

Cobalt ferrite nanotubes and porous nanorods for dye removal

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(Received July 27, 2015, Revised August 4, 2015, Accepted September 7, 2015)

Abstract. CoFe₂O₄ nanotubes and porous nanorods were prepared via a simple one-pot template-free hydrothermal method and were used as an adsorbent for the removal of dye contaminants from water. The properties of the synthesized nanotubes and porous nanorods were characterized by electron diffraction, transmission electron microscopy and x-ray powder diffraction. The Adsorption characteristics of the CoFe₂O₄ were examined using polar red dye and the factors affecting adsorption, such as, initial dye concentration, pH and contact time were evaluated. The overall trend followed an increase of the sorption capacity reaching a maximum of 95% dye removal at low pHs of 2-4. An enhancement in the removal efficiency was also noticed upon increasing the contact time between dye molecules and CoFe₂O₄ nanoparticles. The final results indicated that the CoFe₂O₄ nanotubes and porous nanorods can be considered as an efficient low cost and recyclable adsorbent for dye removal with efficiency 94% for Cobalt ferrite nanotubes and for Cobalt ferrite porous nanorods equals 95% .

Keywords: porous nanoparticles; nanorods; dye removal; waste water treatment

1. Introduction

Nanoscale magnetic materials have aroused extensive attention in the past decades owing to their potential applications in magnetic sensors, high-density recording media, catalysis, and biomedical purposes (Goya *et al.* 2003). However, in the recent years the treatment of wastewater and industrial effluents has become a challenging topic in environmental science and technology (Scha *et al.* 2000). For instance, wastewater containing dyes and pigments; widely used in many industries, can be toxic and even carcinogenic when released into the environment and thus possesses a serious danger to aquatic life. Such environmental problem opened the door for new applications of magnetic nanoparticles since they can adsorb contaminants from the aqueous effluents in a short time and, after adsorption, can be separated from the medium by simple magnetic separation (Muruganandham *et al.* 2006). Magnetic nano- or micro-particulates of iron oxides have long been used in the fields of separations and adsorptions, especially in ion exchange separations (De Lisi *et al.* 2007), enzymes (Rocher *et al.* 2008) or other proteins, nucleic acids (Sari *et al.* 2006) and cell (Chen *et al.* 2007) separations, and dyes removal (Akutsu *et al.* 2004, Morstyn *et al.* 1996). However, removal of color from wastewater is considered a greater

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challenge (Vaskova *et al.* 2006). Most of the dyes, including polar red, are toxic. The effluents containing such materials can cause serious reduction in light penetration and photosynthesis if released into receiving streams. (Wu *et al.* 1999). The toxic nature of the dye is mainly due to the production of hazardous products, such as carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides and hydrogen chlorides upon its decomposition (Ligrini *et al.* 1993). These products are toxic and can lead to severe health problems to all kinds of living organisms including man as well as animals. Thus, polar red dye attracts a noticeable attention to develop effective techniques for its removal. As a matter of fact, many studies extensively investigated various treatment technologies for dye removal. Among these methods are the trickling filter, activated sludge, chemical coagulation (Gong *et al.* 2005), biological treatment, coagulation/flocculation (Vandevivere *et al.* 1998), ozone treatment (Kornaros *et al.* 2006), chemical oxidation (Guibal *et al.* 2007), membrane filtration (Zhao *et al.* 2006), ion exchange (Dutta *et al.* 2001), photo catalytic degradation (Capar *et al.* 2006) and adsorption (Liu *et al.* 2007). But widespread application of these methods can be restricted due to high cost, difficult disposal and regeneration (Vîrlan *et al.* 2013). Nanoparticles have low adsorption capacity of anionic dyes due to repulsion of the negative charge of nanoparticle surface and anionic dyes. Thus, they should be modified (Mahmoodi *et al.* 2014). Metal ferrites are promising materials that can be used in dye removal applications. Cobalt Ferrite is one of the metal ferrites that exhibits unique physical properties such as high Curie temperature, high coercivity, moderate saturation magnetization, excellent chemical stability and mechanical hardness (Rajath *et al.* 2008, Sharma *et al.* 2006). In Addition, this material has a significant higher magnetostriction than metallic Fe or Ni (Gharagozlou *et al.* 2009). This metal ferrite was extensively used in catalysis applications but its use in dye removal wasn't studied much.

