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Original Research Article

KINETIC STUDIES OF MALACHITE GREEN ADSORPTION ON COPPER (II) COMPLEX

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ABSTRACT

The adsorption process of malachite green on Cu (II) -2-aminothiozole complex was investigated at different pH, contact time, initial concentration of malachite green and amount of the Cu (II) complex. The adsorption and kinetic parameters were obtained and tested for different adsorption models and kinetics models by regression analysis method. The results indicated that the data best fit with Freundlich adsorption isotherm and follows pseudo second order kinetics.

KEYWORDS: Adsorption, Malachite Green, Cu (II) Complex, Kinetics, Thermodynamic

Malachite green is an important industrial synthetic dye. Malachite green is widely used dye in leather and textiles industry and also in aquaculture industry to control fish parasite and diseases. It is also used in the food industry and as a bactericide, fungicide and disinfectant. Malachite green is classified as a class II health hazard and they produce toxicity to the aquatic organism like fish, algae, bacteria etc. Its proved to be highly carcinogenic and is banned by many countries. Some conventional methods such as membrane process, ion-exchange, chemical precipitation, electrochemical techniques reverse osmosis, coagulation, ultra-filtration, photooxidation have been used for removal of dyes from wastewater. Most of these methods are expensive due to their high capital and operational costs. The adsorption method has become the most used methods due to its simplicity and cost. The different adsorbents used include copper ferrite nanoparticles alumina and seeds dates etc. The studies on transition metal compounds such as Fe (III) coordinated amino functionalised silica mesoporous silica, Pd-coordinated etc have been investigated but the coordination compounds of Cu (II) have not been studied as yet (Santhi and Manonmani, 2009) (Gurses *et al.*, 2006) (Vijayaraghavan *et al.*, 2006) (Kumar, 2007) (Tewari *et al.*, 2005) (Aazza *et al.*, 2017) (Srivastava *et al.*, 2019).

In the present study Cu (II) complex has been used as a new low cost adsorbents for removal of malachite green from industrial wastewater

MATERIALS AND METHODS

Preparation of Cu (II) -2- aminothiozole Complex

The adsorbent complex Cu L₂ where L is 2-aminothiazole was prepared by the reported method (Srivastava and Srivastava, 1994) (Srivastava *et al.*, 2014). The Methanolic solution of 0.05g of Cu (II) acetate was refluxed with 0.5g of 2- Aminothiozole for

about one hour. The crystalline compound separated out on cooling was filtered, washed with methanol and ether and dried in vacuuo. The salt of malachite green was used as it was purchased by labachemic India. The stock solution of the dye was prepared by dissolving 1g of dye in 1L deionized water. The stock solution were diluted to get the different experimental solution.

Methods

(100g – 500g) of copper (II) complex was equilibrated with 50 ml of malachite green solution of known concentration. The effect of defferent parameters, such as amount of Cu (II) complex, dye concentrations etc. was studied. The initial pH values of the solutions were previously adjusted with HCl (0.1 M) or NaOH (0.1 M) using Labman Digital pH Meter (LMPH10). The optimum conditions for maximum dye removal from aqueous solution were determined.

The amounts of adsorbed dye at equilibrium (q_e) and the adsorption percentage of dye were calculated from equations 1 and 2 respectively.

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Where C_i and C_e Cu(II) are the initial and equilibrium concentrations of dye, respectively; q_e Cu(II) is the equilibrium dye concentration on adsorbent; V (L) is the volume of dye solution and W (g) is the mass of dry adsorbent used.

RESULTS AND DISCUSSION

Effect of Initial pH

The initial pH of an aqueous solution may affect the degree of ionization of the malachite green as well as the surface charge of the malachite green. pH has been related with changes in the structural stability and color intensity of the dye molecule. A 50 ml solution containing 100 mg Cu (II) complex and 5 mg/L of dye solution at 10°C was equilibrated for two hours at different pH. The removal of dye by Cu (II) complex was studied over a range of pH 2–12 and shown in figure 1. The equilibrium dye adsorption capacity indicated that up to pH 7.0, the adsorption capacity increases with increasing pH. The further increase in dye adsorption between pH 7.0 and 12.0 was insignificant. As the maximum pH for dye adsorption by Cu (II) complex was found to be 7.0, this pH was used for further studies.

