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Adsorption Evaluation of Food and Industrial Dyes on Nano copper oxide

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Abstract- In This applicable research, investigating absorption of process of Erythrosine dye on Copper oxide Nano particles Adsorbent was studied. First, prepared dye concentrations of 6, 8 and 12 mg L^{-1} and then effects of parameters such as concentrations of initial dye, time and pH on dye absorption efficiency were investigated.The dye concentrations in different samples were measured via spectrophotometer (505.6 nm for dye Erythrosine wavelength).

The results of absorption studies showed that Erythrosine absorption or removal rates would increase with decreasing the primary dye concentration, increasing reaction time , and decreasing pH on the basis of the results, copper oxide Nano particles can the absorb Erythrosine dye appropriately and efficiency of the process is higher in acidic pH for dye Erythrosine. The maximum dye removal of 93.68 % could be achieved at initial pH 2 using adsorbent dosage of 0.233gr in 50 ml (12 mg L^{-1} dye concentration) and agitation rate of 180 rpm. Effect of different parameters as kinetic parameters, were calculated pseudo-First and second-order kinetic, the Langmuir and Freundlich models Isotherm for absorb of this dye on adsorbent. this results showed that second-order kinetic adherence possessing regression coefficient of $R^2 \geq 0.999$, absorption or removal of Erythrosine on Copper oxide nano particles and different parameters for investigating of process rate of absorption in to be this experience. Equilibrium data fitted well with the Langmuir model for dye with adsorbent.

Keyword: CuO nano particles, Erythrosine dye, Absorption.

Introduction

Contamination of water resources to dye pollutants is considered as an environmental important problem. Due to toxicity and unpleasant appearance, discharging the dye pollutants into surface water resources is undesirable [1,2]. Another adverse effect of discharging dye wastewater into natural flows is prevention of light entrance to water body and it can have negative effects on aquatic plants photosynthetic activity. Moreover, dye wastewater can be increased COD of recipient waters [3]. General acceptance of water and aquatic solutions quality are mainly affected by its dye and dye is the first pollution recognized in wastewater [4]. Nowadays, more than 10000 types of dye are commercially available and are classified into anionic, cationic and non-ionic types used in manufactures process [5].

Textile and dying industries are two main sources of dye wastewater production and treatment of this wastewater are difficult due to synthetic and complex structure of dye [6,7]. Due to their molecular structure, dyes are resistant to light, heat, biological degradation [8]. The common methods have been used for dye removal from wastewater include biological methods (anaerobic treatment) and physicochemical methods such as coagulation, electrocoagulation, floating, filtration, ion exchange, membrane filtration and advanced oxidation [9-15]. However, many of these technologies are expensive, especially when their used for treatment of large wastewater streams. Consequently, adsorption methods using low cost adsorbents have the most potential for application in industrial wastewater treatment, because of their efficiency is proven in the removal of organic and mineral pollutants and economic considerations [16,17].

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and is bonded physically or chemically. The rate at which dye molecules are transferred to the adsorbent may be affected by the transport of dye through the bulk solution to the surface of the adsorbent, the possible adsorption of dye molecules onto this surface, and the diffusion of the dye from the surface to the interior of the adsorbent. Surface chemistry and the distribution of adsorption sites on the surface of the adsorbent play an important role in the adsorption process. Activated carbon is the most widely used adsorbent for dye molecules due to its high porosity for sorption of organic compounds, but its use is becoming limited because of high cost [18].

The objective of the present work is to investigate the adsorption characteristics of CuO Nano-particles for the removal of, Erythrosine dye from aqueous solution which is widely used in textile processing industries. Effects of pH, initial dye concentration and contact time on dye removal were studied. The adsorption data were evaluated using Langmuir and Freundlich isotherm and kinetic parameters for pseudo first-order and pseudo second-order models were determined. Also the adsorption process was confirmed via scanning electron microscopy (SEM) images.