Generally, the properties of the nanomaterials significantly depend on their size, shape and structure. However, Controlling the shape and size of nanomaterials is an ultimate challenge of modern material research (Zavisova *et al.* 2010). According to several researches, it was found that direct synthesis of CoFe₂O₄ nanotubes and porous nanorods is difficult because of the great difference in deposition rate of Co (II) and Fe (III) ions in aqueous solution. In addition, the isotropic structure of cobalt ferrite also causes difficulties in anisotropic growth of nanocrystal. Thus, it remains a challenge to develop simple and effectual approaches to synthesize such nanoparticles.

Our current study was devoted to synthesize Co-Fe nanotubes and porous nanorods via a modified chemical co-precipitation technique with urea as precipitator in the absence of any surfactant. The as-obtained cobalt ferrite nanotubes and porous nanorods were fully characterized and were investigated for their application as an adsorbent for the removal of polar red dye from aqueous solution. Effects of various experimental conditions such as pH, contact time and initial dye concentration, on the adsorption were evaluated through a batch equilibrium technique.

Acid dyes:

The dyeing of untreated wool fabrics was carried out using 1% of concentration of acid dyes using a liquor-to-goods ratio of 30:1 in the presence of 1 g/l egyptol PLM. The conditions of dyeing illustrated. The dyed wool fabric was rinsed thoroughly with running water and air-dried (Wafaa El-Sayed *et al.* 2009)

2. Experimental work

2.1 Synthesis of cobalt ferrite nanotubes and porous nanorods

To synthesize Cobalt Ferrite (CoFe_2O_4) nanotubes and porous nanorods, homogeneous in size, it is vital to keep a molar ratio of Co (II): Fe (III): $(\text{NH}_2)_2\text{CO}$ =1:1:2.7 (CoSO_4 obtained from WINLAB, CoCl_2 , and Urea are obtained from FISCHER, and FeCl_3 obtained from ALPHA chemika), A typical approach modified by us is as follows (Zavisova *et al.* 2010); chemicals were all dissolved in purified deoxygenated water with constant magnetic stirring for 30 min, Then it was added to a Teflon-lined stainless autoclave, which was maintained at $80^\circ\text{--}85^\circ\text{C}$ for 12 h, and cooled to room temperature. Purified and deoxygenated water was added to the precipitate, and decanted after centrifugation at 4000 rpm. Washing was done several times and then the sample was dried in a vacuum at 200°C for 2 h. cobalt ferrite nanotubes was synthesized at the same conditions that used to synthesize porous nanorods but by using cobalt sulphate instead of cobalt chloride at the same conditions.

2.2 Adsorption experiment

The adsorption of polar red (obtained from Ciba-Geigy-Switzerland) from aqueous solution onto the porous nanorods was performed using equilibrium technique. For the determination of adsorption isotherms, 50 ml of dye solution of known initial concentration was shaken with a certain amount of the adsorbent (0.2 g) on a shaker at 30°C . The pH was adjusted to different values, either using HCl or NaOH. Initial dye concentrations were changed in the range of 100 mg L^{-1} to 500 mg L^{-1} . At various time intervals, samples were taken and allowed to settle and further centrifuged at 3000 rpm for 10 min. The concentration of the residual dye was measured using UV-Vis spectrophotometer (USB 650 Fiber Optical Spectrometer Model No. DDS-3X25 USB) at appropriate wavelength corresponding to the maximum absorption of polar red (i.e., 530 nm), and also the effect of CoFe_2O_4 nanotubes and porous nanorods on polar dye was measured. This data was used to calculate the adsorption capacity of the adsorbent. Initial dye concentration in the solution was varied to investigate its effect on the adsorption capacity. Several observations were made at different time intervals, to determine the maximum removal of dye attained. The efficiency (%) of Cobalt ferrite nanotubes and porous nanorods was calculated by the following equations:

$$(\eta = (C_0 - C_e) / C_0 \times 100\%)$$

Where C_0 and C_e are the initial and equilibrium concentrations of dye (mg L^{-1}).

2.3 Characterization

The crystalline structure, size and morphology of CoFe_2O_4 nanotubes and porous nanorods were examined by X-ray powder diffraction (XRD), Transmission electron microscopy and electron diffraction.

