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Nanocrystalline ferrites used as adsorbent in the treatment process of waste waters resulted from ink jet cartridges manufacturing

Abstract: Dye pollution in waste waters causes serious environmental and health risk, legislation problems and is a serious challenge to environmental scientists. In this work the treatment of waste waters resulted from ink jet cartridges manufacturing, using different nanocrystalline ferrites $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) as adsorbent materials, has been investigated. The ferrites were obtained by thermal decomposition at 500°C of the magnesium and copper ferrioxalate coordination compounds. The nanocrystalline ferrites powder was investigated by various methods such as XRD, IR, SEM and EDX. The discoloration of the waste waters has been spectrophotometrically studied. The ferrites could be removed easily after adsorption by using a magnetic filtration process. The results indicated that the maximum adsorption efficiency was obtained after 60 min of treatment, magnesium ferrite showing a higher efficiency than the copper ferrite in the treatment process of waters resulted from ink jet cartridges manufacturing.

Keywords: nanocrystalline ferrites, oxalate, oxides, ink jet, adsorption

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1 Introduction

In order to minimize the waste discharge, the reuse and the recycling terms are also commonly used in the ink–jet cartridges manufacturing. The first step in the remanufacturing of the ink–jet cartridges before refilling is the washing of the remained ink. Consequently at this step results waste waters containing large variety of pollutants such as dyes and surfactants, which are characterized by high toxicity and low degradability [1–5]. The release of these waters in some effluents can reduce light penetration and photosynthesis, causing suffocation of aquatic flora and fauna [6]. Therefore these waste waters must be treated before discharge. In this aim there is a real need to develop an effective and cost viable waste water treatment [7–9]. Numerous methods have been studied for the removal of dyes from waste waters such as: flocculation/coagulation [3,5,10–12], oxidation [1], photocatalysis [13], ultrafiltration [2,8,14], adsorption [6,7,9] and biological processes [4]. Due to the easy of operation most of the researchers focused on the adsorption processes [6,7,9,15]. Anyway, this method presents some drawbacks such as: high cost, difficult disposal and regeneration [1,9]. In order to overcome these drawbacks in this study, adsorbent materials ferrite nanoparticles $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) were used in the removal process of dye from waste waters resulting from inkjet cartridges manufacturing. It was reported that these nanoparticles presented good efficiency as reusable adsorbents due to their reduced obtaining cost, high surface area and easy recovery using their magnetic properties [9,16–20]. The ferrites nanoparticles studied in this paper were obtained by thermal decomposition of coordination compounds at lower temperatures and, its superiority in comparison with other oxalate precursor methods of the mixed oxides [21].

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2 Experimental Procedure

2.1 Materials

All the reagents used for the synthesis of ferrites were analytical grade, including ferric(III) nitrate ($Fe(NO_3)_3\cdot9H_2O$, Mw = 403,95 g mol^{-1}, Merck), magnesium nitrate ($Mg(NO_3)_2\cdot6H_2O$, Mw = 256,41 g mol^{-1}, Merck), copper nitrate ($Cu(NO_3)_2\cdot3H_2O$, Mw = 241,60 g mol^{-1}, Merck), 1,2–ethanediol ($C_2H_4(OH)_2$, Mw = 62,07 g mol^{-1}, Merck) and 2M nitric acid solution (Merck).

The new elaborate method for synthesis of oxalate species is based on the redox reaction:

$$3C_2H_4(OH)_2 + 8NO_3^- + 2H^+ \rightarrow 3C_2O_4^{2-} + 8NO + 10H_2O$$

An aqueous solution of xEG (ethyleneglycol) + $2Fe(NO_3)_3\cdot9H_2O + M(NO_3)_2\cdot6H_2O + yHNO_3$ (2M) with $x \geq 3$ and $y \geq 2$ was prepared and heated in a water bath. The reaction was considered completed when no more gas evolution was observed. The solid reaction products were purified by refluxing from an acetone–water mixture. After filtration, the precipitates were finally washed with acetone and maintained in air until constant mass. The oxides $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) are obtained after the calcinations of the coordination compounds for one hour at 500°C using a heating rate of a 5°C min^{-1}.

The residual solution containing dyes was obtained from a local manufacturer where the empty ink–jet cartridges are refilled.