Experimental Procedure

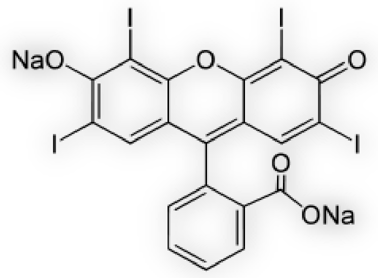
Adsorbent and dye

In this study, CuO Nano-particles adsorbent was used as adsorbent for Erythrosine dye removal from textile wastewater in laboratory scale. The specifications of Erythrosine dye are presented in Table 1. At first, stock solutions 500 mg L^{-1} was prepared from Erythrosine dye and in all steps of examination; desire concentrations were obtained from diluting stock solution. All experiments were carried out using jar apparatus with 200 ml beakers and the beakers were charged with ۵0 ml dye solution.

For synthesis Nano-coordination polymer $[Cu(C_4H_4O_4)$ (bipy) $(H_2O)_2].2H_2O$, First has set 10ml 0.1 M solution of Legend 4, 4′-bipy in Ultrasonic bath. So 10ml 0.1 M solution of Copper chloride salt slowly added and has set against Ultrasonic irradiation for1h. so solution was separated by a Hettich EBA20 centrifuge at 6000 rpm from sediment and was dried. The amount of nano coordination component $[Cu(C_4H_4O_4)$ (bipy) $(H_2O)_2].2H_2O$ The obtained were Sonochemical synthesis in oven at 415 °C for 4 h oven . CuO were obtained after the end of reaction, as calcinations component. Detected by use the images of scanning electron microscopy (SEM).

Molecular formula	$C_{20}H_6I_4Na_2O_5.H_2O$
λ max	505.6 nm
Molecular weight	879.87 g mol^{-1}

Table 1: Erythrosine dye specifications



Scheme 1 . Erythrosine structure

Other chemicals were all of analytical grade from Merck Chemical Company. Distilled deionized water was used for preparation of all solutions. pH adjustments were done using dilute hydrochloric acid and sodium hydroxide solutions. The pH measurements were made by a pH meter (Hach). The agitation process for mixed adsorbent and dye solutions was carried out using shaker (model-Orbital L).

Adsorption studies

Batch sorption equilibrium experiments were performed by adding 0.233 g of CuO nano particles to 50 ml dye solution with desired concentrations and pH at ambient temperature with the stirring rate of 180 rpm. After 15 min, the dye solution was separated from the adsorbent by a Hettich EBA20 centrifuge at 6000 rpm for 5 min. The amount of removed dye was determined by a CECIL 9200 spectrophotometer through monitoring the absorbance variations for all samples at 505.6 nm. The amount of Erythrosine adsorbed onto the CuO Nano-particles, q_e (mg g^{-1}), also known as adsorption capacity was computed using the following equation:

$$q_e = (C_0\ C_e)V / W \qquad (1)$$

Where C_0 and C_e are the initial and equilibrium concentrations of dye, respectively (mg L^{-1}), V is the volume of solution (L) and W is the weight of adsorbent (g). The effect of initial dye concentration, contact time and initial pH on adsorption capacity was studied. The percentage of removed dye in solution for each treatment can be calculated using eq. (2)

$$\text{Dye removal (\%)} = (A. - A/ A.) \times 100 \qquad (2)$$

Where A_0 is the initial dye absorbance and A represents the final absorbance of dye solution. Equilibrium and kinetic studies were performed under optimum experimental conditions.

2.3. Scanning Electron Microscopy studies

Scanning electron micrographs of Nano-copper oxide before and after adsorption process were captured by LEO 1455 VP scanning microscope. The experiment was done with

0.233 g of adsorbent for 50 ml of 12 mg L^{-1} dye solution at pH 2 within 90 min contact time. The stirring rate was fixed at 180 rpm and Separation procedure was the same.

Results and Discussion

Effect of contact time on dye removal in different concentrations

Recognizing equilibrium contact time is essential for absorption process design and rapid sorption is among desirable parameters. Results of effect of contact time on Erythrosine dye removal in different concentrations are shown in Fig. 1. Based on results, as contact time increases, the dye removal efficiency increases too. In initial minutes of experiment, dye was quickly removed and high quantity of dye concentrations were removed in few minutes and then the dye removal was increased constantly with increasing contact time up to reach to 95.44% in 90 min. According to results, 90 min was obtained as equilibrium contact time; at this time, due to saturation of absorption sites on absorbent, dye removal efficiency won't have any changes.