2.4 Results and discussion

2.4.1 Characterization of prepared CoFe_2O_4 nanotubes and porous nanorods

In order to understand the formation mechanism of the CoFe_2O_4 nanotubes and porous

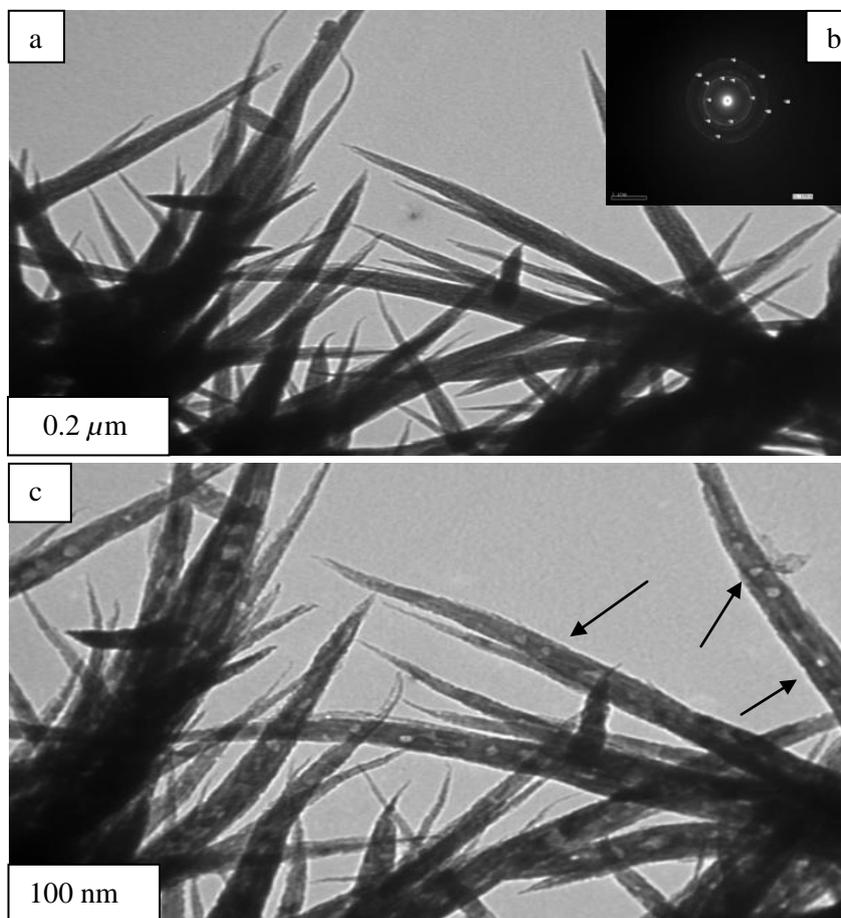


Fig. 1 (a) TEM images of CoFe_2O_4 porous nanorods, (b) in the frame is EDX pattern of the porous nanorods, (c) TEM images of CoFe_2O_4 porous nanorods shows porous nanoparticles with size 4-14 nm

nanorods, time-dependent experiments were carried out at 80-85°C during which samples were collected at different time intervals from the reaction mixture. At the beginning of the reaction, urea after heating over 80°C decomposes to CO_2 and NH_3 (Eq. (1)). In the reflux condition, CO_2 can be released, so only NH_3 reacts with water and produces hydroxyl ions (Eq. (2)).



Then Fe^{3+} reacts with OH^- ions and yellow precipitate can be observed, indicating the generation of $\text{Fe}(\text{OH})_3$ (Eq. (3)).



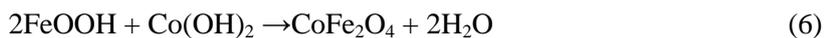
$\text{Fe}(\text{OH})_3$ is transformed into goethite $\text{Fe}(\text{OOH})$ (Eq. (4)), which is usually in the shape of needle



Since the solubility of $\text{Fe}(\text{OH})_3$ is much smaller than $\text{Co}(\text{OH})_2$, with enhancement of the pH value, $\text{Fe}(\text{OH})_3$ is first precipitated.



After reaction of the nanoparticles is formed (Eq. (6)).



