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Nanocrystalline Copper Ferrite Particles: Synthesis, Characterization and Their Application for the Removal of Reactive Red 141

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1- Introduction

Reactive dyes are generally described by the presence of azo chromophores (−N=N–) or phthalocyanine chromophore (including copper, nickel or other metals) and aromatic rings, which are toxic and mutagenic to living organisms. Several dye removal and degradation techniques have been developed including physical, chemical and biochemical methods along with the photocatalytic degradation process. Among various treatment techniques, adsorption by magnetic nano sorbents is a water remediation technology which can lead to rapid and efficient wastewater stream removal. After sorption, it is easy to separate sorbent from the water media using a magnetic separator. Copper ferrite, $CuFe_2O_4$, has an inverse spinel structure in which octahedral sites are occupied with Cu^{2+} ions while Fe^{3+} ions are equally distributed between tetrahedral and octahedral sites. In this research, copper ferrite nanostructure was synthesized using the solvothermal method and used for the removal of reactive red 141. The effect of different parameters, i.e., pH of solution, temperature, adsorbent dosage and initial concentration of pollutant on the removal of reactive red 141were also investigated.

2- Materials and methods

All chemicals were of analytical grade and used without further purification. Mili-Q water was used with a resistivity of at least 18.2 MΩ.cm^{-1}. Copper ferrite ($CuFe_2O_4$) nanocrystals were obtained using the solvothermal method in the polyol media. Briefly, $FeCl_3.6H_2O$ (5 mmol) and $CuCl_2.2H_2O$ (2.5 mmol) were dissolved in 40 mL of ethylene glycol. Sodium acetate (3.6 g) was added to the above solution under vigorous stirring for 30 minutes. The as-prepared slurry was sealed into Teflon–lined autoclave and maintained at 180 °C for 12 h. After cooling to the room temperature, the black precipitate ($CuFe_2O_4$) was collected magnetically, washed several times with water and dried in a forced-convection oven at 60 °C overnight.

In adsorption studies, a certain amount of adsorbent (copper ferrite) was transferred to the reactor containing 200 mL of RR141 aqueous solution at different known concentrations. The adsorption of pollutant per unit gram of adsorbent, q_e, was evaluated using the following equation:

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{1}$$

where V is the solution volume, C_0 is the initial adsorbate concentration in the solution, C_e is the solute concentration in the bulk phase at equilibrium condition and M is the adsorbent mass.

3- Results and discussion

The X-ray diffraction patterns of $CuFe_2O_4$ sample are shown in Fig.1. The XRD peaks could be identified with the cubic $CuFe_2O_4$ phase (ICDD-01-077-0010, space group Fd-3m, *a*=*b*=*c*=8.37 Å).

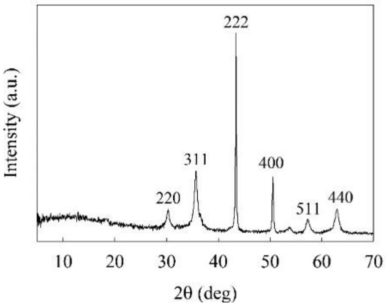

Fig. 1: XRD patterns of $CuFe_2O_4$ nanoparticles.

The morphology and structure of $CuFe_2O_4$ nanoparticles were investigated by the transition electron microscopy (TEM). The TEM results confirmed the nanosized and distorted surface morphology.

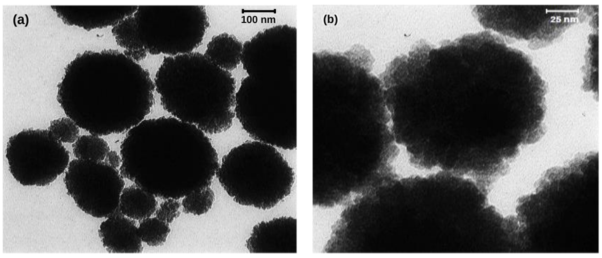

Fig. 2. Low magnification (a) and high magnification (b) TEM images of $CuFe_2O_4$ nanoparticles.

It was found that the size of nanoparticles varied from 50 to 200 nm. Also, high magnification TEM images indicated the spherical morphology of $CuFe_2O_4$ nanoparticles.

The effect of initial pH on the adsorption of RR141 onto $CuFe_2O_4$ nanoparticles was investigated. As shown in Fig. 3, the complete removal of RR141 was observed in acidic media after 10 min (pH=3.0±0.5).

Fig. 4 presents the effect of contact time on the removal of RR141 for three different amounts of $CuFe_2O_4$ (0.025, 0.05 and 0.1 g) over 1-60 min using 200 mL of 20 mgL^{-1} RR141 under natural pH of RR141 solution (pH = 5.0±0.5) and room temperature (T=30±1 °C).

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Accordingly, removal efficiencies of 50.19%, 68% and 96.35% for 0.025, 0.05 and 0.1 g of $CuFe_2O_4$ nanoparticles were measured after 20 min, respectively.

