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Research Article

ADSORPTION EVALUATION OF FOOD AND INDUSTRIAL DYES ON NANO COPPER OXIDE

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ABSTRACT
The aim of this laboratory research is to investigate the absorption of Indigo carmine dye process on adsorbent Copper oxide nano particles. The Indigo carmine dye adsorption by Copper oxide nanoparticles was carried out using variables parameters such as connect time, pH and initial dye concentration. The dye concentrations in different samples were measured via spectrophotometer (283.6 nm for dye Indigo carmine wavelength). The results of the absorption process indicated that Indigo carmine absorption or removal rates would increase by decreasing the primary dye concentration, increasing reaction time, and increasing pH. It was also found that Copper oxide nano particles can absorb Indigo carmine dye appropriately. Moreover, the efficiency of the process is higher in acidic pH for dye Indigo carmine. In addition, maximum dye removal of 98.40% could be achieved at initial pH 12 using adsorbent dosage of 0.233gr in 50 ml (6 mg L^{-1}dye concentration) and agitation rate of 180rpm. Also the effect of different parameters such as first and second order of pseudo kinetic reactions and the Langmuir and Freundlich Isotherm models were calculated to identify the absorption of the dye on the adsorbent. The studied dye absorption isotherm was fitted by Langmuir model (R^2=0.928) and was followed by second order kinetic reactions. Our finding led to the conclusion that Indigo carmine dye absorption/removal rates would increase by decreasing primary dye concentration, increasing reaction time, and increasing pH.

Keywords: *CuO Nano Particles, Indigo Carmine Dye, Absorption*

INTRODUCTION
Nowadays there are about 100000 Commercial dyes and most of them are abandoned in the environment. About 10 to 15% commercial dyes enter the environment by sewage.
Many reports have been conducted about eliminating chemical contaminants and various metals from water sources and industrial agricultural and domestic sewage. In particular, heavy metal absorbance such as silver and Copper on organic and mineral absorbance surfaces. In recent years, many works have been performed to eliminate dyes (Gottlieb *et al.,* 2003; Birhanli and Ozmen, 2005). Dye is one of the most important contaminates of industrial sewages, especially loom sewages.
The existence of insoluble dye materials in loom sewages disrupts biological filtration. Most dyes are stable against light and heat due to technology which I used in making them resistant to whitening materials, sun light and oxidation. So, they cannot be separated in common sewage filtration systems (Sanghi and Bhattacharya, 2002).
Artificial dyes are used widely in different industries such as loom, paper, hide, printing and cosmetics. Discharge of dye sewages creates serious problems in environment, because of their high toxicity and ability to accumulate in the environment. Also, complex aromatic structures make them even more so it is difficult to eliminate them from depleted dehydrations into acceptor waters (Yao *et al.,* 2010; Mishra *et al.,* 2010).
Environmental contamination from various organic chemical dye by compounds emitted by developing chemical industries has become a serious threat. Toxic and hazardous compounds especially heavy metals, entering the environment cause serious problems for humans and other organisms. These elements are not biologically dissoluble and are are mobilizable and able to accumulate in the texture of live organisms (Quintelas *et al.,* 2009; Maleki *et al.,* 2011; Barati *et al.,* 2010). Activities such as chemical production, agriculture and mining can release these metals into environment (Maleki and Zarasvand, 2008).

MATERIALS AND METHODS

Specifications of Indigo Carmine Dye

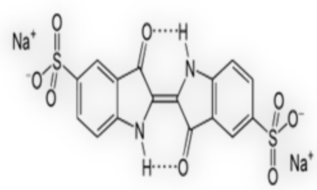
In this study, CuO Nano-particles are used as adsorbent for Indigo carminedye removal from textile wastewater at laboratory scale.

The specifications of Indigo carminedye: this dye have molecular formula $C_{16}H_8N_2Na_2O_8S_2$, molecular mass 466.36 mg $L^{-1}$and it is light blue solid with 10 g L^{-1} solubility in 25°C and melting point >300°C. The chemical structure of this dye is depicted in Table 1.

Product CuO Nano-Particles Adsorbent

For synthesis Nano-coordination polymer [Cu(C4H4O4)(bipy)(H2O)2]. 2H2O, 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 centrifuged by a Hettich EBA20 at 6000 rpm and separated sediment was dried. An amount of nano coordination component [Cu(C4H4O4)(bipy)(H2O)2]. 2H2O that obtained using So, no chemical synthesis is placed in oven at 415 °C for 4 h. CuO were obtained after the end of reaction from calcinations component and Detected by use the images of scanning electron microscopy (SEM).