The nanotubes and porous nanorods have been synthesized by hydrolysis of Co^{2+} and Fe^{3+} solution in the presence of urea at 80°C for 12 h. Fig. 1(a), and (c) are the typical images of the porous nanorods, from which we can see that the product is mainly composed of uniform rod-like porous structures. Fig. 1(b) is the selected area electron diffraction (SAED) pattern of the porous nanorods, which confirms that the sample is single crystal and have a cubic crystal structure. Fig. (1): (a) TEM images of the porous nanorods, (b) in the frame is EDX pattern of the porous

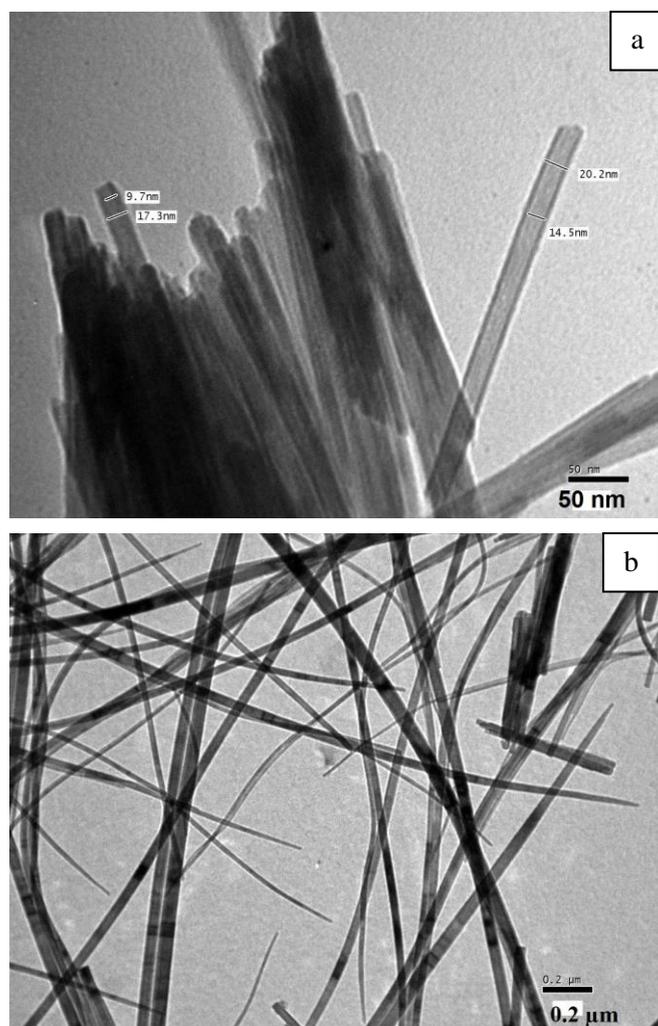


Fig. 2 TEM images of CoFe_2O_4 nanorods shows the nanotubes inner and outer radii with size 9-20 nm

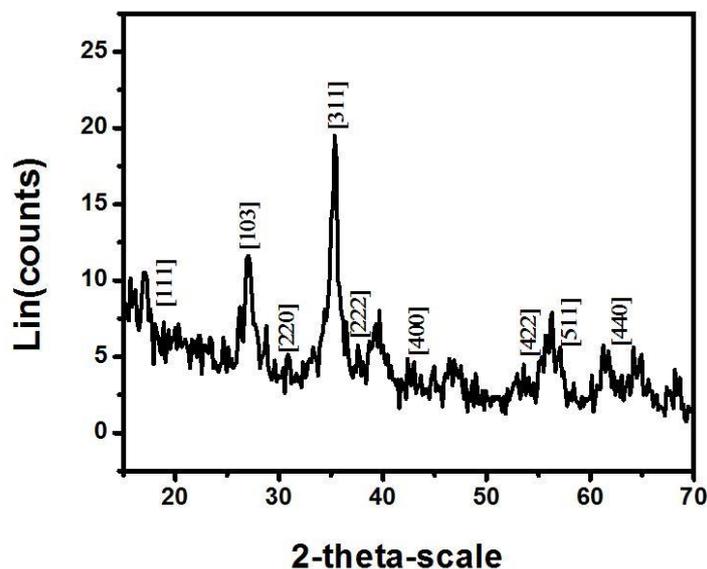
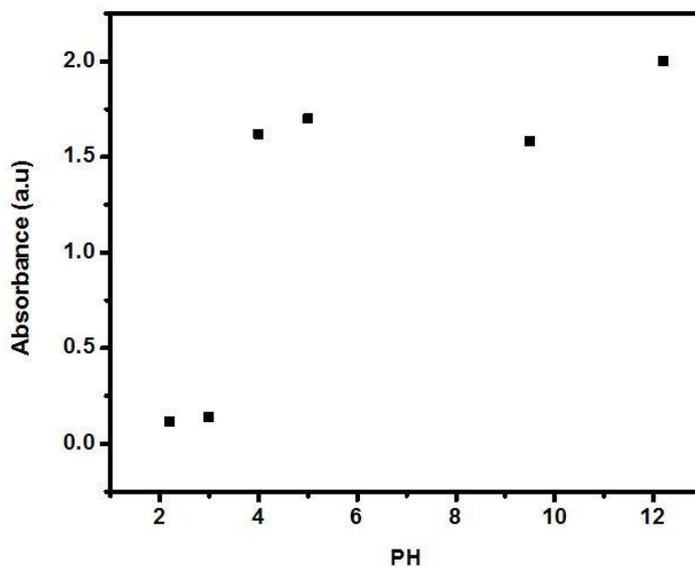
Fig. 3 XRD spectra for CoFe_2O_4 porous nanorods

