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Cationic Surfactant Assisted synthesized Copper(II)oxide Nano particles for the Removal of Anionic dyes-Adsorption Isotherms and Kinetics

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ABSTRACT

CTAB assisted synthesized copper(II) oxide nano particles have been successfully used as adsorbent for the removal of anionic dye (Congo red) from aqueous solutions. Batch adsorption studies were conducted using spectrophotometer at the maximum wave length of the dye (500 nm). Langmuir adsorption isotherms are calculated. Results confirm the pseudo second order kinetics. Thermodynamic parameters reveal the spontaneity and exothermic nature of the reaction.

High lights

- CuO-CTAB nano particles are proved to be best adsorbents for the adsorption process.
- The anionic dyes (Congo red) can be best removed from aqueous solutions by using adsorption technique.
- At the optimum conditions of the adsorbate and adsorbent the isotherms, kinetics and thermodynamic parameters are calculated.

Keywords: Surfactant CTAB, CuO nano particles, Adsorption, Congo red.

INTRODUCTION

Dyes are used in large quantities in many industries including textiles, leather, cosmetics, paper, printing, plastic, pharmaceuticals and food etc. to colour their products, which generates waste waters. The textile industry alone can account for the one third of the total dye stuff production [**1, 2**]. It is necessary to eliminate dyes from waste water before it is discharged as these dyes are also toxic and even carcinogenic. In recent years adsorption techniques has become more popular for waste water treatment in the removal of pollutants. Adsorption is influenced by many factors such as dye/ adsorbent interaction, adsorbent's surface area, particles size, temperature, pH and contact time.

Copper oxide nanoparticles are of technological interest due to their physical and chemical properties, and can be applied in high temperatures supper conductors, catalysis, batteries, gas sensors, solar energy conversion.

Surfactants can act as shape directing agents [**3, 4**]. Surfactants involved in the synthesis process can control the shape and size of resulting CuO nanoparticles at room temperature. The introduction of cetyltrimethyl ammonium bromide (CTAB) as cationic surfactant can control the growth rate of various faces of CuO nanoparticles. The electrostatic interaction takes place between CTA^+ cationic and $Cu(OH)_6^4-$anionic. The cationic CTA^+ condense in to aggregates in which counter ions $Cu(OH)_6^4-$are interrelated in the interfaces between the 6 head group to form CTA^+ - $Cu(OH)_6^4-$pair. The present work explains the batch adsorption studies, adsorption isotherm and kinetics with respect to the anionic dye Congo red with CuO-CTAB nanoparticles as adsorbent and the results are discussed in detail.

MATERIALS AND METHODS

All the chemicals used were of analytical grade and the stock solutions were prepared from deionized Millipore water.

Preparation of stock solution of Congo red: The 1000 ppm (1000 mg L^{-1}) stock solution of dye was prepared by dissolving 1.0 g of Congo red in 1L of deionised water. Required initial concentration of the dye was prepared by diluting the stock solution in accurate proportion. The concentration of Congo red dye was monitored before and after the adsorption using UV Visible spectrophotometer of Perkin Elmer Make.

Synthesis of CuO-CTAB nano particles: The CuO-CTAB nano particles were prepared using wet chemical synthesis method [5]. The black colored CuO-CTAB nano particles were obtained was stored in air tight container until further use.

Method: Batch adsorption studies were conducted using CuO-CTAB nano particles for the removal of anionic dye Congo red at corresponding λ_{max} of 500 nm. Studies were performed at various initial pH equilibrium, time and adsorbate/adsorbent concentrations. Kinetic studies and isotherms adsorption models are performed for the better understanding of the adsorption mechanism.0.1N HCl and 0.1N NaOH solutions were used for the pH adjustments. The extent of removal of dye has been calculated by using the following equations.

$$\text{Amount adsorbed (q)} = \frac{X}{m} = \frac{(Co - Ce)}{m}$$

$$\text{Percentage (\%) removal} = \frac{(Co - C)}{Co} X\ 100$$

Where, C_O and Ce are initial and equilibrium concentrations of the dye before and after the adsorption.

RESULTS AND DISCUSSION

Effect of pH: pH of dye solution plays a crucial role in the whole adsorption process [6]. It affects the surface charge of the adsorbent, the adsorbed material degree of ionization, and the dissociation of

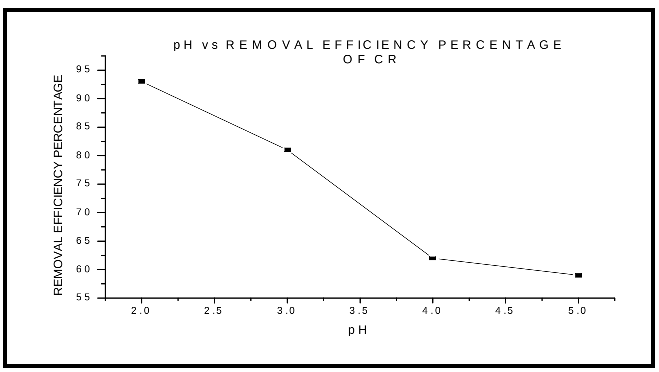

Figure 1. Effect of pH on the adsorption of Congo red (20 mg L^{-1}) by CuO-CTAB nano particles (300 mg) at 300K.

active group on the figure 1 reveals the effect of pH on the adsorption of Congo red dye on to CuO-CTAB nano particles. According to figure 1 acidic pH was favorable for the adsorption is due to the electrostatic attraction between Congo red dye and CuO-CTAB nano particles. Hence pH 2 is favorable for adsorption of Congo red dye.