Table 1: Indigo Carmine Dye Specifications

Molecular Formula	$C_{16}H_8N_2Na_2O_8S_2$
Molecular Structure	

Procedure

At first, 500 mg L^{-1}stock solutions was prepared from Indigo carmine dye and in all steps of the examination; desired concentrations were obtained from diluting stock solution. Batch sorption equilibrium experiments were performed by adding 0.233 g of CuO nano particles to 50 ml dye solution with desired concentrations and a pH at ambient temperature with a 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 283.6 nm. The percentage of removed dye in solution for each treatment can be calculated using eq. (1)

Dye removal (%) = (A. − A/ A.) ×100. (1)

Where A, is the initial dye absorbance and A represents the final absorbance of dye solution.

RESULTS AND DISCUSSION

1. ***Study of Concentration Effect on Indigo Carmine Absorbance by Using Copper Oxide Nono Particulates:*** The adsorption of indigo carmine dye by CuO Nano-particles was studied at different initial concentrations (6, 8, and 12 mg/L-1). Figure 2 shows the plots for the effect of initial concentration and contact time on the adsorption of indigo carmine dye by CuO Nano-particles. The equilibrium condition was achieved within 90 min for dye concentrations. The results show that an increase of dye concentration from 6 to 12 mg L^{-1}, decreased removal efficiency decreases from 98.40 % to 94.55%.

2. Balance Isotherms and Adsorption

Adsorption is a mass transporting process, in which different mixtures are competing to achieve balance. In a bi-components system that includes an absorber and soluble, a soluble concentration graph in the solid phase, describes q_e (mg g^{-1}) against the soluble concentration factor in solution C_e (mg L^{-1}) at constant temperature of on absorbance isotherm. The simplest theoretical model for monolayer adsorption due to Langmuir line raised equation can be shown as (Maleki and Zarasvand, 2008; Shirmardi *et al*., 2012).

$C_e /q_e = 1/Q_m.K_L + (1/Q_m)$ Ce (2)

Where, q_e is the amount of dye adsorbed on CuO Nano-particles at equilibrium, C_e is the equilibrium concentration of dye solution, K_L 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.

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

$q_e = K_F .C_e\ 1/n$ (3)

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 shown that the magnitude of the 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

$\text{Ln } q_e = \ln K_F + 1/n \ln C_e$ (4)

(A) (B)

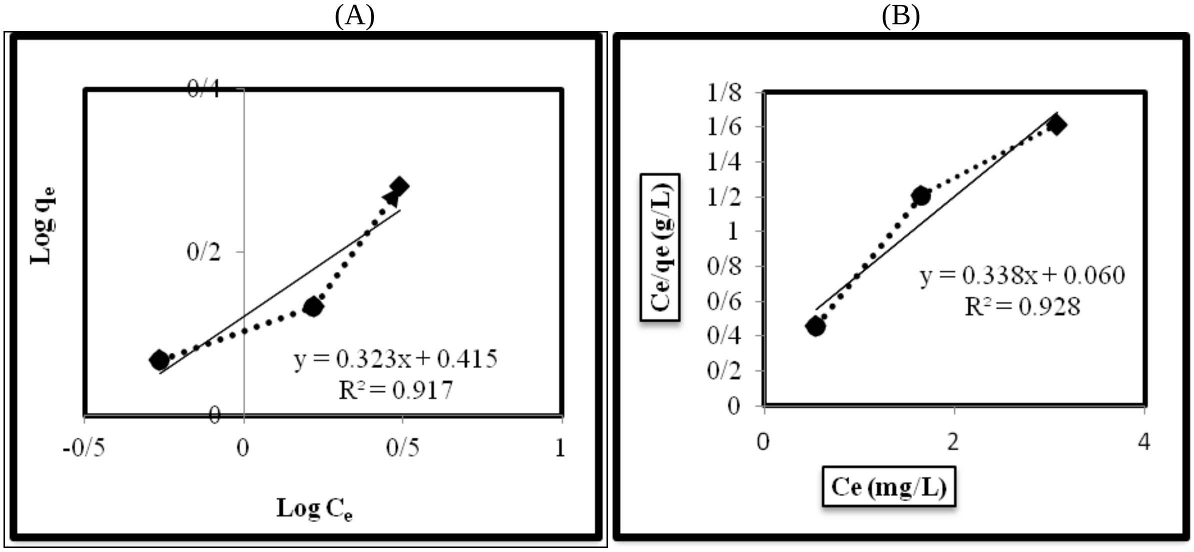


Figure 1: Langmuir (A) and Freundlich (B) Isotherm Plot for Indigo Carmine Dye Adsorption on Copper Oxide Nano Particles