The minimum removal of dye was thus found at around pH 2, which is attributed to the H⁺ ions competing favorably with the cationic groups of the dye molecule for adsorption sites on Cu (II) complex.

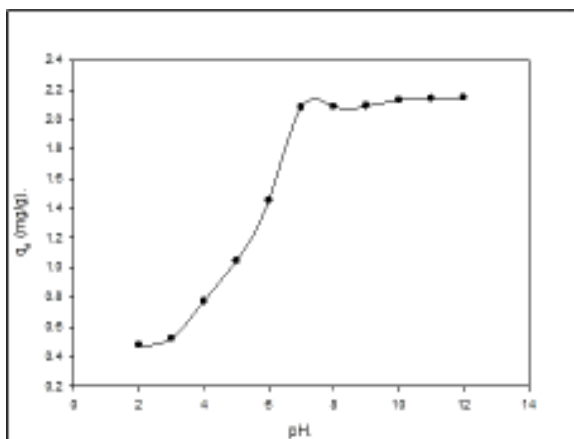


Figure 1: Effect of pH on adsorption of dye

Effect of Amount of Cu (II) Complex

Fig. 2A represents the percentage adsorption of dyes by increasing the amount of Cu (II) complex. The variation is 94% to 97% by increasing the amount of copper (II) complex from 100 mg to 500 mg at pH 7. Obviously, it may be attributed to the increase in surface area of the adsorbent under the given experimental condition and which in turn increases the binding site. However, the adsorption per unit gram of adsorbent is observed to reduce with increasing amount of Cu (II) complex as shown in Fig. 2(B) which decreases from 2.40 to 0.4 per gram adsorbent.

Several factors may be responsible for this effect such as availability of solute, electrostatic interactions and interference between binding sites.

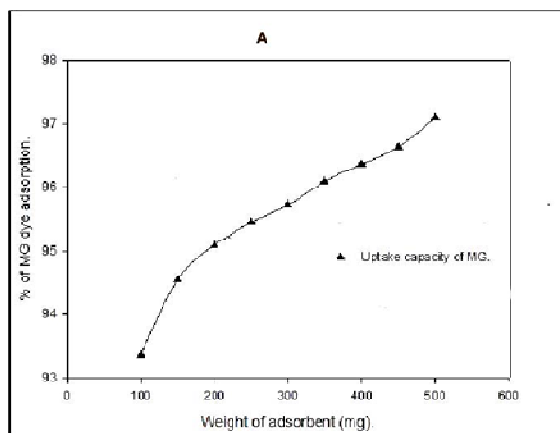


Figure 2A: Effect of amount of adsorbent on adsorption of adsorbate

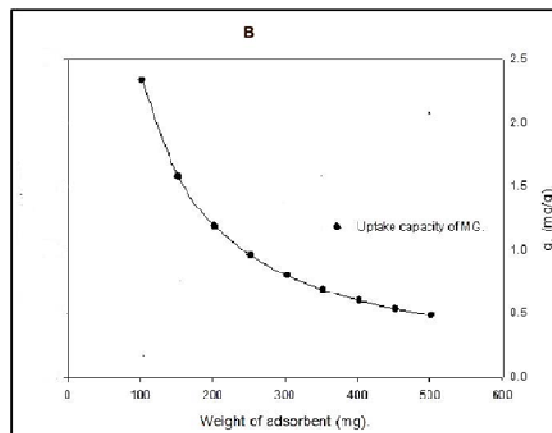


Figure 2B: Effect of amount of adsorbent on adsorption of adsorbate

Effect of Temperature

The effect of temperature on the adsorption capacity of dye was studied at 10, 20, 30, 40, and 50°C and the results were shown in Table 1. The results show that the adsorption capacity decreased with temperature increase from 10°C to 50°C. The equilibrium adsorption of the dye decreased with increasing temperature suggesting that adsorption of dye by Cu (II) complex was an exothermic process following the mechanism of physical adsorption at low temperature.