2.2 Apparatus and procedure

The FTIR spectra (KBr pellets) of the ferrites were recorded on a Vertex 70 BRUKER–FTIR spectrophotometer in the range 400–4000 cm^{-1}. The oxides were characterized by X–Ray diffraction (XRD) analysis. The powder X–Ray diffraction patterns of the obtained oxides were recorded at room temperature with a XRD using a Rigaku Ultima IV diffractometer, using Cu K_α radiation (λ = 1.5418 Å). SEM images were recorded using a Quanta FEG 250 microscope, equipped with an EDAX/ZAF quantifier.

The obtained ferrites powders were used as adsorbent material in the removal process of dye from waste water from the ink–jet cartridges remanufacturing. The waste waters before and after treatments with the ferrites were analyzed through UV–VIS spectrophotometry using a Varian Cary 50 spectrophotometer. The spectra were recorded in the range of 300–800 nm. In order to determine the efficiency of the studied adsorbent in the removal process of dye from waste waters the influence of the solid: liquid (S:L) ratio and contact time, upon the removal efficiency, was studied. In order to determine the optimum S:L ratio, 25 mL of residual waters was treated with various quantity of adsorbent materials (0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 g). The samples were shaken for 1 hour using a Julabo SW23 shaker, and after were filtered and the resulting solutions were again analyzed through UV–VIS spectrophotometry. After establishing the optimum S:L ratio the influence of the shaking time (15, 30, 45, 60, 90 and 120 min) upon the adsorption capacity was determined. The degree of adsorption was determined based on the following equation:

$$\eta = \frac{(Ads_{init} - Ads_{fin})}{Ads_{init}}100 \qquad (1)$$

where:
η represent the removal degree of dye, %;
ads_{init} represent the initial absorbance of the dye present in the waste water at 625 nm;
ads_{fin} represent the absorbance of the dye present in the waste water at 625 nm, after treatment with the studied ferrites.

3 Results and discussion

3.1 Characterization of nanocrystalline ferrites

The synthesis method of the coordination compound $[Fe_2M^{II}(C_2O_4)_4(OH_2)_6]$ (M^{II} = Mg, Cu) is based on the redox reaction between 1,2-ethanediol and nitrate ion, in the presence of nitric acid (2M) [21].

The oxides $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) are obtained after the calcinations of the coordination compounds at 500°C. The ferrites were identified by IR and XRD.

The IR spectra (Fig. 1) show two intense absorption bands ν_1 and ν_2, corresponding to the vibration of tetrahedral and octahedral complexes, which are indicative of formation of spinel structure being in agreement with the literature data [22,23,24]. The higher frequency band ν_1 is in the range 530–640 cm^{-1} and the lower frequency band ν_2 is in the range 400–480 cm^{-1}.

In Fig. 2 are presented the XRD patterns of the products obtained after independent calcinations in the furnace at 500°C in static air atmosphere. For both products the XRD patterns show the presence of the characteristic peaks of pure $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) ferrites which were identified using JCPDS 04–012–0916 and JCPDS 04–013–7127, respectively.

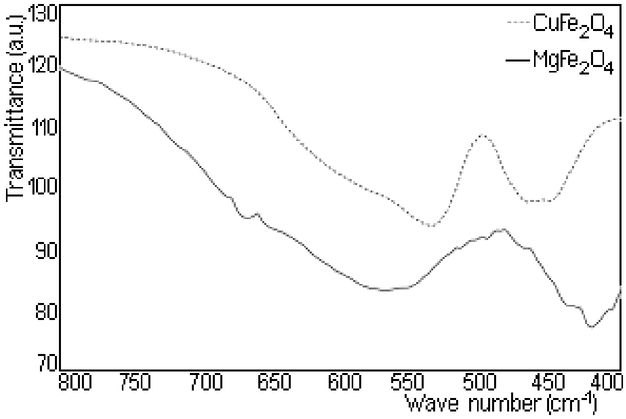

Figure 1: FTIR spectra of $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) ferrites obtained after the calcinations at 500ºC for 1h of the coordination compounds.