Table 2: Langmuir and Freundlich Adsorption

Langmuir			**Freundlich**		
$(C_e/q_e = (1/K_L\ Q_m) + C_e/Q_m)$			$(\text{Ln } q_e = \ln K_F + (1/n) \ln C_e)$		
q_m, mg g^{-1}	K_L, L mg^{-1}	R^2	K_f, mg g^{-1}	n	R^2
2.958	5.649	0.928	2.600	3.095	0.917

3. Adsorption Kinetics

To obtain information about the factors that affect reaction rate it is necessary to investigate the kinetics. Two synthetic models are used widely as resources in the elimination process, include first and second order kinetics models. Initially absorbance of color molecules is very fast and decreases gradually until balanced. Results of this study are presented in the following figures to determine the mass transportation and speed controlling mechanisms kinetics empirical data are matched to linear forms of first and second kinetics models, based on (5), (6) equations.

$\text{Log}(q_e\text{-}q_t) = \log q_e - k_1 t/2.303$ (5)

$t/q_t = 1/k_2 q_e^2 + t/q_e$ (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 indigo carmine dye on Copper oxide nano particles are tabulated in Table 2. Results show that the sorption data could not be fitted with this model. Where, K_2 is the rate constant of second-order sorption (g $mg^{-1}min^{-1}$).

