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Copper (II) Oxide particles as Adsorbent for Removal of Alkali Blue; Isotherm and Kinetic Studies

M. A. Ibrahim* and **M. B. Ibrahim**

Department of Pure and Industrial Chemistry, Bayero University, P.M.B. 3011, Kano, Nigeria

*E-mail address: mibrahim042@gmail.com , mbibrahim.chm@buk.edu.ng

ABSTRACT

Adsorption behaviour of copper (II) oxide particles (CuO-Ps) for the removal of Alkali Blue (AB) was studied. Different adsorption variables such as contact time, initial concentration and pH for the adsorption process were investigated by batch adsorption studies. FTIR was carried out to determine the functional groups present at the surface of the particle with functional groups such as $-\text{OH}$, $\text{C}=\text{C}$, $\text{C}-\text{H}$, $\text{C}\equiv\text{C}$ detected. The percentage removal and optimum contact time for the removal of AB was 84.8% at 10 min. The experimental isotherms data were analyzed using Langmuir, Temkin, Freundlich and Dubinin-Radushkevich (D-R) isotherms and it was observed that AB fits closely to Langmuir with R^2 value of 0.884. Kinetics studies shows that the adsorption process fits better to pseudo-second order with the experimental values of q_e 4.242 been closer to the calculated values of the q_e 4.108. Effect of pH shows that it adsorb better at the initial pH of 5.30. Lower value of mean square energy of 0.707 kJ/mol indicates that the adsorption process is physical. The results indicated that copper (II) oxide particle can be used as a low-cost adsorbent for the removal of AB from aqueous solutions.

Keywords: Adsorption, Kinetics, Isotherm, FTIR, Copper (II) Oxide particles

1. INTRODUCTION

Adsorption is considered as one of methods of choice in water treatment as it gives the best results in removing different types of coloring materials (Sulaymon *et al.* 2009). This treatment has no side product as the pollutants are adsorbed on the surface of the adsorbent and in many cases, can be regenerated and reused (Dahri *et al.*, 2015). The most widely used adsorbent is activated carbon due to its great potential for the removal of dyes. However, its preparation and regeneration costs have encouraged the application of alternative materials (Crini, 2006; Hameed, 2009). Nowadays, a wide variety of materials have been used for the development of cheaper and effective adsorbents such as agro-wastes (Okeola and Odeunmi, 2010), banana peels (Ali and Sa'eed, 2015), and pine needles (Malik *et al.*, 2015) in the treatment of various types of wastewater especially for dye-based wastewater.

Dyes commonly used in industries such as in food, textiles and papers industries consist of stable molecules resistant to light, chemical and other kinds of exposure can be considered as mutagens to human and can also easily accumulate in the living tissues. Alkali Blue dye AB is one of the only few dyes used in microscopy which are after chromed with a mordant. It is used in a method for elastic fibres. Alkali Blue belongs to the anionic class of dyes. The removal of dyes from industrial wastewater are important both environmental and water reuse concerns. Therefore, the aim of this study is to investigate the potential of Copper (II) Oxide particles as an adsorbent for the removal of AB dye from the aqueous solution.

2. MATERIALS AND METHODS

2. 1. Synthesis of Copper (II) Oxide Particles

Synthesis of Copper (II) oxide particle was carried out based on the method employed by Mayekar *et al.* (2014). Polyethylene glycol (PEG) was used instead of polyvinylpyrrolidone (PVP) which also plays the same role to stabilize the aggregation of the metal ion. For the synthesis of copper (II) oxide particles, 7.68 g of copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was mixed with 2.4 g of polyethylene glycol (PEG) and 200 ml of distilled water. The solution was stirred using magnetic stirrer and heated until it reaches 60 °C. 1.0 M of sodium hydroxide solution and 1.0 M hydrochloric acid were used to adjust the pH of the solution to 7.0 (Neutral). Sodium hydroxide solution was added drop by drop followed by heating and stirring for two hours. Brownish black precipitate was formed. It was centrifuged and oven dried at 50 °C for eight hours to get copper (II) oxide powder. The FTIR of the particles both before and after adsorption was conducted.