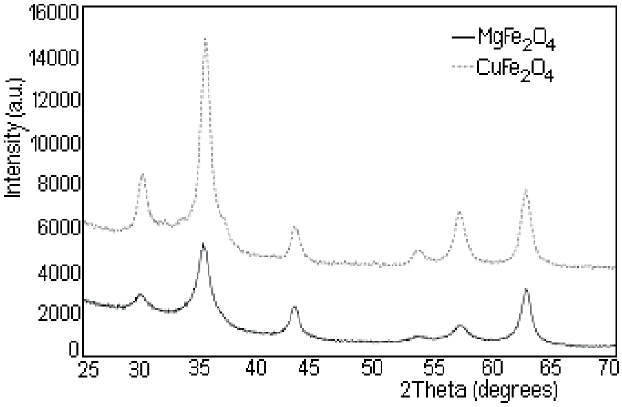

Figure 2: XRD patterns of $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) ferrites.

The average crystallites size was evaluated using Scherrer's formula [25]:

$$d_{XRD} = [0.91\lambda/(\beta\cos\theta)] \times 57.32 \qquad (2)$$

where: d_{XRD} is the crystallite size;
λ the wave length (Cu K_α);
β the corrected half–width obtained using α quartz as reference and the Waren formula, and
θ is the diffraction angle of the most intense diffraction peak.

The lattice parameter "a" was calculated using formula:

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad (3)$$

where: h, k, l are the Miller indices of the crystal planes;
d_{hkl} is the inter planer spacing.

As mentioned before, a heating treatment of the two coordination compounds performed at 500°C determines the formation $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) ferrites characterized by a lattice parameter at 8.41/8.40 Å ($MgFe_2O_4$/$CuFe_2O_4$) and an average crystallites size of 79/90 Å ($MgFe_2O_4$/$CuFe_2O_4$).

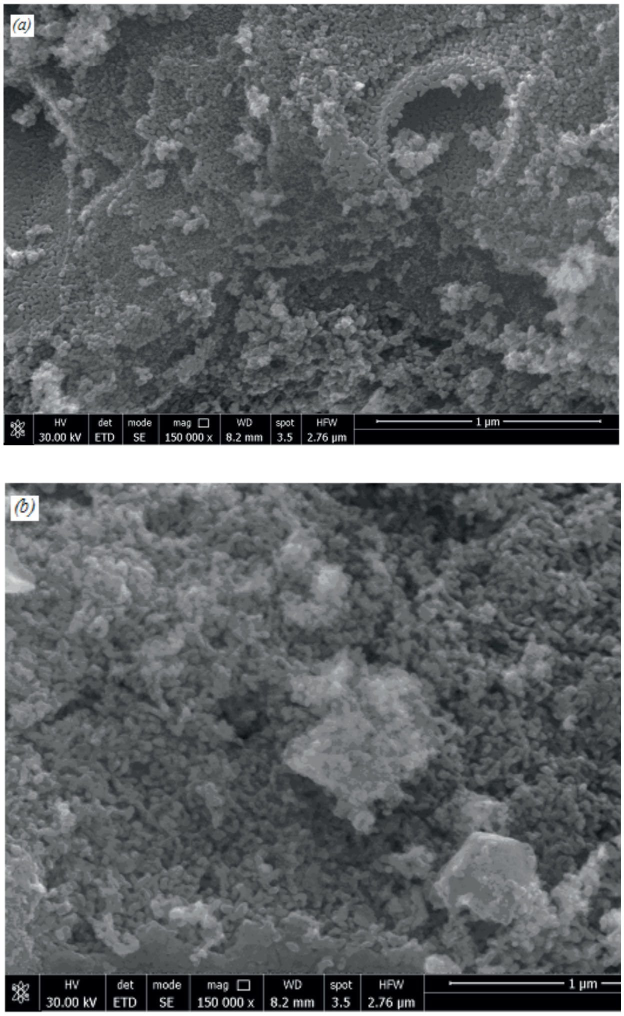

Figure 3: SEM images of $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) ferrites: (a) $MgFe_2O_4$ and (b) $CuFe_2O_4$.

Note that lattice parameter values are close to those reported by literature, while the average crystallites sizes are lower than the ones reported by literature for ferrites obtained by other methods [26–28], the adsorption maximum capacity is strongly influenced by ferrites particles size [16,29].

The SEM images (Fig. 3) show that the ferrites consist of agglomerated spherical particles with 10–30 nm average particle size.

Qualitative and quantitative EDX analyzes showed a high purity and corresponding stoichiometry of the products analyzed.