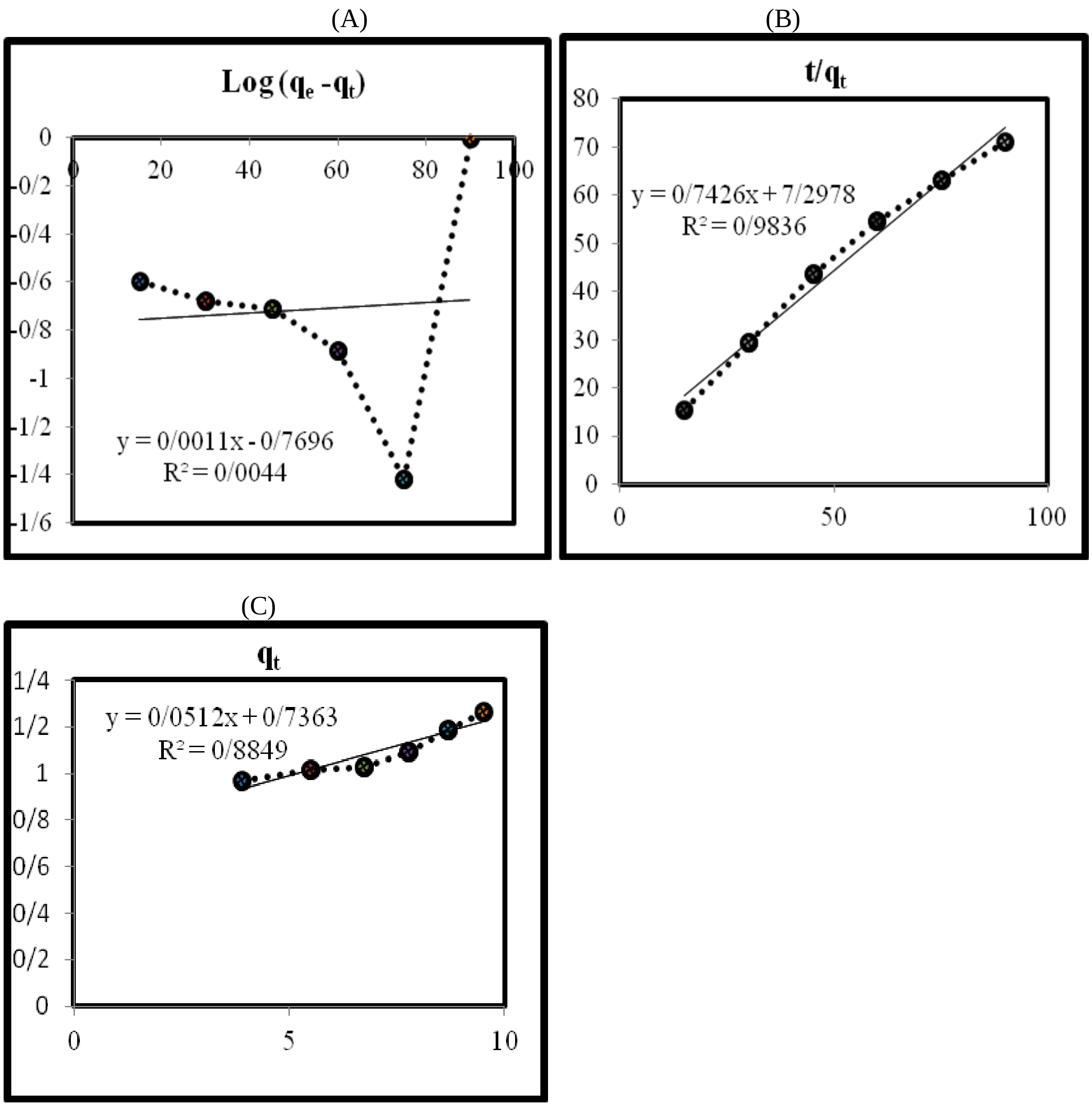


Figure 2: Pseudo First Order (A) and Pseudo Second-Order (B) Adsorption Kinetics and Intra Particle Diffusion (C) of Indigo Carmine Dye onto Copper Oxide Nano Particles; pH 12, 25 °C, Initial Dye Conc. of 6 mg L^{-1} and Rate of 180 rpm

Table 3: Comparison of the First and Second-Order Adsorption Rate Intra Particle Diffusion Constants and Calculated and Experimental q_e Values for Different Initial Dye Concentrations

Parameter	First-order kinetic model				Second-order kinetic model			Intra particle diffusion		
	$(\text{Log}(q_e\text{-}q_t) = \log q_e - k_1t/2.303)$				$(T/qt=1/k_2q_e^2 + t/q_e)$			$(\text{Ln } q_e = \ln Q_m - K_e^2)$		
	q_e (exp) (mg/g)	k_1 (1/min)	q_e (cal) (mg/g)	R^2	k^2 (g/ mg/ min)	q_e (cal) (mg/g)	R^2	Intra particle rate constant k_{id}, (mg g^{-1})	y Intercept (mg g^{-1}), min$^{-1/2}$	R^2
Initial dye concentration (mg/l)										
6	1.226	0.002	0.170	0.004	0.075	1.347	0.983	0.051	0.736	0.884
8	1.644	0.00	0.330	0.001	0.047	1.773	0.976	0.073	0.873	1.238
12	2.434	0.002	0.590	0.018	0.197	1.029	0.971	0.113	0.858	0.85

Results
These results showed that absorption of indigo carmine dye followed second-order kinetic adherence possessing a regression coefficient of $R^2 \geq 0.928$. In relations to the absorption or removal of indigo carmine on Copper oxide nano particles and the different parameters investigated affecting the process rate of absorption, the equilibrium data fitted well with the Langmuir model for dye with adsorbent.

Discussion
CuO Nano-particles can be applied as a suitable and low-cost adsorbent for the removal of indigo carmine dye from wastewater. The effects of various factors such as contact time, pH and initial dye concentration were investigated for different dye concentrations of 6, 8 and 12 mg L^{-1}. The results of absorption studies show that indigo carmine absorption rates would increase by decreasing the initial dye concentration, increasing reaction time, and increasing pH. On the basis of the results, absorption of indigo carmine dye by, CuO Nano-particles is a more appropriate and efficient process in higher in the higher the basic PH.

Conclusion
The initial adsorption equilibrium was achieved within 90 min at pH 12 (optimum pH) for all concentrations of indigo carmine. The kinetics of the adsorption was found to follow a pseudo second-order rate equation. Under the experimental conditions (C.=6 mg L^{-1}, adsorbent dosage of 0.233gr in 50 ml of dye solution, pH=12 and agitation rate of 180 rpm) maximum dye removal of 98.40 % was attained.

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