2. 2. Batch Adsorption Experiment

Different adsorption variables such as pH, contact time and initial dye concentration on the adsorptive removal of the dye were investigated in batch mode. In each experiment, 100 mL of dye solution in a 120 mL bottle was agitated and stirred at 300 rpm along with a fixed mass of the particles at an initial concentration of 10 mg/L, initial pH of the dyes and at a particles at an initial concentration of 10 mg/L, initial pH of the dyes and at a constant temperature of 30 ± 2 °C. The mixture was then centrifuged and the residual concentration of the dye was determined spectrophotometrically using UV-Visible spectrophotometer (Model Hitachi 2800) at a corresponding λ_{max} of the dye; 581 nm (80 %, Merck). 1.25 g of AB was

dissolved in 1000 ml of distilled water to prepare the standard solution. The obtained experimental data at various times and concentration were fitted to different models to evaluate and calculate the kinetics and isotherm parameters. The solution pH was adjusted by the addition of dilute aqueous solutions of HCl and NaOH (0.1 M). The removal efficiency and adsorption capacity of the adsorbent were calculated from equations (1) and (2) respectively:

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where: C_0 (mg/l) and C_e (mg/l) are the initial concentration and concentration of the adsorbate at equilibrium, C_t is the dye concentration at any time, V is the volume of the solution (L) and M is the mass of the adsorbent (g) (Guo *et al.*,2015).

3. RESULTS AND DISCUSSIONS

3. 1. Effect of Contact time

The effect of contact time was studied by varying the agitation time in the range of 5 to 120 minutes for 10.00 mg/L dye initial concentration at room temperature ($30\text{ }^\circ\text{C} \pm 3\text{ }^\circ\text{C}$) and 0.2 g of the particles. The equilibrium time, percentage dye removal and the amount of dye adsorbed at any time and at equilibrium was observed.

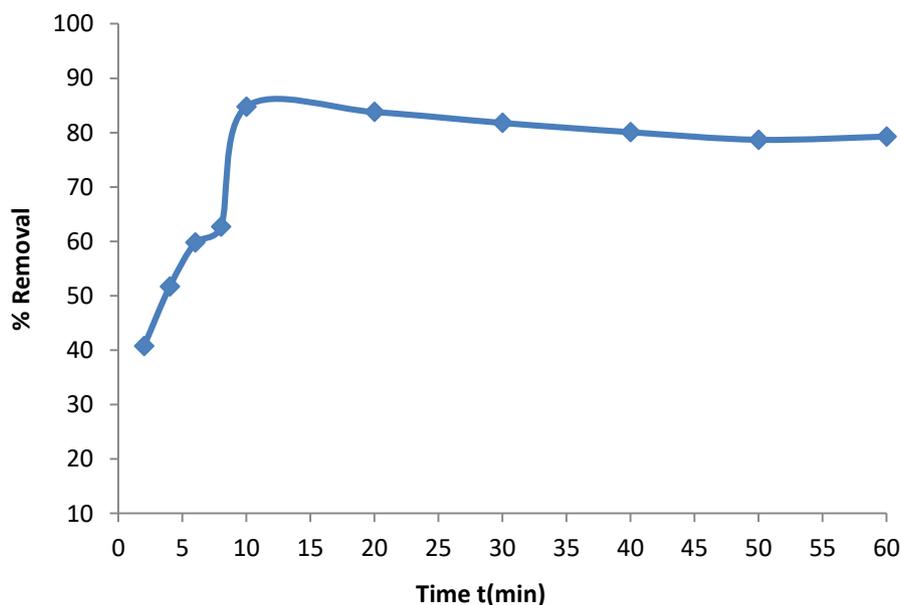


Fig. 1. Effect of contact time on the removal of AB dye

For the adsorption process equilibrium was attained after 10 minutes with maximum removal percentage of about 84.8 % (Fig. 1) which is due to high interaction between adsorbent and the dye, and also the availability of more active sites on the particles for the dye adsorption. At a time above 10 minutes the percentage removal decreases which may due to fact that all the active site have been occupied. This is in agreement with Gao and Mei (2002), which reported that the interaction between Alkali blue and bovine serum albumin interaction was completed within the first 10 minutes at room temperature.

3. 2. Adsorption Kinetics

Kinetic studies were employed in order to investigate the mechanism of the adsorption process and its potential rate controlling steps. The adsorption kinetics of the dye was analysed by the pseudo first order, pseudo second order, Elovich kinetic and intraparticle diffusion models.