Fig. 4 Shows the effect of pH on absorbance (a.u) value

nanorods, (c) TEM images of CoFe_2O_4 porous nanorods shows porous nanoparticles with size 4-14 nm. Fig. 2 (a), (b) TEM images of the nanotubes shows the nanotubes inner and outer radii with size 9-20 nm.

Fig. 3 Shows the XRD pattern of the sample, which is quite identical to pure porous nanorods indicating that the sample has a cubic crystal system. Characteristic peaks of impurities are also observed.

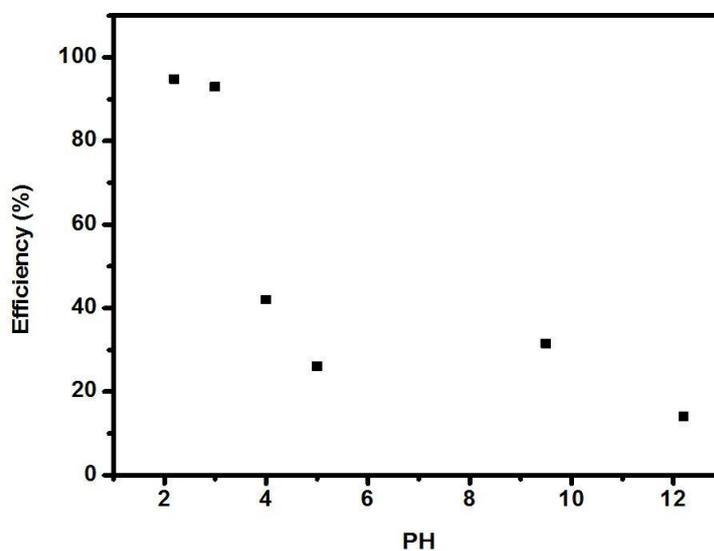


Fig. 5 Shows the effect of pH on efficiency (%) value

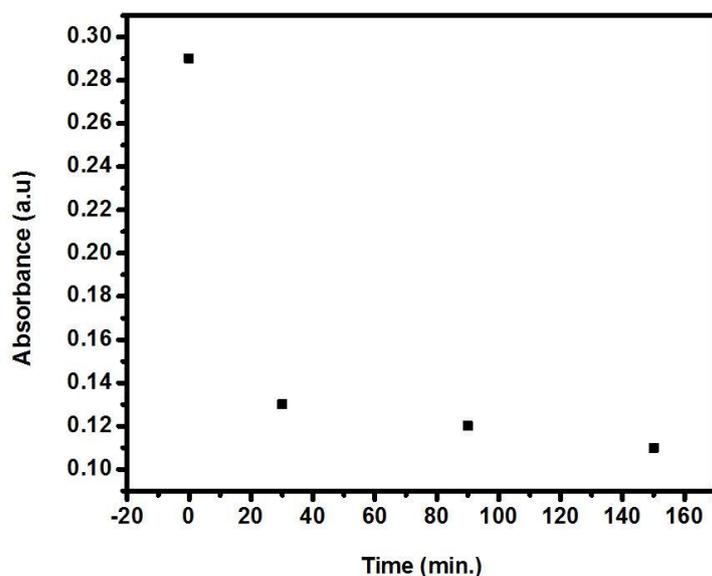


Fig. 6 Shows the relation between the contact time (min.) and the absorbance (a.u) values of polar red dye