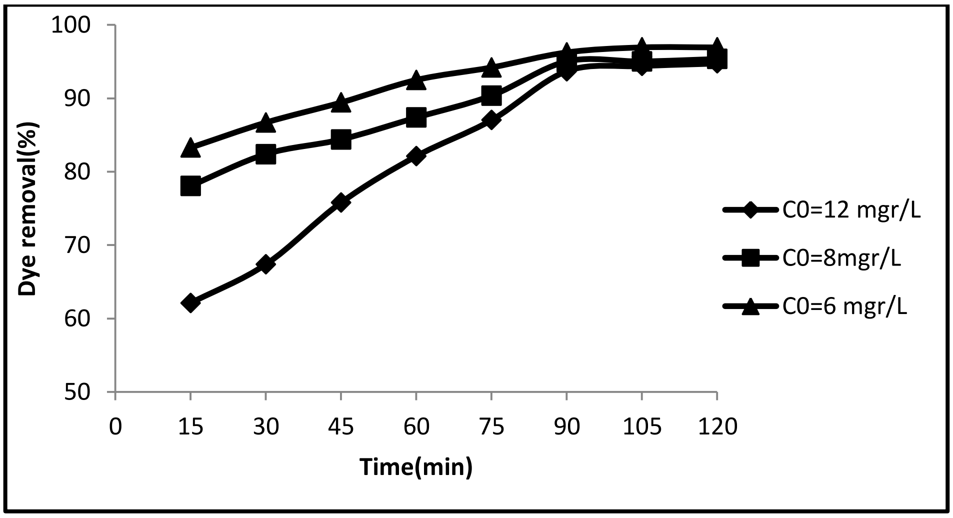


Figure 1. Effect of contact time for different dye concentrations on dye removal by Copper oxide nano particles; pH 2, 25 °C, agitation rate of 180 rpm and 0.233 g adsorbent in 50 ml of dye solution.

Effect of different concentrations on dye removal

The equilibrium condition was achieved within 90 min for 6, 8 and 12 mg L^{-1} dye concentrations. The effect of initial dye concentration on the ability of CuO Nano-particles to adsorb dyes from solution suggested that the percentage color removal of Erythrosine decreased when the initial dye concentration increased.

In batch absorption systems, available adsorbent initial concentration in solution plays an important role as a driving force which overcomes mass transfer resistance of adsorbate between Aqueous and solid phase. In the present study, the adsorption experiments are performed to study the effect of dye initial concentration by varying it from 6 to 12 mg L^{-1}, while maintaining the CuO Nano-particles amount 0.233 g and obtained results are presented in Fig. 2. The results showed that with increase of dye concentration from 6 to 12 mg L^{-1}, the removal efficiency decreases from 95.44 % to 93.68%. The decrease in removal efficiency can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. The increase in adsorption capacity with increase in dye concentration may be due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher concentration.

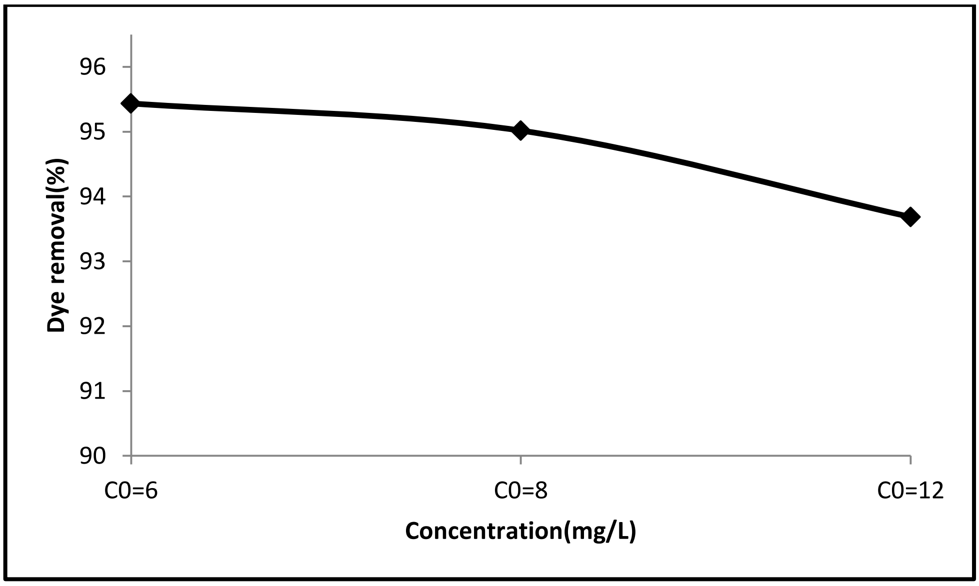


Figure 2. Effect of different dye concentrations on dye removal by Copper oxide Nano-particles; pH 2, 25 ºC, agitation rate of 180 rpm and 0.233 g adsorbent in 50 ml of dye solution.