From Table 1, there is disagreement between q_e (equilibrium adsorption capacity) experimental and the q_e calculated values from pseudo first order. Also the calculated correlation coefficient (R^2) is very low when compared to that of other kinetic models in Table 1. This shows that the adsorption of AB onto CuO-Ps do not follow the pseudo first-order kinetics.

Table 1. Kinetics parameters for adsorption of AB on CuO-Ps

q_e exp. (mg/g)	Pseudo-first order		Pseudo-second order		Intraparticle diffusion		Elovich	
	$\ln (q_e - q_t) = \ln q_e - k_1 t$		$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$		$q_t = k_{diff} t^{1/2} + C$		$q_t = \frac{1}{\beta} \ln (t) + \frac{1}{\beta} \ln (\alpha \beta)$	
4.242	$q_{e,cal.}$ (mg/g)	1.061	$q_{e,cal.}$ (mg/g)	4.108	C (mg/g)	2.424	A (mg/g.min)	20.035
	k_1 (min ⁻¹)	0.035	k_2 (g/mg.min)	0.175	k_{diff} (mg/g.min ^{-1/2})	0.255	B (mg/g)	1.762
	R^2	0.359	R^2	0.997	R^2	0.548	R^2	0.719

Conditions: ($C_o = 10$ mg/L, $m = 0.2$ g , $T = 303$ K)

The q_e experimental and the q_e calculated values from the pseudo second- order kinetic model for the adsorption process is very close to each other as shown in Table 1. Also the calculated correlation coefficients (R^2) is also close to unity for pseudo-second order kinetic than the other tested kinetic models. Therefore, the adsorption can be approximated more appropriately by pseudo second order kinetic model (Sumanjit *et al.*, (2012).

The values of constants α (initial adsorption rate) and β (desorption constant) are recorded in Table 1. In the adsorption process, adsorption predominate desorption ($\alpha > \beta$). From the R^2 values it can be concluded that for the adsorption of AB dye onto CuO-Ps Elovich equation is not applicable.

From Intra particle diffusion plot, the line did not pass through the origin showing that intraparticle diffusion is not the only rate limiting step. The intercept of the plot C revealed the boundary layer effect for the adsorption (Nuengmatcha *et al.*, 2016). The value of C was high resulting in more surface adsorption of the dye. Therefore, both surface adsorption and intraparticle diffusion mechanisms were simultaneously operating in the adsorption behaviors using the CuO-Ps adsorbent.

3. 3. Effect of Initial Concentration

The effect of initial concentration of AB on the removal efficiency by CuO-Ps adsorbent for concentration of 10, 20, 30, 40, 50, 100, 150, 200, 250 mg/L was studied and respective result are shown in Fig. 2.

The optimum concentration for adsorption of AB onto CuO-Ps is 30 mg/L. As is shown, the removal percentage of AB dye was found to increase to a certain level (30 mg/L) then decreases at higher concentration, this may be attributed to lack of available active sites required for the high initial concentration of the dye (Abechi *et al.* 2011). The adsorption sites took up the available solute more quickly at low concentrations (Abechi *et al.* 2011).

