J. Nanoanalysis., 5(4): 249-254 Autumn 2018

ORIGINAL RESEARCH PAPER

Exclusion of heavy cations from wastewater using activated carbon/ $NiFe_2O_4$ nanocomposite prepared via co-precipitation method

Mahdi Ranjeh[1] and Mehdi Mousavi-Kamazani[2,*]

[1] Department of Chemistry, College of Science, Semnan University, Semnan, Iran
[2] New Technology Faculty, Semnan University, Semnan, Iran

Received: 2018-08-21 Accepted: 2018-09-29 Published: 2018-10-01

ABSTRACT

First, crystalline $NiFe_2O_4$ powder was synthesized on a nanoscale dimension by a simple one-step co-precipitation chemical route, and then used to produce activated carbon/$NiFe_2O_4$ nanocomposite. The structure and morphology of the as-prepared composite was characterized by X-ray diffraction (XRD) pattern, transmission electron microscope (TEM) and Fourier transform infrared (FT-IR) spectroscopy. Eventually, the as-prepared composite was used for exclusion of heavy cations from wastewater in different conditions. A significant absorption capacity (250 mg g^{-1}) showed that this nanocomposite could be useful for the removal of heavy cations from wastewater.

Keywords: *Carbon/$NiFe_2O_4$; Exclusion; Heavy Cation; Nanocomposite*

How to cite this article
Ranjeh M., Mousavi-Kamazani M. Exclusion of heavy cations from wastewater using activated carbon/$NiFe_2O_4$ nanocomposite prepared via co-precipitation method. J. Nanoanalysis., 2018; 5(4): 249-254. DOI: 10.22034/jna.2018.544277

INTRODUCTION

Ecological crisis of environmental pollution has been criticized for different issues. One of the major issues is the pollution caused by metals or their species in the environment. Heavy metal pollution affects flora, fauna and other abiotic components of the ecosystem [1]. Of course, many attempts have been made to remove them (e.g., "Low-cost adsorbents for heavy metal uptake from contaminated water: a review") [2]. One of the most attractive class of materials for technological applications is nano crystalline ferrites, which possess a general formula MFe_2O_4 (M = divalent metal ion, e.g. Ni, Co, Cu, Mn, Mg, Zn, Cd, etc.). Nickel ferrite ($NiFe_2O_4$), which has an inverse spinel structure, has been intensively examined as one of the magnetic nanomaterials. The divalent cations (Ni^{2+}) location in the crystal structure has a close relationship with the magnetic properties of the nickel ferrite. However, nickel ferrite exhibits super-paramagnetic behavior and is widely used as gas-sensor, magnetic fluids, catalysts, magnetic storage systems, photo magnetic materials, magnetic resonance imaging, site-specific drug delivery and microwave devices [3–11]. In one case, the removal of divalent cations of nickel and lead, and the oxyanions of hexavalent chromium were tested by the developer's adsorbents. The adsorption equilibrium and kinetics data were fitted to various models to evaluate and compare the performance with an activated carbon [12]. Another case studied the magnetic and electrical response of the soul-gel synthesized $NiFe_2O_4$ nanoparticles. Changes in the impedance plane plots with temperature were discussed and correlated to the microstructure of materials. Thermally activated hopping carriers between Fe^{3+}-Fe^{2+} and Ni^{2+}-Ni^{3+} ions were determined in terms of a decrease in the sample resistance and a change in the conduction mechanism around 318 K [13]. Chinnasamy et al. showed that Nano crystalline $NiFe_2O_4$ exhibits a mixed spinel structure with Ni^{2+} ions occupying

* Corresponding Author Email: *m.mousavi@semnan.ac.ir*

both (A) and (B) sites. It was also found that $NiFe_2O_4$ nanoparticles with a mixed spinel structure exhibit interesting electrical, magnetic, gas, and humidity sensing properties [14]. Nano-sized $NiFe_2O_4$ is one type of ferrite that has been studied extensively. It shows peculiar structural and magnetic properties. Small particle size promotes a mixed spinel structure, whereas the bulk form is an inverse spinel. As far as the magnetic properties of these materials are concerned, spin glass like behavior can be considered as the most interesting property that leads to high field irreversibility, shift of the hysteresis loops, and anomalous relaxation dynamics [15]. This study described a new process based on the use of co-precipitation technique for the synthesis of pure $NiFe_2O_4$ nanoparticles and activated carbon/$NiFe_2O_4$ nanocomposite. Moreover, the study investigated the exclusion of heavy cations from wastewater. According to the opinion of the present study' researchers, a good efficiency has not been achieved in the previous methods; however, the method developed here showed a good efficiency with the use of less material, which is economically feasible.

EXPERIMENTAL

Materials and physical measurements

$Fe(NO_3)_3.9H_2O$ (Merck), $Ni(NO_3)_2.6H_2O$ (Aldrich), NaOH (Merck), and ethanol (Merck) were used in this study. X-ray diffraction (XRD) patterns were recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered Cu Kα radiation at a scan range of $10<2\theta<80$. Philips EM208 field emission transmission electron microscope operated at 100 kV was used to perform transmission electron microscopy. Fourier transform infrared (FT-IR) spectra were obtained on Magna-IR, spectrometer 550 Nicolet with 0.125 cm^{-1} resolution in KBr pellets in the range of 400-4000 cm^{-1}.