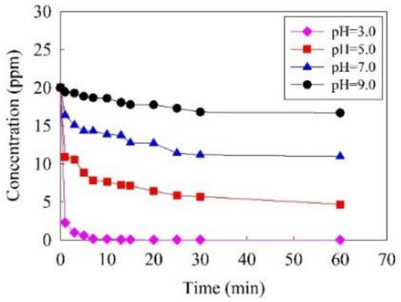

Fig. 3. Effect of initial pH of the solution on the sorption of RR141 using $CuFe_2O_4$ nanoparticles.

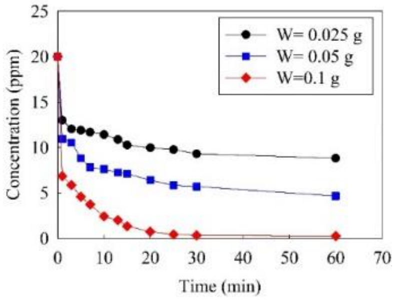

Fig. 4. Effect of contact time and adsorbent loading on the removal of RR141 using $CuFe_2O_4$ nanoparticles.

Fig. 5 shows the RR141 removal at different initial concentrations (10-50 mg. L^{-1}) over 120 min using 0.025 g of adsorbent under natural pH of the RR141 solution (pH = 5.0±0.5) and at room temperature (T=30±1 ºC). The results exhibit that the adsorption capacity raised with increased initial concentration. The high removal efficiency in the applied concentration range over a short time demonstrates that there are plenty of accessible active sites on the surface of sorbent. The maximum adsorption capacity obtained was about 144.8 mg RR141/g $CuFe_2O_4$.

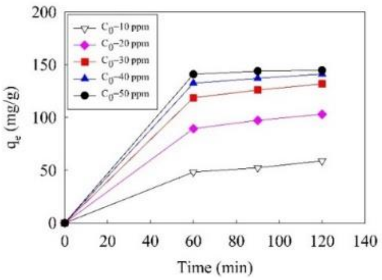

Fig. 5: Effect of initial concentration for the removal of RR141 using $CuFe_2O_4$ nanoparticles (pH = 5.0±0.5, T=30±1 ºC, amount of sorbent=0.025 g).

The well-known Langmuir and Freundlich adsorption isotherm models were used to investigate the adsorption of RR141 on $CuFe_2O_4$ nano adsorbent. The linear form of Langmuir isotherm is obtained from the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \left(\frac{1}{q_m}\right) C_e \qquad (2)$$

where C_e (mg. L^{-1}) is the equilibrium concentration of the adsorbate, q_e (mg. g^{-1}) is the adsorption per unit mass of adsorbent and q_m (mg. g^{-1}) and K_L (L. mg^{-1}) are Langmuir constants. The linear form of Fruendlich isotherm is as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3)$$

where K_f is roughly an adsorption capacity indicator and (1/n) is the adsorption intensity. Here, values of n > 1 represent favorable adsorption conditions. The data related to Langmuir and Freundlich isotherms are listed in Table 1.

Table 1: Isotherm parameters of Langmuir and Freundlich model for the adsorption of RR141 onto $CuFe_2O_4$ nanoparticles.

Langmuir			Freundlich		
R^2	K_L	q_m	R^2	n	K_F
0.998	0.22	166.66	0.922	2.73	45.55

The consistency of results with the Langmuir model (R^2=0.998) is higher than that of the Freundlich model (R^2=0.922).

To analyze the adsorption kinetic models, Lagergren's pseudo-first order and Ho's pseudo-second order models were used for the experiment data. The adsorption kinetics of RR141 on $CuFe_2O_4$ nanoparticles is best illustrated by the pseudo-second order rate kinetics, which fits well with our results (Table 2).

Table 2: Kinetic parameters of Ho's pseudo-second order models for the adsorption of RR141 onto $CuFe_2O_4$ nano adsorbents.

		q_e		R^2	k_2
		predicted	Experimental		
T=30 ºC	W=0.025 g	87.72	89.44	0.997	0.006
	W=0.05 g	62.89	61.36	0.998	0.007
	W=0.1 g	40.49	39.5	0.999	0.02
T=40 ºC	W=0.025 g	89.29	95.92	0.998	0.01
	W=0.05 g	60.98	65.48	0.999	0.02
	W=0.1 g	39.06	39.5	0.999	0.043
T=50 ºC	W=0.025 g	96.15	113.44	0.999	0.01
	W=0.05 g	62.11	67.28	0.999	0.022
	W=0.1 g	39.68	39.78	0.999	0.069

4- Conclusion

$CuFe_2O_4$ nanoparticles were prepared, characterized and successfully applied for the RR141 dye remediation from aqueous media. The adsorption of RR141 onto $CuFe_2O_4$ changed the initial pH solution. The removal efficiency improved up to 100% in the acidic media (pH=3) after 10 min. Two isotherm models, Freundlich and Langmuir, were tested for the experimental results. The results were fitted with the Langmuir model. The RR141 adsorption rate fitted with the pseudo-second order kinetic model where the rate limiting step was assumed to be chemical adsorption between the adsorbate and the adsorbent. $CuFe_2O_4$ nano adsorbent was easily manipulated by a low strength external magnetic field, which allowed easy recovery from the aqueous media.