2.4 Factors affecting dye adsorption

2.4.1 Influence of pH

The influence of pH on adsorption capacity was studied over a range of pH values from 2 to 11. It was observed that the dye absorbance increased when pH increased from 3 to 5 and then the absorbance was not significantly altered beyond 7. This can be confirmed from the data on the absorbance curve in Fig. 4. In addition, it was clear that the efficiency of dye removal increased in

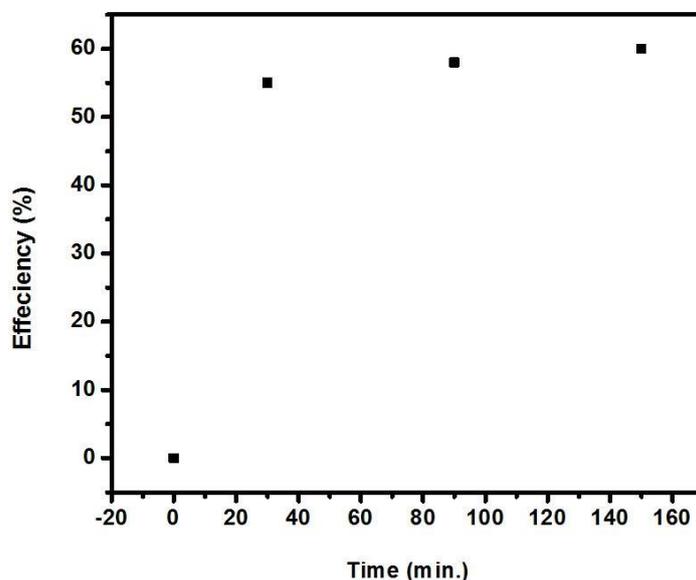


Fig. 7 Shows the effect of time (min.) on efficiency (%) value

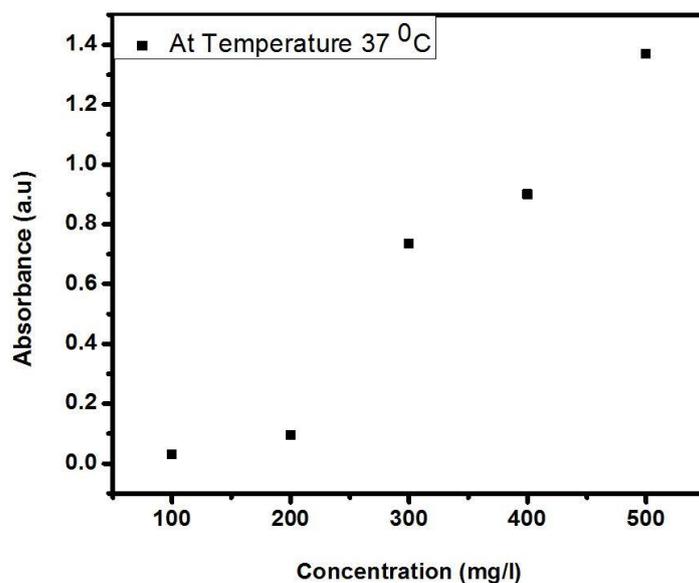


Fig. 8 Shows the effect of concentration C (mg/l) on absorbance (a.u) at temperature 37°C

the acidic pH where it reached its maximum of 95% dye removal at pH 2, as shown in Fig. 5. The efficiency then started to decrease as the pH increased.

Therefore, the fact that polar dyes adsorbed on cobalt ferrite porous nanorods adsorbent increased with decreased pH values suggested that one of the contributions of cobalt ferrite nanorods adsorption toward polar dyes resulted from electrostatic attraction between the charged cobalt ferrite porous nanorods adsorbent surface and the polar dyes.