Effect of pH

pH is a very important parameter in absorption process and affected on absorption capacity, dye solubility, solution chemistry and surface of absorbent pore. As shown in Fig.

2, when pH solution increases from 2 to 12, dye removal efficiency with CuO Nano-particles decreases from 93.68 to 14.52%. In other studies, maximum Erythrosine dye removal on CuO Nano-particles was achieved at pH solution less than 5. At high pH, Low adsorption capacity is due to competition between hydroxyl ions and negative charge of dye ions on adsorption sites.

The effect of pH on dye removal was investigated in the range of 2-12. pH influence on the adsorption of Erythrosine dye in contact time different on the CuO Nano-particles is shown in Fig. 4. The percentage of dye removal for various pH amounts in contact time different calculated from equation (2) is shown in Fig. 4. Solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbent.

At lower pH values, the percentage color removal of hydrolyzed reactive dye was relatively high, which may be attributed to the presence of positive charge produced via ionization of functional groups of adsorbent and significantly high electrostatic attraction. At pH values lower than 2, hydronium ions would significantly compete with dye ions for the adsorption sites of CuO Nano-particles and consequently inhibiting the adsorption of dyes.

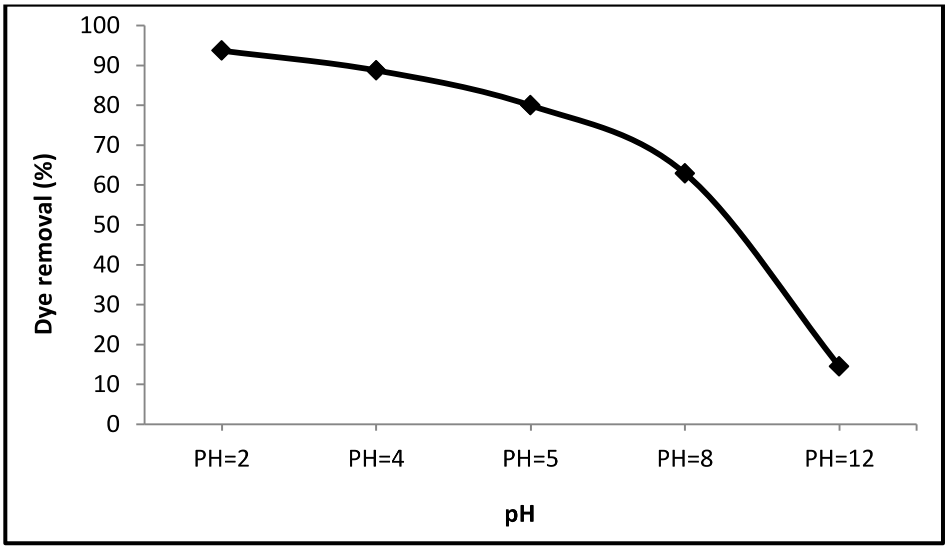


Figure 3. Effect of pH on the removal of Erythrosine; 25 ºC, agitation rate of 180rpm and 0.233 gr adsorbent in 50 ml of 12 mg L^{-1} dye solution.