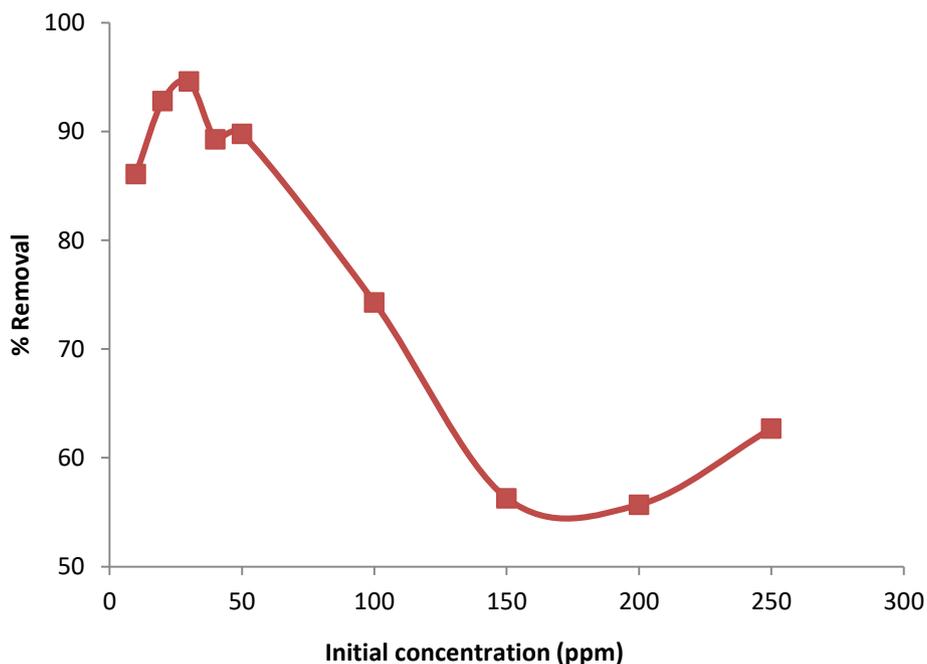


Fig. 2. Effect of Initial dye Concentration on the removal of AB.

3. 4. Adsorption Isotherm

The nature of the adsorption process is explained by the dimensionless parameter R_L which could be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or

irreversible ($R_L = 0$) (Erhayem *et al.*, 2015). From Table 2, the value of R_L of 0.055 which is less than 1, shows that the adsorption process is favourable (Ibrahim and Ibrahim, 2018; Sampranpiboon *et al.*, 2014). K_L (L/mg) is the Langmuir constant related to the affinity between an adsorbent and adsorbate (Tran *et al.*, 2016). The values of K_L for adsorption of AB onto CuO-Ps is high, indicating that the particle have high affinity to the dye. The R^2 value for the adsorption of AB is higher than that of other models tested, this shows that adsorption of AB onto CuO-Ps fits better with Langmuir isotherm.

It was reported that the Freundlich isotherm constant can be used to explore the favourability of adsorption process. The adsorption process is said to be favourable when the value of n_F satisfies the condition $1 < n_F < 10$, otherwise it is unfavourable (Ibrahim and Ibrahim, 2018; Ibrahim and Sani, 2014). The values of n_f for AB is within the range $1 < n_f < 10$, indicating favourable physical adsorption. In Temkin isotherm, the value of A_T 1.225 for AB shows that AB has good adsorption potential or binding potential to the particles (Kalalagh *et al.*, 2011).

The Temkin heat of adsorption B_T values of 6.249 J/mol for AB being less than 80 kJ/mol indicates a favourable physical adsorption as described by Inglezakis and Zorpas (2012). From D-R isotherm results, the magnitude of E is used for estimating the type of adsorption mechanism. If the magnitude of E is between 8 and 16 kJ/mol, it is indicated that the adsorption process is chemical adsorption, while for value of $E < 8$ kJ/mol; the adsorption process is physical in nature (El-Araby *et al.*, 2017). The values of mean square energy E of 0.707 kJ/mol for AB being < 8 kJ/mol further indicate a successful physical adsorption.

Table 2. Adsorption Isotherms parameters for adsorption of AB on CuO-Ps

Langmuir		Freundlich		Temkin		D – R	
$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$		$\log q_e = \log K_f + \frac{1}{n_f} \log C_e$		$q_e = B_T \ln A_T + B_T \ln C_e$		$\ln q_e = \ln(X_m) - \beta \epsilon^2$	
K_L (L mg ⁻¹)	0.0686	n_f	2.116	A_T (L/mg)	1.255	X_M (mg/g)	21.12
R_L	0.055	k_f (mg/g)	3.8150	b_T	396.5	E (J/mol)	707
Q_M (mg/g)	34.36	R^2	0.8635	B_T (J/mol)	6.249	R^2	0.798
R^2	0.884			R^2	0.870		

3. 5. Effect of pH

The initial pH value of the solution is one of the most important factors influencing dye adsorption. This is because the pH value determines the number of hydrogen ions capable of competing with the positively charged dye ions for the active sites on the adsorbent. In this

research the pH of the dyes was varied from 2 to 12. The initial pH of the dye was measured and adsorption was carried out for the initial pH value. Initial pH of AB dye measured was found to be 5.30.

Effect of pH on the removal of AB is shown in Fig 3. It was observed that increase in pH (from 2 to 5.30) causes the adsorption to increase from 90.1 to 94.6%, and then decreases to 83.7 in the pH 12. The decrease in removal later observed is probably because of the accumulation of the dye cations in the interfacial region causes the development of a positive charge, which inhibit further adsorption of the dye.

