and serious environmental problems [1,2]. Synthetic dyes, since of their reasonable cost of producing and easily soluble in water, are widely used in the industry of textile. The synthetic dyes are easier to apply with synthetic fibers like rayon, polyester and acrylic and natural fibers such as silk, cotton and wool [3].

In wastewater treatment technology, various methods have been employed to remove pollutants from aqueous solutions including electrochemical treatment, precipitation, evaporative recovery, adsorption, ion exchange, membrane separation and reverse osmosis [4,5]. Adsorption has been considered to be one of the most extensively used methods for the removal of organic and inorganic pollutant from polluted water [6]. Adsorption by solids reduces the toxicity of the contaminated water or eliminates dyes from industrials effluents [7]. Among adsorption process, adsorption onto the metal oxides has been proven to be one of the effective and reliable treatment method [8,9]. It was reported that Fe_2O_3 could be employed for the removal of acid red 27 dye from the wastewater [10]. Kong and Zhang studied the adsorption of methylene blue and Congo red onto the magnetic Fe_3O_4 core-shell nanoparticles [11]. It was also found that acid and basic dyes can be adsorbed by ZnO and the total adsorption of the dyes approximately 10% chemisorption and 90% adsorption of lower energy [12]. This study reports the results of removal of acid alizarin black (AAB) from polluted water by adsorption onto zinc oxide (ZnO) under different operating conditions.

2. MATERIALS AND METHODS

2.1 Materials

Acid alizarin black (AAB) was purchased from Hopkin and Williams Ltd, UK, and used as received to prepare solutions that used in this research. A stock solution of AAB (1000 mg/L) was prepared on a daily basis in distilled water and other concentrations (10, 20, 30, 40, 50, 60 and 70 mg/L) were prepared by dilution the stock solution of AAB. The stock solution of AAB (1000 mg/L) was covered and stored in a dark place. Zinc oxide (ZnO) was purchased from Alpha Chemika, India. Nitric acid (HNO_3) and sodium hydroxide (NaOH) were purchased from Fisher-Scientific, UK. Various molarities of HNO_3 and NaOH were used to adjust the pH value of solutions between 2 and 12 using pH meter.

2.2 Adsorption Isotherm

10 mg of ZnO was used as adsorbent and four solutions of AAB with initial concentration 10, 20, 30, 40, 50, 60 and 70 mg/L were used. This involved using 200 mL of AAB in a reactor and placed on a stirrer for better mixing for 24 min. Samples were taken at a specific schedule, 2 mL of sample, using a glass syringe with 10 mL. A set of experiments is performed to study the effect of initial dye concentration, adsorbent dose, temperature and pH of the solution. For separating adsorbents from the taking sample before analysis, a centrifuge was used. The samples were analysed using spectrophotometer with maximum absorbance (643 nm).

The following equation was used to calculate the percentage of AAB removal:

$$\% \, Removal = \frac{C_o - C_e}{C_o} * 100 \, \% \qquad (1)$$

Langmuir, Freundlich and Temkin models were applied for describing the adsorption of AAB on ZnO.

The Langmuir model can be written in a nonlinear form as in below equation [13]:

$$q_e = \frac{Q_m \, b \, C_e}{1 + b \, C_e} \qquad (2)$$

Where C_e is the equilibrium concentration of sorbent (mg/L), Q_m is the maximum sorption capacity (mg/g), q_e is the mass of AAB adsorbed per unit mass of adsorbent at equilibrium (mg/g), b is the Langmuir adsorption constant (L/mg). In order to obtain Q_m and b values, a linear equation can be obtained by rearranging the equation 1 for Langmuir-1 as in equation 3 and for Langmuir-2 as in equation 4 [14]:

$$\frac{C_e}{q_e} = \frac{1}{b\,Q_m} + \frac{C_e}{Q_m} \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m} \quad (4)$$

The Freundlich isotherm, on the other hand, can be represented by the equation 5:

$$q_e = K_f\, C_e^{\,1/n_f} \quad (5)$$

For non-ideal adsorption and when the surface is heterogeneous the Freunlidh isotherm is used [15]. Where n_f is the Freundlich coefficient and K_f is the Freundlich constant. A linear equation is used to determine K_f and n_f:

$$lnq_e = lnK_f + \frac{1}{n_f} lnC_e \quad (6)$$

The Temkin isotherm is represented by equation 7:

$$q_e = \left(\frac{RT}{B}\right) \ln(K_T C_e) \quad (7)$$

Where B is the constant related to the heat of sorption and K_T is the Temkin isotherm constant, R is the gas rate constant (8.314 J K^{-1},mol^{-1}) and T is the temperature in K.