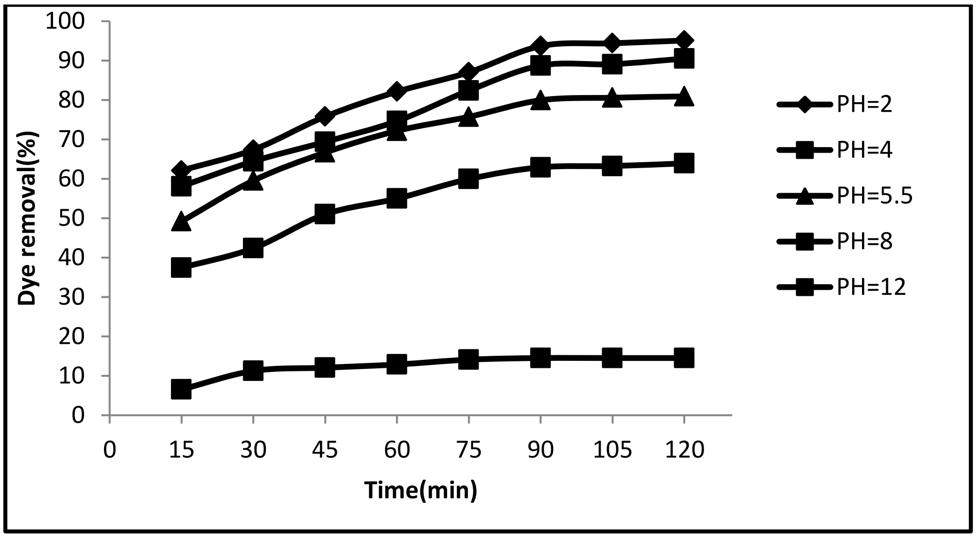


Figure 4. Effect of pH different time on the removal of Erythrosine; 90 min contact time, 25 ºC, agitation rate of 180rpm and 0.233 gr adsorbent in 50 ml of 12 mg L^{-1} dye solution.

3.4. Adsorption equilibrium isotherms

Basically, adsorption is a mass transfer process in which atoms or molecules move from a bulk phase onto a solid or liquid surface. Adsorption equilibrium at a definite temperature is usually presented in the form of adsorption isotherms, which are useful for selecting the most appropriate adsorbent and also for predicting the performance of adsorption processes. Many systems can be model by a number of the classical isotherms such as Freundlich and Langmuir together with more sophisticated isotherms [19, 20].

The Langmuir equation is applicable to homogeneous adsorbing sites where the adsorption of each molecule onto the surface has equal sorption activation energy. Langmuir adsorption model assumes that there is no interaction between adsorbed species and predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent [21]. The simplest theoretical model for monolayer adsorption due to Langmuir line raised equation can be shown as [22].

$$C_e/q_e = 1/Q_m.K_L + (1/Q_m)C_e \qquad (3)$$

Where qe is the amount of dye adsorbed on CuO Nano-particles at equilibrium, C_e is the equilibrium concentration of dye solution, KL is the equilibrium constant, and Q_m is the maximum adsorption capacity. The linear plot of C_e/q_e versus C_e demonstrates that the adsorption obeys Langmuir isotherm model and values of Q_m and K_L for a specific adsorption system can be determined From the slope and the intercept of a plot. Langmuir equation (eq.3) has been successfully applied to many adsorption processes for acid dyes**,** reactive dyes, direct dyes and basic dyes [23-26]. Even in some literature the applicability of Langmuir model for adsorbents has been emphasized [27].

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich isotherm expresses reversible adsorption process and predicts that the dye concentrations on the adsorbent will increase so long as there is an increase in the dye concentration in the liquid. The related equation can be given by

$$q_e = K_F . C_e^{1/n} \qquad (4)$$

Where q_e is solid phase adsorbate concentration in equilibrium (mg g^{-1}), C_e is liquid phase adsorbate concentration in equilibrium (mg L^{-1}) and 1/n is heterogeneity factor indicating the adsorption intensity. It has been revealed that the magnitude of heterogeneity factor indicates the favorability and capacity of the adsorbent/adsorbate systems. K_F is Freundlich constant (L g^{-1}) and can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbents for a unit equilibrium concentration. A linear form of the Freundlich expression can be given by

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (5)$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ provides the determination of K_F and 1/n.