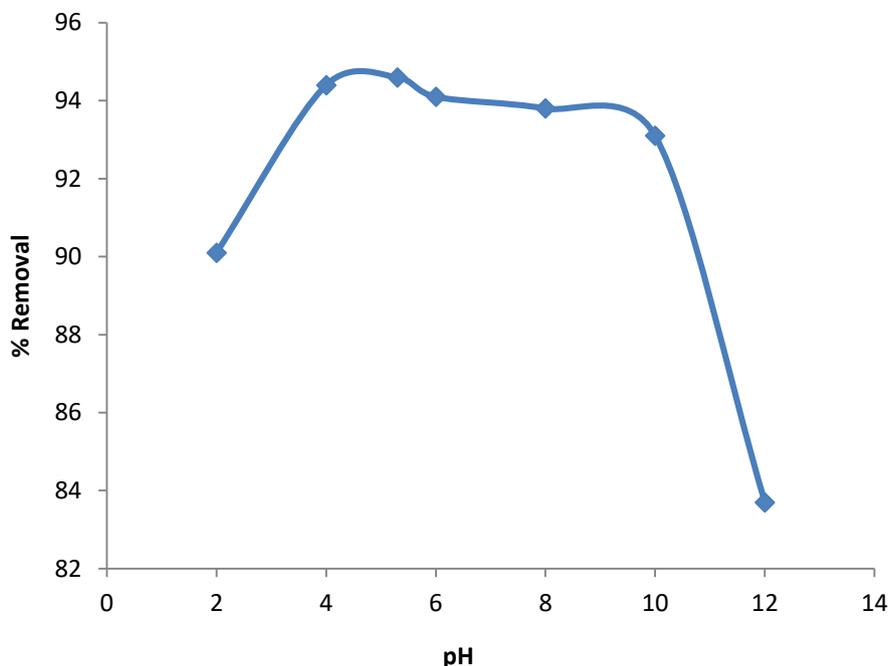


Fig. 3. Effect of pH on the removal of AB.

3. 6. Fourier Transform-Infrared (FT-IR) Characterization

The type of functional groups bonded to the CuO-Ps surface are important in understanding the mechanism of adsorption of ionic adsorbates onto the substrate (Patnukao *et al.* 2008). FT-IR spectra of CuO-Ps and after adsorption with Alkali Blue was taken and compared with that of CuO-Ps before adsorption to obtain information on the nature of the possible adsorbent-adsorbate interactions. The spectra of the samples showed the presence of several functional groups such as -OH, C≡C, C=C and C-H.

The functional groups could act as chemical of binding agents where hydroxyl group dissociate negatively charged active surface (Ibrahim and Ibrahim, 2018). The FT-IR summary from the spectra of the CuO-Ps both before and after adsorption with AB is shown in Table 3. They demonstrated that after the adsorption, shifting occurs both to higher and lower wave numbers. This shifting indicated that there were binding processes taking place on the surface of the substrate (Stuart, 2004).

Table 3. FT-IR results of CuO-Ps both before and after adsorption with AB.

Peaks	$\bar{\nu}$ (cm ⁻¹)		Functional Group Assignment
	Before Adsorption	After Adsorption with AB	
1	3420	3413 (-7)	Bonded -OH
2	2880	2925 (+45)	Aliphatic C-H group
3	2199	2177 (-22)	C≡C group
4	1599	1581 (-18)	C=C stretching
5	1350	1343 (-7)	-OH bending
6	1097	1033 (-64)	C-O stretching

NB: Values in parenthesis shows the changes in the wavenumber (cm⁻¹) after the respective dye adsorption.

4. CONCLUSIONS

In this research, copper (II) oxide particle has been synthesized and used as an effective adsorbent for the removal of AB dye from aqueous solutions. The effects of variables, such as initial dye concentration, contact time and pH were studied. Isotherm modeling revealed that the Langmuir equation described the adsorption of AB.

The adsorption process fit successfully to pseudo-second-order kinetic model.

The values of mean free energy indicate that the adsorption process to be physical in nature. The band in the FTIR spectra of the adsorbent after adsorption shifted at the peaks indicating the possibilities of the functional groups to be involved in the adsorption process.

In view of these results, it can be concluded that synthesized CuO-P can be utilized as a low-cost and effective adsorbents in the removal of AB from aqueous solutions.

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