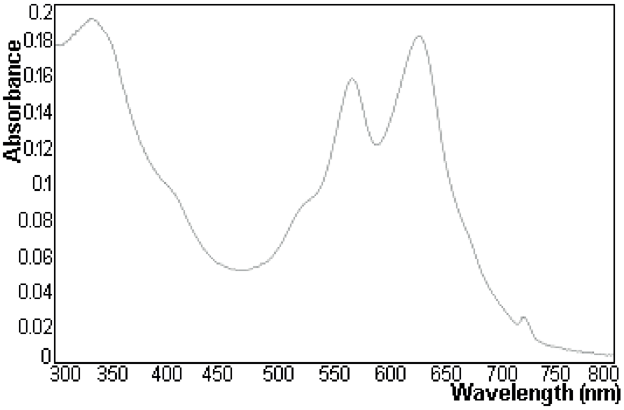

Figure 4: UV–VIS spectrum of the used waste water.

3.2 Use of obtained ferrites as adsorbent materials

The obtained ferrites were used in the removal process of dyes from waste waters resulting during the ink–jet cartridges manufacturing. The used waste water was analyzed through the UV–VIS spectrophotometry and the obtained spectrum between 300–800 nm is presented in Fig. 4. The studied water is a colored one which contains three colors at three specific wavelengths: 625, 564 and 333 nm. Because the color which absorbs at 625 nm presents the higher peak, which means is in the higher proportion, therefore in subsequent studies this wavelength was used to obtain absorption values. The influence of the S:L ratio upon the efficiency of the adsorption process of dye onto the studied ferrites is presented in Table 1.

From the experimental data it can be observed that the use of a higher quantity of copper ferrite didn't lead to a higher degree of separation of dye from aqueous solution. In the case of magnesium ferrite the increasing of the S:L ratio leads to the increasing of the adsorption process efficiency. This influence is not significant for a S:L ratio higher than 0.05 g of ferrite in 25 mL of waste waters. Therefore further studies are conducted at this S:L ratio for both studied ferrites.

The influence of the stirring time upon the efficiency of the adsorption process of dye onto the studied ferrites is presented in Table 2. It can be observed that for both studied ferrites the highest removal efficiency of the dye from waste waters is obtained in the first 60 min of stirring. At higher stirring time the increasing of the adsorption process efficiency is not significant, therefore is not recommended to work use a higher stirring time from the economic point of view. Also it can be noticed that the magnesium ferrite present a higher efficiency compared with the copper ferrite in the removal process of dye from the real waste water. This could be explained by the fact that the particles sizes of the magnesium ferrite are smaller than those of the copper ferrite; therefore the surface contact between the adsorbent and adsorbate is higher. The fact that the particle size of the nanoferrites influences the adsorption performance was also should by other researchers [17].

Table 1: The influence of the S:L ration upon the adsorption process efficiency.

S:L ratio, g of adsorbent: mL of waste waters	Adsorption process efficiency, %	
	$MgFe_2O_4$	$CuFe_2O_4$
0.02:25	47.1	60.8
0.03:25	67.8	60.6
0.04:25	76.1	61.1
0.05:25	96.9	60.7
0.06:25	97.3	59.5
0.07:25	97.9	68.2

Table 2: The influence of the stirring time upon the adsorption process efficiency.

Stirring time, min	Adsorption process efficiency, %	
	$MgFe_2O_4$	$CuFe_2O_4$
15	49.93	22.07
30	68.71	47.06
45	82.09	52.35
60	96.9	60.7
90	98.3	71.86
120	98.9	73.66

4 Conclusions

Nanocrystalline $M^{II}Fe_2O_4$ (M^{II} = Mg, Cu) ferrites with spinel structure were obtained after the calcinations of magnesium and copper ferrioxalate coordination compounds at 500°C. The FTIR spectra showed two characteristic metal oxygen vibrational bands responsible for the spinel oxides. The X–Ray diffraction patterns prove that at 500°C the spinel phase was obtained. The average particle size of oxides was in the range of 10–30 nm, as revealed by XRD and SEM techniques.

The nanoferrites obtained by thermal decomposition at 500°C of the magnesium and copper ferrioxalate coordination compounds show good adsorptive properties based on particles size. The obtained ferrites presented good efficiency in the removal process of dye from a real waste water. The highest degree of separation of the dye from the waste water resulted from the ink–jet cartridges remanufacturing is obtained when is used a S:L ratio of 0.05 adsorbent in 25 mL of waters for 1 h of shaking. In case of use of magnesium ferrite is achieved the total removal of dyes from the waste waters.

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