3. RESULTS AND DISCUSSION

3.1 Effect of Contact Time

The contact time effect was studied for an initial concentration of AAB (20 mg/L) and 10 mg of ZnO. Fig. 1 shows that the adsorption of AAB was occurred very quickly from the beginning of the experiments during the first 20 min, then a slight increase occurred until 25 min where the maximum adsorption of AAB on ZnO was observed. There was no further increase in the adsorption of AAB beyond 25 min and it was fixed as an equilibrium time.

3.2 Effect of Dye Concentration

The effect of dye concentration on adsorption of AAB on ZnO is shown in Fig. 2. The experimental results of AAB adsorption on ZnO were obtained at various concentration (10, 20, 30 and 40 mg/L). It was indicated that the dye removal percent from the solution decreased with increase in initial AAB concentration. However, as the initial dye concentration increased, the actual amount of AAB adsorbed per unit mass of ZnO increased, as a results of increased concentration gradient between adsorbate in solution with higher concentration of dye and adsorbate in the adsorbent (see Fig. 3).

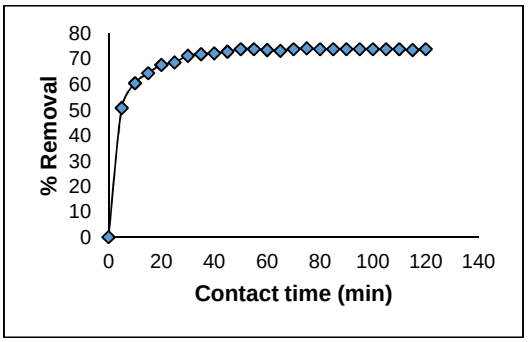

Fig. 1. Effect of contact time on adsorption of AAB on ZnO (ZnO = 10 mg, T = 20℃, V = 200 mL, pH = 6)

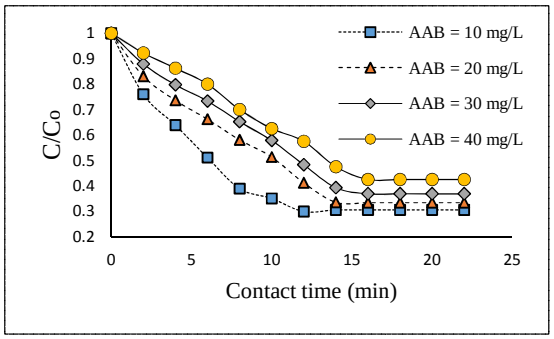

Fig. 2. Effect of initial dye concentration on adsorption of AAB on ZnO (C_o=20 mg/L, ZnO = 10 mg, T = 20°C, V = 200 mL, pH = 6)

3.3 Effect of pH

The effect of pH on adsorption of AAB on ZnO is shown in Fig. 4. The initial pH of the solution plays an important role in controlling the adsorption process of dye onto suspended particles [16]. The surface charge of the adsorbents and the degree of ionization of dye are affected by the pH of the solution owing to the protonation and deprotonation of the active functional groups [17]. Since the hydrogen ion (H^+) and hydroxyl ion (OH^-) are strongly adsorbed to the surface of adsorbent, the adsorption of other ions is affected by the pH of the solution. Through the point of zero charge

(pH_{pzc}), the point at which the net charge of the adsorbent is zero, the understanding of the mechanism of adsorption can be explained [18]. The pH_{pzc} for the same was estimated preciously for the same product of ZnO which was about 8.6 [19]. The surface of ZnO particles are negatively charged above this pH value, while they are positively charged below this pH value [20]. Since AAB dye is consider as an anionic dye, it could be adsorbed on the surfaces of ZnO particles easily below its pH_{pzc}, according to a simple surface charge model [21]. Fig. 5 shows the effect of pH on removal percentage. It was found that the best pH for this system were 7 and 8.