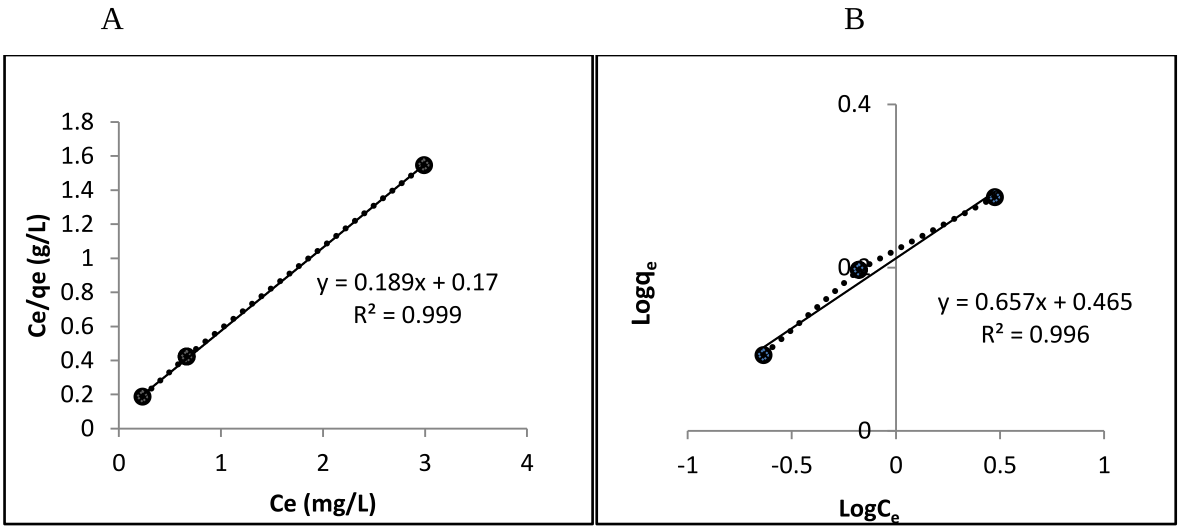


Figure 5. Langmuir (A) and Freundlich (B) isotherm plot for Erythrosine dye adsorption on Copper oxide nano particles.

Table 2: Equations and results of isotherms calculations

Isotherm	Equations	Linear form	R2	Constant	Value
Longmuir	$q_e = Q_m K_L C_e/1 + K_L C_e$	$C_e/q_e = (1/K_L Q_m) + C_e/Q_m$	*0.999*	K_L(L/mg)	*1.112*
				Q_m(mg/g)	*5.291*
Freundlich	$q_e = K_F.C_e^{1/n}$	$\ln q_e = \ln K_F + (1/n) \ln C_e$	*0.996*	K_f (mg/g)	*2.917*
				n	*1.522*

Adsorption kinetics

The study of adsorption kinetics is essential for investigation of solute uptake rate which controls the retention time of adsorption at the solid-solution interface. The results would be of undeniable importance for the process optimization in industry. The kinetics of Erythrosine dye adsorption on the Copper oxide nano particles was analyzed using pseudo first-order rate expression and pseudo second order model [28]. High correlation coefficient for pseudo second-order equation indicated that the pseudo second-order model could successfully describe the kinetic of Erythrosine dye adsorption on Copper oxide nano particles.

Pseudo first order model

The Langergren equation a pseudo second-order equation, describes the kinetics of adsorption process as follows

$$\mathrm{Log}(q_e-q_t)= \log q_e - k_1 t/2.303 \qquad (6)$$

Where q_t is the amount of dye adsorbed (mg g^{-1}) at time t, q_e is the amount of dye adsorbed at equilibrium, and K_1 is the rate constant of first-order sorption (min^{-1}). The pseudo first-order kinetics constants for the adsorption of Erythrosine dye on Copper oxide nano particles are tabulated in Table 3. Results showed that the sorption data could not be fitted by this model.

3.5.2. Pseudo second-order model

The second order kinetic model can be given by

$$t/q_t = 1/ K_2.q_e^2 + (1/q_e).t \qquad (7)$$

Where K_2 is the rate constant of second-order sorption (g mg^{-1} min^{-1}). The plot of t/q_t versus (Fig. 7) showed a linear relationship with high regression coefficient ($R^2 \geq 0.999$).

Kinetics parameters are tabulated in Table 3. The linear plot of t/q_t versus t shows a good compliance between experimental and theoretical q_e values (Table 3).

The correlation coefficient for the pseudo second-order model is significantly higher than that of pseudo first-order model indicating the fitness of adsorption data into this equation and also demonstrated that the chemical sorption is the rate determining step instead of mass transfer. Similar observations have been reported for adsorption of dyes.