Table 1: Effect of Temperature

Temperature in °C	10	20	30	40	50
q _e (mg g ⁻¹)	2.25	2.10	2.05	2.0	1.9

Effect of Contact Time

The Plot shown in fig 3 indicates that the maximum adsorption capacity reaches in 180 min where the equilibrium is attained. However, the initial adsorption process was quite rapid and it was not much significant after a certain time.

Effect of Initial Dye Concentration

Adsorption of dye onto Cu (II) complex was measured at the equilibrium time for six different initial concentrations of dye solution at adsorbent amount of 500mg. The percentage of adsorption of dye adsorbed at equilibrium increases from 95 to 98% for an increase in initial dye concentration from 5 to 30 mg L⁻¹. Where a higher initial dye concentration provides to overcome all resistances of the dye between the aqueous and solid phases, On the other hand, the percentage adsorption shows a decreasing trend as the initial concentration of the dye is increased. Under those condition that is ions present in the adsorption medium interact with the binding sites. At higher concentrations, because of the saturation of the adsorption sites, the percentage adsorption of the dye by Cu (II) complex shows a decreasing trend.

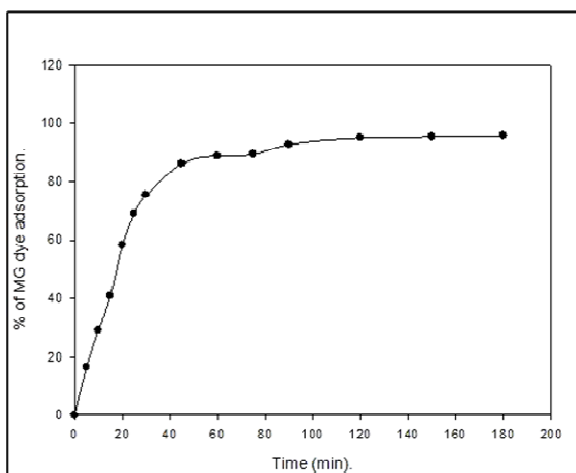


Figure 3: Effect of time on adsorption of dye

Adsorption Isotherms

The amount of dye adsorbed per unit gram of Cu (II) complex was determined as shown in Eq. (1). Langmuir & Freundlich adsorption isotherms were used for the evaluation of adsorption data. Langmuir adsorption isotherm assumes monolayer adsorption, which is presented by the equation:

$$q_e = \frac{q_{max} b C_e}{(1 + b C_e)} \tag{3}$$

where q_e and q_{max} are the equilibrium and maximum dye adsorption capacities, respectively; C_e the equilibrium dye concentration and b the Langmuir

equilibrium constant.

The Freundlich model is presented as:

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F and n are the Freundlich constants which is characteristic of the system.

Langmuir-Freundlich model is presented as:

$$q_e = \frac{q_{max} C_e^\beta}{K + C_e^\beta} \tag{5}$$

Where K is the saturation constant, β is the cooperative binding constant.

The adsorption isotherms for dye on Cu (II) complex at different temperatures are presented in Figure 4.