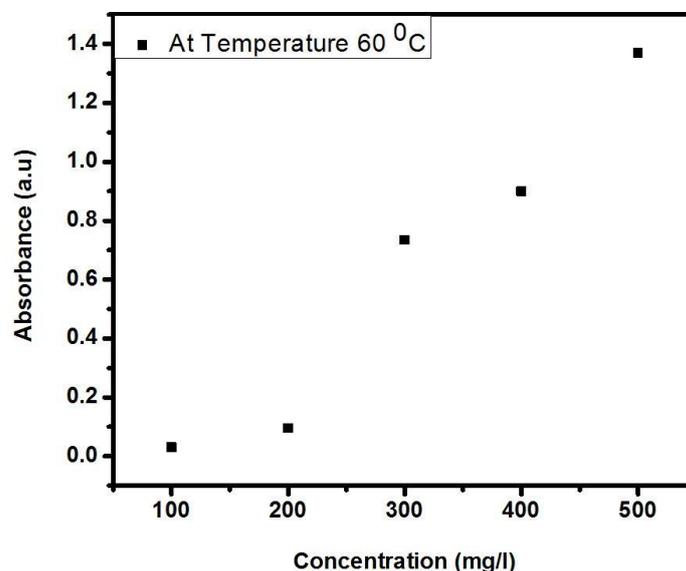


Fig. 9 Shows the effect of concentration C (mg/l) on absorbance (a.u) at temperature 60°C

2.4.2 Influence of time

Time is another important variable that can affect the adsorption process. The absorbance value decreased by increasing the values of time from 30, 90, to 150 mins. Fig. 6 shows the relation between the contact time and the absorbance values of polar red dye. It was observed that for CoFe_2O_4 porous nanorods about 63% of the adsorption capacity was reached within 150 minutes of mixing adsorbent and polar red solution. The results in terms of dye removal efficiency of porous nanorods are shown in Fig. 7.

2.4.3 Influence of concentration

The adsorption capacity is considered a function of the initial concentration of dye. As expected, the overall trend was decreasing of the sorption capacity with increasing dye concentration values from 100 to 500 as shown in (Figs. 8, 9) since the maximum capacity was reached, and all the active sites of the nanorods were occupied by the dye molecules. Larger surface areas of cobalt ferrite; obtained by increasing the nanorods concentration, not only caused higher removal capacities but also enhanced adsorption rate. However, in the same conditions, if the concentration of polar dye in solution was bigger, active sites on the adsorbent were surrounded by much more polar dye ions. Hence the adsorption quantity for polar dye decreased with the increase of dye concentrations. In addition, the dye removal efficiency decreased from 95% to 47% for an increase in the initial concentration, while the adsorbent dose was kept constant at 0.2 g.

Overall, we found that the prepared cobalt ferrite porous nanorods had high affinities for polar dye and the electrostatic attraction between the dye molecules and charged cobalt ferrite surface might be the predominant adsorption mechanism.

2.4.4 Influence of temperature

We varied the exposure temperatures of the experiment to study the effect of thermodynamics

on the dye removal efficiency. A relation was constructed between concentration and absorbance values at different temperatures of 37°C and 60°C as shown in Fig. 8 and Fig. 9 respectively. However, non significance difference was observed and the results indicated that temperature didn't influence the dye adsorption capacity of the porous nanorods.

3. Conclusions

The nanorods were successfully synthesized through hydrolysis of FeCl₃ and CoSO₄, or FeCl₃ and CoCl₂ solutions containing urea as stabilizer (different molar ratio Co²⁺/Fe³⁺/urea). Depending on the experimental condition, nanorods of different size, composition and magnetic properties were prepared. The results showed that porous CoFe₂O₄ porous nanorods can be used as an effective adsorbent for removing polar red from aqueous solution. Results showed that the synthesized porous could effectively remove high concentrations of polar red dye in a short contact time for cobalt ferrite nanotubes equal 94% and for cobalt ferrite porous nanorods equal 95% .

The amount of dye adsorbed was found to vary with initial pH; contact time and polar red concentration. The best pH values for favorable dye adsorption were in the range of 2-4. The dye adsorption equilibrium was attained after 60 min and the maximum adsorption capacity obtained was 100 mg of dye for 0.2 g CoFe₂O₄ porous nanorods.

The final results indicated that the CoFe₂O₄ nanotubes and porous nanorods can be considered as an efficient low cost and recyclable adsorbent for dye removal with efficiency 94% for Cobalt ferrite nanotubes and for Cobalt ferrite porous nanorods equals 95% .

Acknowledgments

We thank Department of Materials Science, Royal Institute of Technology, Stockholm SE-100 44, Sweden.

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