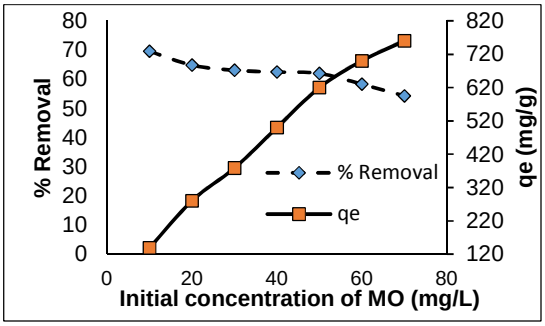

Fig. 3. Effect of initial dye concentration on removal percent and adsorption capacity of AAB (ZnO = 10 mg, T = 20℃, V = 200 mL, pH = 6)

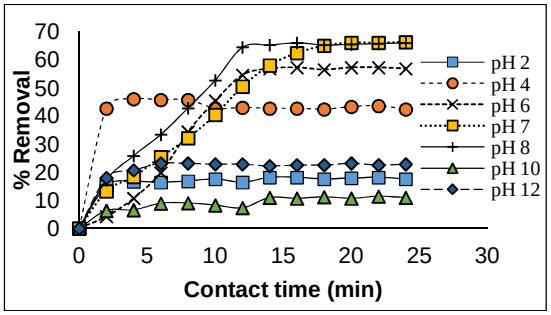

Fig. 4. Effect of pH on removal percent of AAB (C_o = 20 mg/L, ZnO = 10 mg, T = 20℃, V = 200 mL)

3.4 Effect of ZnO Dose

The effect of ZnO dose in range 0.01-0.1 g/L of dye solution (C_o = 20 mg/L) on dye removal percent is shown in Fig. 6. The dye removal was favoured as the amount of ZnO increased. A large adsorbent dose, as expected, reduces the saturation of the adsorption sites, since dye molecules are more shared per adsorbent unit due to an increase in total adsorbent surface and adsorption sites availability. AAB dye can easily access the adsorption sites and the q_e is high when the adsorbent dose is small. A similar behavior was found for the dye adsorption on different adsorbents such as pumpkin seed hull [22], jackfruit peel [23], papaya seeds [16] coir pith [24] etc. In this research, the ZnO dose of 70 mg/L was found to be appropriate for efficient AAB adsorption.

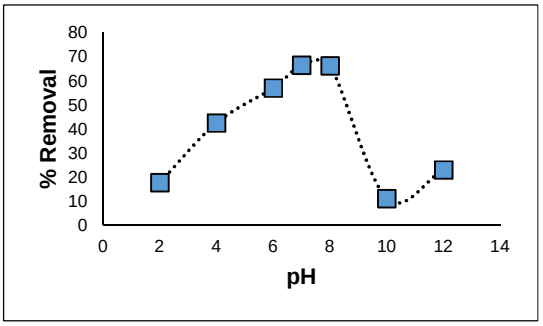

Fig. 5. Effect of pH on removal percentage (C_o = 20 mg/L, ZnO = 10 mg, T = 20℃, V = 200 mL)

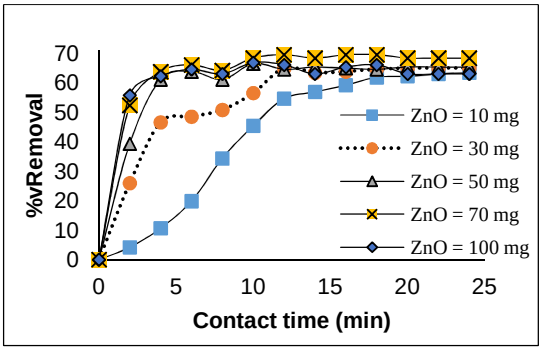

Fig. 6. Effect of ZnO dose on removal percentage of AAB (C_o =20 mg/L, V = 200 mL, pH = 6)