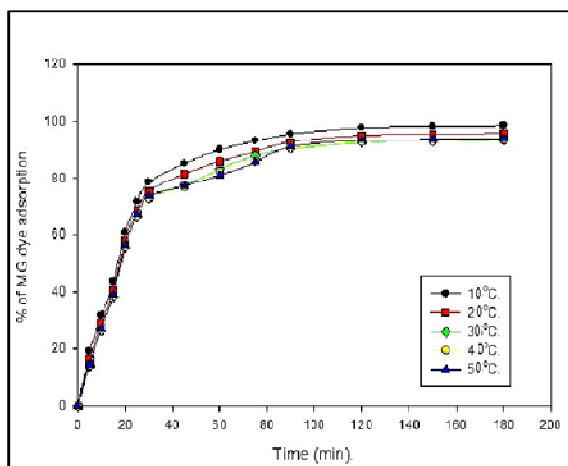


Figure 4: Effect of initial concentration on adsorption of adsorbate

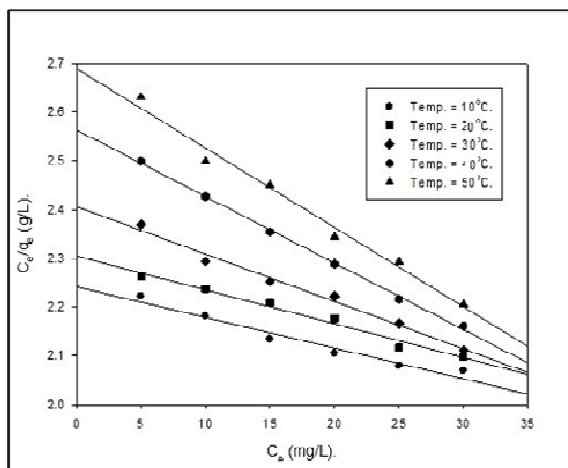


Figure 5: Langmuir adsorption isotherm for dye at different temperature

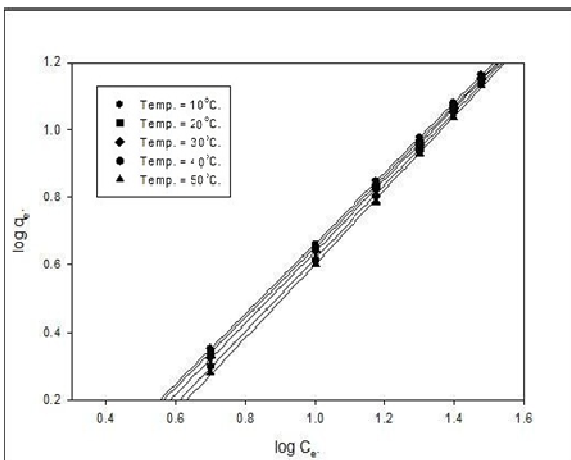


Figure 6: Freundlich adsorption isotherm for dye at different temperature

A plot of C_e/q_e versus C_e (eqn.-3) at different

Table 2: Langmuir and Freundlich Adsorption Isotherm at different temperature

Parameters	Temperature (°C)				
	10	20	30	40	50
Langmuir					
q_{max} (mg g ⁻¹).	158.98	143.88	102.71	73.15	61.31
B (L mg ⁻¹).	0.0061	0.0053	0.0040	0.0030	0.0028
R ² .	0.9594	0.9792	0.9862	0.9984	0.9847
Freundlich					
n.	0.9597	0.9588	0.9434	0.9251	0.9141
K_f (mg L ⁻¹ⁿ g ⁻¹ L ¹ⁿ).	0.4189	0.4084	0.3805	0.3464	0.3231
R ² .	0.9999	0.9998	0.9998	0.9996	0.9996

Thermodynamic Parameters of Adsorption

From table 3 its clear that ΔG° values of 13825.821, 14138.771, 13880.155, 13620.662 & 13710.478 mol⁻¹ were obtained at 10, 20, 30, 40 and 50°C, respectively. The fig 7 represent plot of $\log b$ us $1/T$. The value of ΔH° and ΔS were determined from the

temperature on the basis of Langmuir adsorption isotherm from the measurement of data is shown in figure 5. The graph is plotted in linearized form and value of q_m and langmuir constant b were evaluated and recorded in Table 2.