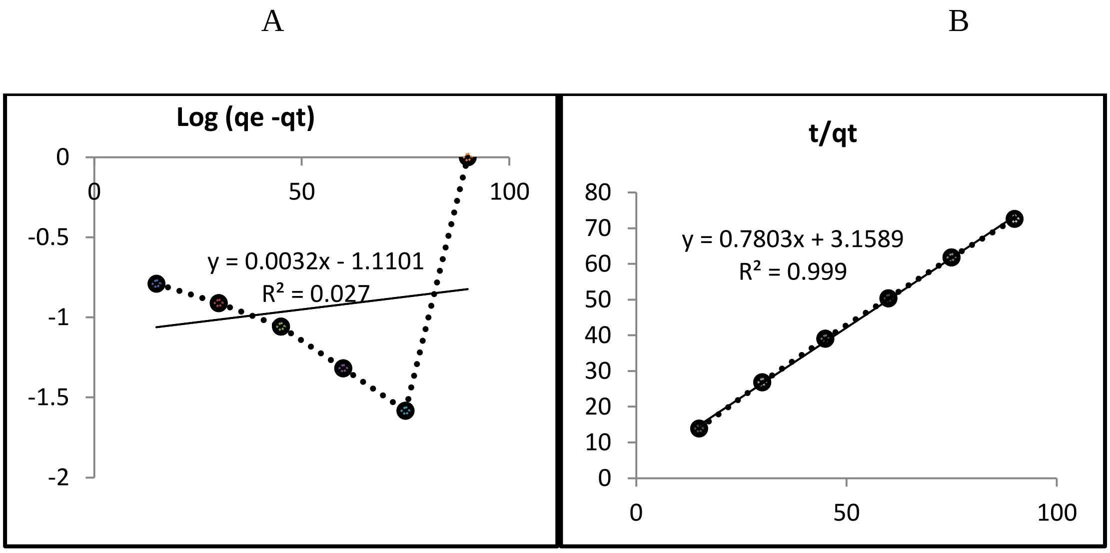


Fig. 6. Pseudo first order (A) and Pseudo second-order (B) adsorption kinetics of Erythrosine dye onto Copper oxide nanoparticles; pH 2, 25 °C, Initial dye conc. of 6 mg L^{-1} and rate of 180 rpm.

Table 3: Equation and result from kinetics calculations at pH 2

Kinetics	Equations	Linear form	R^2	Constant	Value
Pseudo first order	$dq_{t/dt} = k_1 (q_e-q_t)$	$Log(q_e-q_t)= \log q_e - k_1 t/2.303$	*0.027*	K_1	*0.006*
				q_e (calc)	*0.077*
Second order	$dq_{t/dt} = k_2 (q_e-q_t)2$	$t/q_t=1/k_2 q_e^2 + t/q_e$	*0.999*	K_2	*0.192*
				qe (calc)	*1.282*

qe(exp.) (mg g^{-1})	1.239

Scanning Electron Microscopy (SEM) analysis

Scanning Electron Microscope is a type of electron microscope capable of creating high resolution magnified images of sample surface. The production of magnified images is due to using electrons instead of light waves which also provides SEM images with characteristic three dimensional appearance and useful for judging the surface structure of the sample. The shape, size, porosity and arrangement of the particles making up the object that are lying on the surface of sample can be well determined by scanning electron microscopy.

The SEM image of original CuO Nano-particles shows the presence of significant number of pores providing a suitable position for dyes to be adsorbed. SEM images after Erythrosine dye adsorption demonstrated that the pores and cavities of adsorbent were efficiently packed with dyes (Fig. 6).