3.5 Effect of Temperature on Adsorption and Thermodynamics

The adsorption of AAB on ZnO was studied at temperature of 20, 30, 40, 50 and 60℃. Fig. 7 shows the effect of temperature on adsorption of AAB dye on ZnO. The free energy (ΔG) of adsorption was calculated from bellow equation [14]:

$$\Delta G = -RT \ln b \qquad (8)$$

Where: T is the temperature (K), R is the gas constant (8.314 J/mol) and *b* is the Langmuir constant. The entropy (ΔS) and enthalpy (ΔH) of adsorption were calculated at different temperature by using Van't Hoff equation [22]:

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

From the plot of ln *b* versus *1/T* show Fig. 8, the ΔS and ΔH were calculated from the slope and intercept, respectively, with these parameters being given in Table 1.

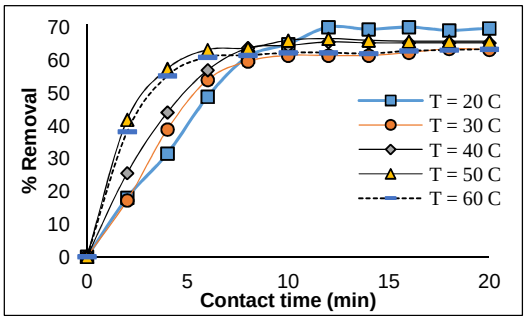

Fig. 7. Effect of Temperature on adsorption of AAB on ZnO (C_o =20 mg/L, ZnO = 10 mg, pH = 6)

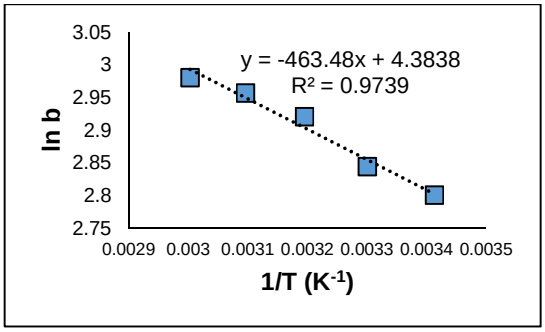

Fig. 8. Plot of *lnb* versus *1/T* for estimation of thermodynamic parameters (C_o =20 mg/L, ZnO = 10 mg, V = 200 mL, pH = 6)

As shown in Fig. 7, the capacity of adsorption increased at higher temperatures, which indicates that dye adsorption was an endothermic process in this system.

Table 1. Thermodynamic parameters for AAB adsorption on ZnO under different temperatures

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
293	-6.6	3.85	36.45
303	-7.1		
313	-7.6		
323	-7.9		
333	-8.3		

3.6 Adsorption Isotherms

The adsorption capacity of ZnO for AAB dye can be determined by measuring equilibrium isotherms. Adsorption isotherms, for the analysis and design of an adsorption system, plays a crucial role in the predictive modeling procedures. According to the linear form of Langmuir-1, Langmuir-2, Freundlich and Temkin, adsorption isotherms were analysed. Fig. 9 shows all of the isotherm analyses results. The experimental results are well represented by the Langmuir-1 and Freundlich model more than the others. Table 2 shows isotherm constants for AAB dye on ZnO.

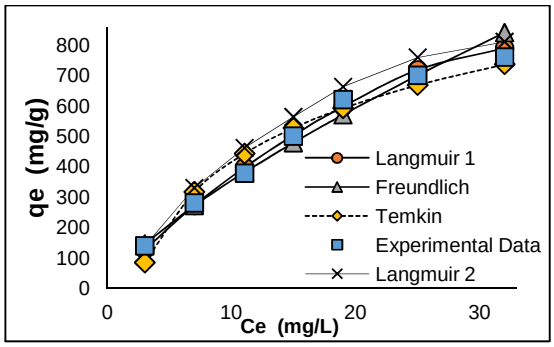

Fig. 9. Experimental data and theoretical isotherms for ZnO (ZnO = 10 mg, T = 20℃, V = 200 mL, pH = 6)