Effect of Dye Concentration: To explore the adsorption capacity of CuO - CTAB nano particles for Congo red a fixed amount of nano particles (0.5 mg) was agitated with different concentrations of dye solutions (10, 20, 30 and 40 mg L^{-1}). Figure 2 shows the effect of Congo red and can be seen that with the increase in the initial concentration , the removal efficiency of dye decrease with increase in dye concentration, dye removal efficiency decreased because fixed amount of adsorbent has limited capacity and active sites[7, 8].

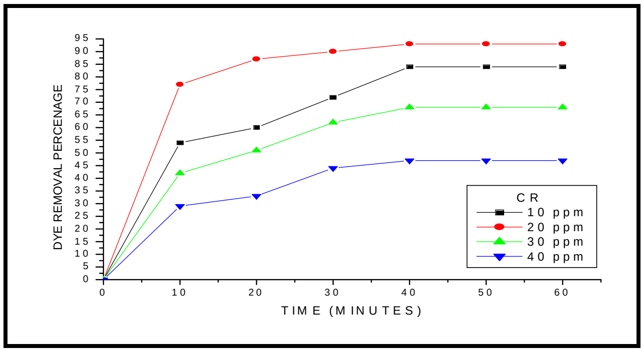

Figure 2. Effect of dye concentration on the adsorption of Congo red by CuO-CTAB nano particles (300 mg) at 300K.

Effect of contact time: Figure 2 represents the changes of dye removal (%) in different contact time vs the adsorbent dosage. It can be seen that the studied conditions have strong effect on the kinetic of the dye adsorption. Since the equilibrium time for Congo red was obtained at 40 min for adsorption using CuO-CTAB nanoparticles.

Adsorption Isotherm: To optimize the design of an adsorption system for dye removal, various isotherm equations such as Langmuir and Freundlich have been used to describe the equilibrium characteristic of adsorption. Langmuir theory assumes that the specific homogenous sites within the adsorbent are responsible for the sorption. The Langmuir isotherm is represented using linear equation

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$$

Where, q_e, C_e, K_L and Q_o are the amount of adsorbed dye on the adsorbent at equilibrium (mg g^{-1}), the equilibrium concentration of the dye solution (mg L^{-1}), Langmuir constant(L g^{-1}) and maximum adsorption capacity (mg g^{-1}) respectively. A dimension less constant called the equilibrium parameters R_L can be used to describe essential characteristic of the Langmuir isotherm determined using the equation. $R_L = \frac{1}{(1+K_L C_0)}$ Where C_o is the highest initial dye concentration and K_L is Langmuir Constant. The nature of the adsorption process could be either unfavorable (R_L>1), Linear (R_L=1) Favorable (O<R_L<1) [9]. The Langmuir plot is shown in figure3. According to table 1 adsorption isotherm data fitted well to the Langmuir isotherm with coefficient correlation of 0.996 for Congo red with R_L values between 0 and 1.

Adsorption kinetics: In order to investigate the adsorption mechanism pseudo first order, pseudo second order and intra particle diffusion equations are followed. The linear form of pseudo second order model is given by

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

Where, k_2 is the equilibrium rate constant of pseudo second order (g mg min^{-1}) [10].

Table1. Values of Freundlich and Langmuir adsorption isotherms for the adsorption of Congo red (20 mg L^{-1}) by CuO-CTAB nano particles (300 mg) at 300K.

Lagmuir Isotherm	Values	Freundlich Isotherm	Values
Qmax calculated (mg g^{-1})	6.5	n	0.56
K_L (L mg^{-1})	1.061	K_F (L mg^{-1})	0.244
R^2	0.991	R^2	0.925
Qobs (from exp)(mg g^{-1})	6.2	--	--

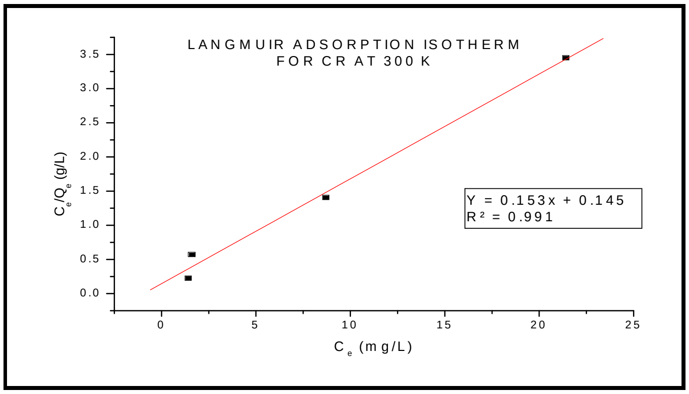

Figure 3. Langmuir adsorption isotherms of Congo red (20 mg L^{-1}) by CuO-CTAB nano particles (300 mg) at 300K.