Both K_f and n were calculated by plotting $\log q_e$ versus $\log C_e$ (Freundlich adsorption isotherm ; eqn- 4) at different temperature (Figure 6) and the values were recorded in Table 2.

The linear regression analysis was carried out and the correlation coefficient R^2 for both the models were also mentioned in the table 2. It was evident that the R^2 values approximately 0.9999 in case of Freundlich adsorption isotherm model showed that it is the best fit model.

plot and found to be -0.001989 J/ mole and -48.845 J/ degree/ mole respertively. The negative entropy value led as to conclude that the disorder at solid/ liquid interface decreasing during the adsorption process while the negative inthalpy is indicative of exothermic adsorption process. i e, the adsorption sites are activated by decrease in temperature.

Table 3: Thermodynamic parameters of adsorption

T (K)	b (L m g ⁻¹)	ln b	ΔG° (J mol ⁻¹)	ΔH° (J mol ⁻¹)	ΔS° (J deg ⁻¹ mol ⁻¹)
283	2.8055 x 10 ⁻³	-5.879	13825.821	-0.001989	-48.8545
293	3.0152 x 10 ⁻³	-5.8068	54138.771		-48.2552
303	4.0466 x 10 ⁻³	-5.5125	13880.155		-45.8091
313	5.3315 x 10 ⁻³	-5.2552	13620.662		-43.5165
323	6.0632 x 10 ⁻³	-5.0765	13710.478		-42.4473

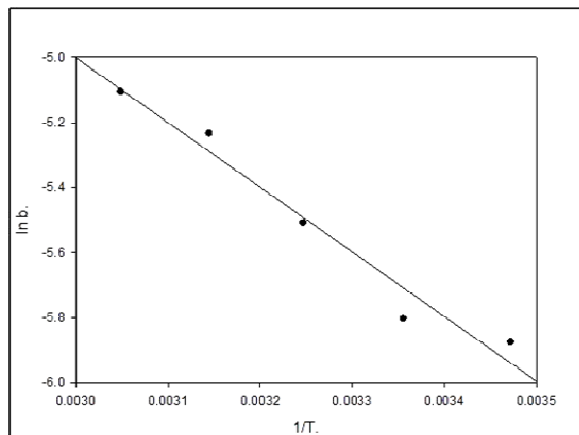


Figure 7: Adsorption for dye on adsorbent at different temperatures

Adsorption Kinetics Studies

Kinetics of dye adsorption governs the rate that determines the residence time and it is one of the important characteristics defining the efficiency of an adsorbent. The kinetic profiles of dye adsorption onto the Cu (II) complex were described in this section.

Kinetics of Adsorption Process

In order to investigate the kinetics of adsorption processes for adsorption of dye on Cu (II) complex, the data obtained from experiments were simulated using pseudo first and second order kinetic models.

The pseudo-first-order rate equation of Lagergren is presented as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

Where k_1 (min^{-1}) is the pseudo-first-order reaction rate constant. The pseudo-first-order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites. A straight line of $\ln(q_e - q_t)$ versus t indicates the application of pseudo-first-order kinetics model. In a true pseudo-first-order process, $\ln q_e$ should be equal to the intercept of a plot of $\ln(q_e - q_t)$ against t .

The pseudo-second-order equation, another equation used for kinetics analysis, which is based on the sorption equilibrium capacity, may be expressed in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where k_2 is the pseudo-second-order rate equilibrium constant ($\text{g mg}^{-1} \text{min}^{-1}$). A plot of t/q_t against t should give a linear relationship for the applicability of the pseudo-second-order kinetics model.

The principle behind the adsorption kinetics involves the search for a best model that well represents the experimental data. The experimental data were used to draw the pseudo first order and second order plot for different dye concentration i.e. 5mg/L, 10mg/L, 15mg/L, 20mg/L, 25mg/L, 30mg/L .and presented in figure 8 and 9 respectively.