Table 2. Isotherm constants for AAB dye on ZnO

Langmuir-1			Freundlich		
Q_m (mg/g)	b (L/mg)	R^2	n_f	K_f (mg/g(mg/L)$^{(1/n)}$)	R^2
798	0.022	0.97	1.34	63.8	0.9898
Temkin				**Langmuir-2**	
q_e (mg/g)	K_T (L/g)	B	R^2	Q_m (mg/g)	b (L/mg)	R^2
736.7	1.004	277.56	0.96	772	0.048	0.956

Table 3. Comparison of the pseudo first and second order adsorption parameters for different dye concentrations

Initial concentration (mg/L)	First order model			Second order model		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	K_2 ($g.mg^{-1}min^{-1}$)	R^2
10	266.8	0.127	0.9307	275.3	0.002	0.9908
20	498.07	0.196	0.9607	503.41	0.0017	0.9937
30	753.12	0.305	0.8234	741.6	0.0013	0.9972
40	785.32	0.179	0.7542	779.7	0.0011	1

3.7 Adsorption Kinetic

The pseudo first order kinetic given by Svenska and Langergen was used to determine the rate constant of adsorption [25]:

$$\ln(q_e - q_t) = lnq_e - k_1 t \quad (10)$$

Where k_1 is the rate constant adsorption (min^{-1}), q_e and q_t are the amount of AAB adsorbed in (mg/g) at equilibrium and at time t, respectively. For different concentrations of AAB, k_1 values were calculated from the plots of $(q_e - q_t)$ with t, as shown in Fig. 10.

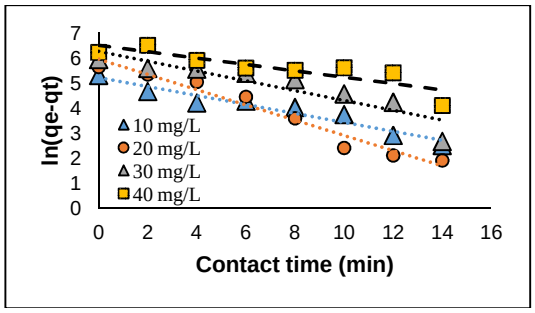

Fig. 10. Pseudo first-order kinetics for adsorption of AAB by ZnO (ZnO = 10 mg, T = 20°C, V = 200 mL)

The pseudo second order equation, on the other hand, based on adsorption equilibrium is expressed as follows [26]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

Where k_2 is the equilibrium rate constant of pseudo second order sorption (g $mg^{-1}min^{-1}$). Equation (11) gives linear form by plotting t/q_t versus t, will give a straight line with intercept $1/kq_e^2$ and slope $1/q_e$ (as shown in Fig. 11). This figure shows a good agreement between calculated and experimental q_e values, show Table 2. For the second order kinetic model, the correlation coefficients are higher than 0.99 indicating the applicability of this equation and the second order nature of the adsorption process of AAB on ZnO.

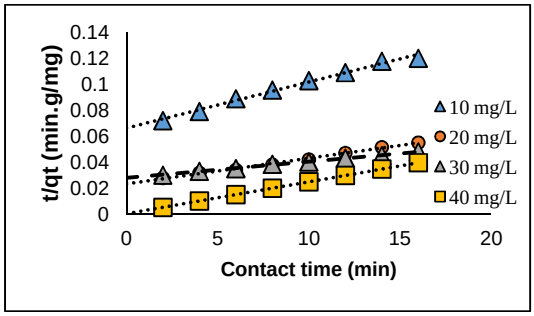

Fig. 11. Pseudo second order kinetics for adsorption of AAB by ZnO (ZnO = 10 mg, T = 20°C, V = 200 mL)

4. CONCLUSIONS

The adsorption of AAB dye, under different operating condition, onto ZnO was studied in this research. The operating conditions were contact time, initial dye concentration, quantity of adsorbent, temperature and pH of the solution. The most effective improvements on the adsorption of AAB were recorded when 10 mg/L of dye was used. It was found that the increasing of ZnO amount increased the removal percentage. The best pH for the adsorption was recorded to be 7 and 8. It was also found that increasing temperature insignificantly increased the removal percentage. Langmuir, Freundlich and Temkin isotherms were studied to analyse the removal data of dye. The positive value of enthalpy indicates that the dye adsorption onto ZnO was endothermic. The adsorption process of AAB follows the pseudo second order kinetic expression.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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