According to table 2 pseudo second order kinetic model with higher correlation coefficient and closer experimental, q_e calculated fitted well with experimental data. Linear relationship presented in between t/ q_t and contact time (t). Figure 4 confirms the pseudo order kinetic model.

Table 2. Pseudo second order kinetic model for the adsorption of Congo red (20 mg L^{-1}) by CuO-CTAB nano particles (300 mg) at 300K.

Pseudo Second Order	Congo Red
Q cal (mg g^{-1})	6.5
Qobs ((mgg^{-1})	6.2
k_2 (g mg min^{-1})	0.0626
R^2	0.999

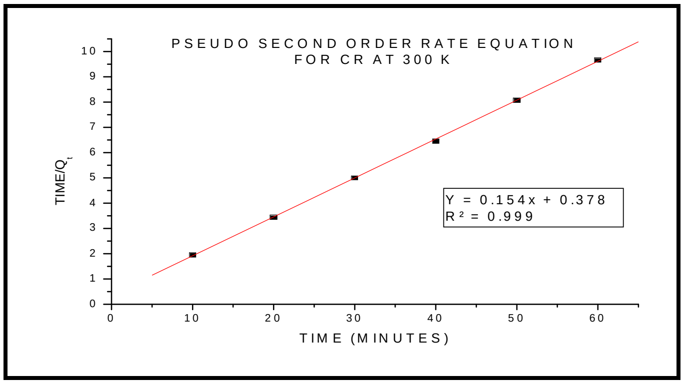

Figure 4. Pseudo second order kinetic model for the adsorption of Congo red (20 mgL^{-1}) by CuO-CTAB nano particles (300 mg) at 300K.

Thermodynamic parameters: The effect of temperature on adsorption of Congo red by CuO-CTAB can be explained on the basics of thermodynamic parameters such as change in Gibb's free energy (ΔG^o), Enthalpy (ΔH^o) and entropy (ΔS^o). Thermodynamic parameters are expressed by following equations.

$$K_e = \frac{C_{adsorbate}}{C_{Adsorbent}}$$

$$\Delta G^o = -RT \ln K_e$$

$$\ln Kc = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

Where, K_e is the equilibrium constant at temperature T, R is universal gas constant and C adsorbate, C adsorbent are equilibrium concentration of adsorbate on the adsorbent solution respectively [11]. The value of thermodynamic parameters is given in table 3 (Figure 5). The negative value of ΔG^o confirms the exothermic nature of the process.

Table 3. Thermodynamic parameters for the adsorption of Congo red (20 ppm) by CuO-CTAB nano particles (300 mg) at 300K

Thermodynamic parameters	Congo red
ΔH (kJ mol^{-1})	-27.43
ΔS(k joule/K)	-0.00144
ΔG (kJ mol^{-1})	-26.998

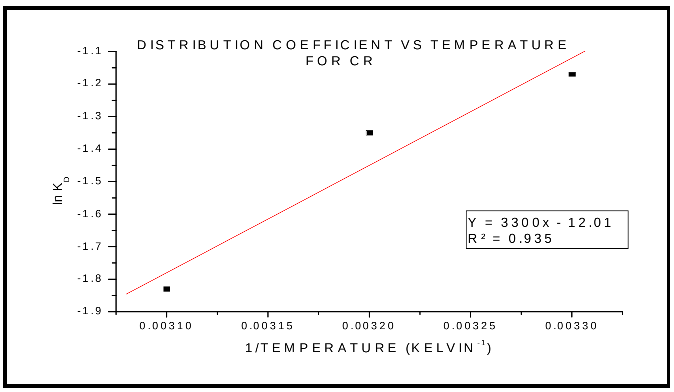

Figure 5. Calculation of thermodynamic parameters for the adsorption of Congo red (20 ppm) by CuO-CTAB nano particles (300 mg) at 300K.

The negative value of ΔS^o corresponds to decrease in degree of freedom of the adsorbed species owing to association, fixation or immobilization and suggests no significant change in the interval structure of CuO-CTAB during the adsorption of the dye.

APPLICATION

Cationic assisted synthesized nano particles (CuO-CTAB) are best applied for the removal of anionic dyes from aqueous solutions. As the surfactants can enhance the surface morphology of the adsorbent the adsorption technique is extended for other anionic dyes.

CONCLUSION

In this study low cost environmentally friendly, adsorption capacity CuO-CTAB nano particles are used as adsorbents for the removal of dye from aqueous solutions by adsorption process with a removal efficiency of more than 90%. The removal efficiency is dependent on the initial concentration, pH and temperature of the solution. Based on this study, the optimum conditions for an effective removal of dyes adsorption on to surfactant assisted metal oxide nano particles can be tuned. Additionally, the adsorption thermodynamics analysis revealed that the process was spontaneous and fits the pseudo second-order kinetic model.

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