The rate constant of adsorption is determined. The value of q_e determined experimentally $q_{e(\text{exp})}$, calculated $q_{e(\text{cal})}$, correlation coefficient together with the adsorption rates k_1 and k_2 are shown in Table 4. The correlation coefficients for the first order kinetic model were determined and compared with that of second order kinetic model. It is seen that the correlation coefficient of first order kinetic are lower than in the case of second order kinetic model (Table 4). This shows that kinetics of MG dye adsorption by Cu (II) complex are better described by pseudo- second order kinetic model rather than pseudo-first order. Also, $q_{e(\text{cal})}$ using pseudo-second order kinetic model is in par with $q_{e(\text{exp})}$ which has been obtained experimentally

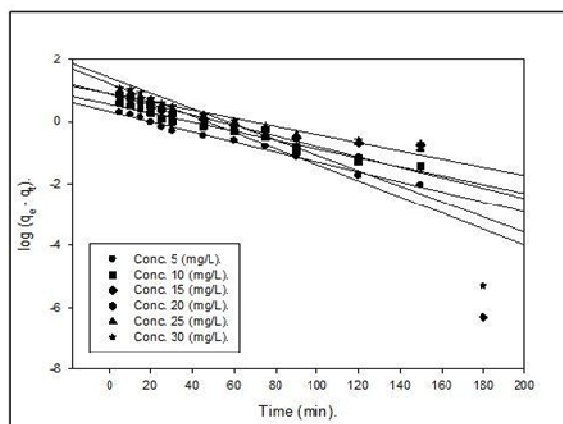


Figure 8: pseudo-first order for different initial concentrations of dye

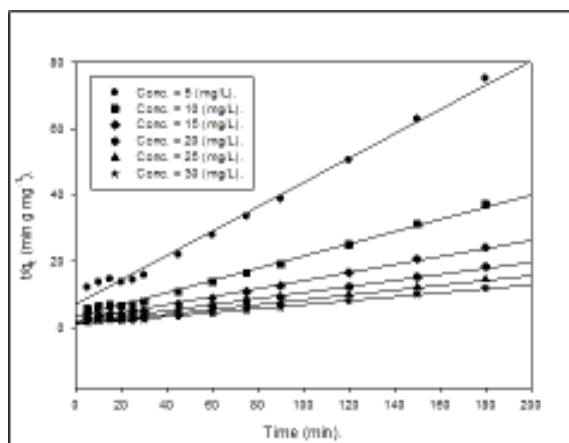


Figure 9: pseudo-second order for different initial concentrations of dye

Table 4: First order & second order kinetic data

Initial concentration (mg/L)	q _e (exp) (mg/g)	Pseudo-first order rate constants				Pseudo-second order rate constants			
		k ₁ (min ⁻¹)	q _e (cal) (mg/g)	R ²	ε (%)	k ₂ (g/mg min)	q _e (cal) (mg/g)	R ²	ε (%)
5	2.3932	0.01617	2.2629	0.9892	5.4450	0.3664	2.3781	0.9915	0.6303
10	4.8364	0.01436	4.4716	0.9760	7.5418	0.1836	4.8063	0.9931	0.6225
15	7.4045	0.0114	6.4532	0.9259	12.8472	0.1209	7.3589	0.9929	0.6161
20	9.7727	0.01682	9.2994	0.9668	4.8426	0.0912	9.7122	0.9930	0.6194
25	12.3409	0.01310	11.1733	0.9561	9.4608	0.0728	12.2650	0.9940	0.6147
30	14.9591	0.01323	13.5766	0.9182	9.2421	0.0597	14.8668	0.9914	0.6171

CONCLUSION

The present study indicated that Cu (II) - 2 - aminothiazole complex may be used as a effective adsorbent for rapid adsorption of malachite green from its neutral aqueous solution.

The adsorption process follows pseudo-second-order adsorption kinetics and thermodynamic parameters indicated that it is an exothermic process and follows Freundlich adsorption isotherm.

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