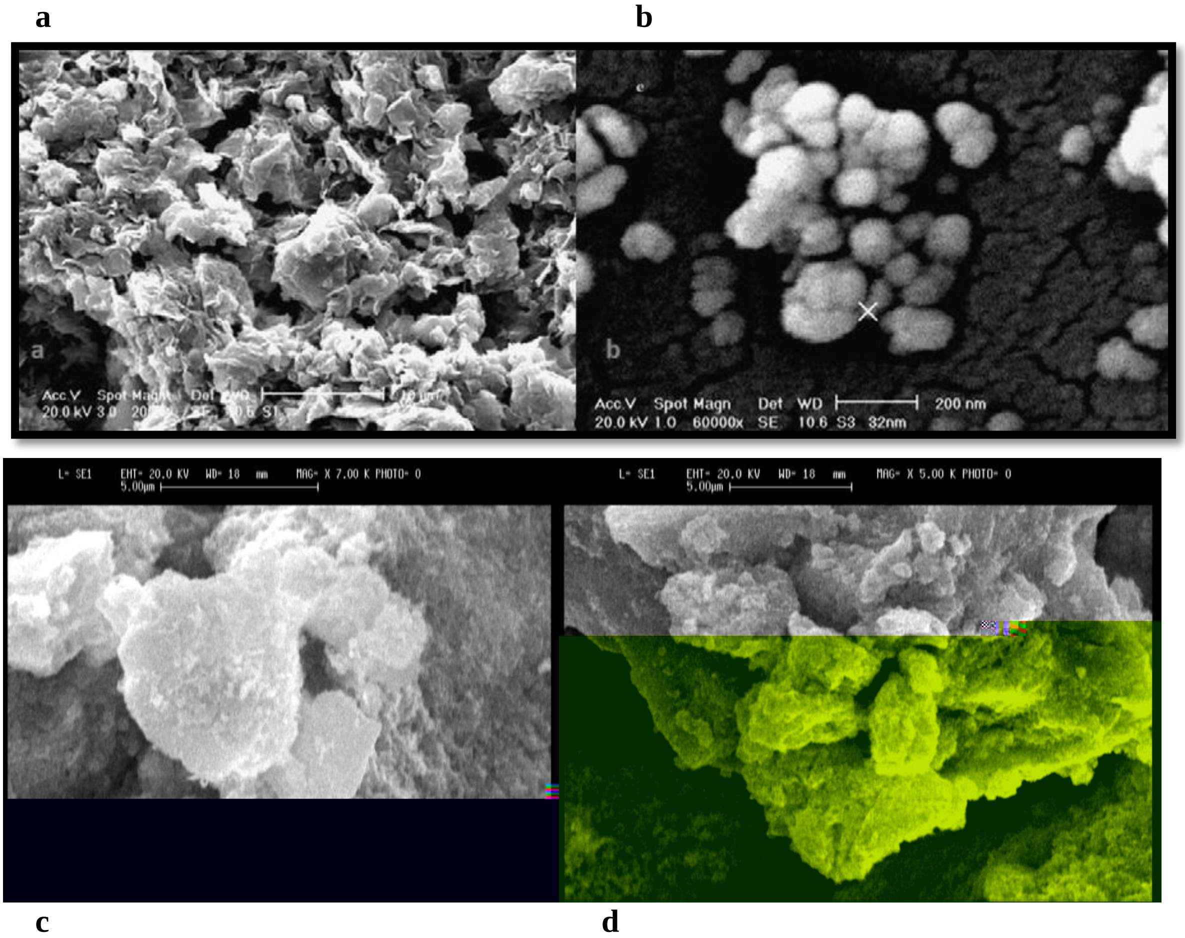


Fig.7. Scanning electron micrographs of (a) original CuO nano particles, (b,c,d) dye adsorbed CuO nano particles with Erythrosine. conditions: pH 2, 0.233 g in 50 ml of adsorbent, 12 mg L^{-1} of initial dye concentration, equilibrium time of 90 min, agitation rate of 180 rpm, 25 ± 1 ºC and particle size of 32 nm.

Conclusions

CuO Nano-particles can be well applied as a suitable and low-cost adsorbent for the removal of Erythrosine dye from wastewater. Equilibrium and kinetic evaluations at ambient temperature revealed that the sorption process obeyed Langmuir isotherm model. The initial adsorption equilibrium was achieved within 90 min at pH 2 (optimum pH) for all concentrations of Erythrosine. The kinetics of the adsorption was found to follow a pseudo second-order rate equation. Under the experimental conditions (C_0=6 mg L-1, adsorbent dosage of 0.233 g in 50 ml of dye solution, pH 2 and agitation rate of 180 rpm) maximum dye removal of 95.44 % could be attained. The adsorption capacity was found to increase significantly with decrease in the adsorbate, pH. According to the results, low-cost CuO Nano-particles, being a cheap and available material, could be an alternative for some costly adsorbents in the removal of dyes in wastewater treatment process. As the investigations about the adsorption properties of CuO Nano-particles, have been much limited, so it was considered to be important to study on the ability of this to remove dyes from industrial wastewater. The feasibility of using CuO Nano-particles as an adsorbent for the treatment of solution containing other types of dyes is an important purpose to study in further investigations.

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