Synthesis of $NiFe_2O_4$ nanoparticles

Two g of NaOH was dissolved in 100 cc of distilled water and heated to boiling point. Then, a 50 cc solution of $Fe(NO_3)_3.9H_2O$ (5.494 g) and $Ni(NO_3)_2.6H_2O$ (1.977 g) in water was prepared and added to the boiling solution. The mixed solution was then refluxed at 100 °C for 2.5 h. Finally, the resulting product was separated from the water and dried at 90 °C for 10 h.

Preparation of activated carbon/$NiFe_2O_4$ composite

Activated carbon/$NiFe_2O_4$ composite was synthesized by a facile refluxing route in solution of NaOH. In a typical procedure, a certain amount of activated carbon was added into 150 mL alkaline solution containing 3.4 g sodium hydroxide, and stirred at room temperature for 35 min to get the activated carbon suspension. The suspension was then maintained at 120 °C to keep the boiling state. 50 mL metal nitrate solution (aqueous) was prepared by dissolving $Fe(NO_3)_3.9H_2O$ (5.494 g) and $Ni(NO_3)_2.6H_2O$ (1.977 g) in distilled water. The solution was poured as quickly as possible into the above boiling suspension. Then, the mixture solution was refluxed at 100 °C for 2.5 h. The resulting product was separated from water through a simple magnetic procedure and then dried at 90 °C for 10 h.

Removal of heavy cations by activated carbon/$NiFe_2O_4$ composite

Researchers of the present study added 0.1 g of activated carbon/$NiFe_2O_4$ composite to 25 ml of a

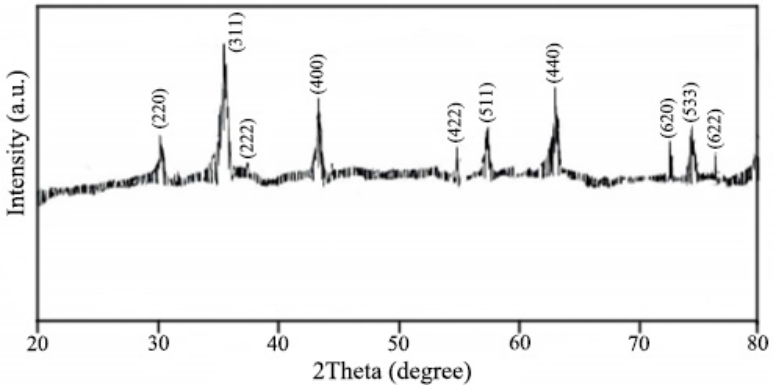

Fig. 1. XRD pattern of the as-synthesized $NiFe_2O_4$ nanoparticles

50 ppm solution of heavy cations and stirred for 5 h. The solution was then smooth and reached 100 cc with 1% nitric acid. Ultimately, absorption was read by AAS (Atomic Absorption Spectroscopy). Table 1 shows the results of the studies.

RESULTS AND DISCUSSION

Fig. 1 depicts XRD pattern of the as-synthesized $NiFe_2O_4$ nanoparticles. The diffraction peaks observed in the figure are in good agreement with cubic phase of $NiFe_2O_4$ (space group fd3m and JCPDS: 10-0325). The sharp and strong diffraction peaks in the figure indicate that the as-prepared product is well crystallized. In addition, no diffraction peaks from other species such as Fe_2O_3 or NiO could be detected, showing that the obtained sample is pure. The crystallite size diameter (D) of the as-obtained products has been calculated by Scherer equation [16]:

$$D(hkl) = k\lambda/\beta cos\theta \quad (1)$$

where D is the crystallite size, as calculated for the (hkl) reflection, k is the wavelength of Cu Kα radiation (0.154 nm), k is a constant related to the crystal shape (0.94), and β is the value of full width at half-maximum intensity (FWHM). Crystallite sizes of the as-prepared $NiFe_2O_4$ particles was found to be 21 nm. The lattice constants of all the samples are calculated using the following relation [17, 18]:

$$a = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$$

The values are consistent with the earlier reported values of 0.833 nm for nano $NiFe_2O_4$ [19] and 0.8339 nm for the bulk $NiFe_2O_4$ [20], which prove the efficiency of the synthesis technique provided here.

Figs. 2a and b shows the FT-IR spectra of the as-prepared $NiFe_2O_4$ and activated carbon/$NiFe_2O_4$, respectively. A broad absorption band at about 3400 cm^{-1} represents a stretching mode of H_2O molecules and OH groups [21, 22]. Two other principle absorption bands in the range of 400 - 600 cm^{-1} are also observed in the FT-IR spectra. The first band is around 500 cm^{-1} and the second one is around 585 cm^{-1}, which can be attributed to

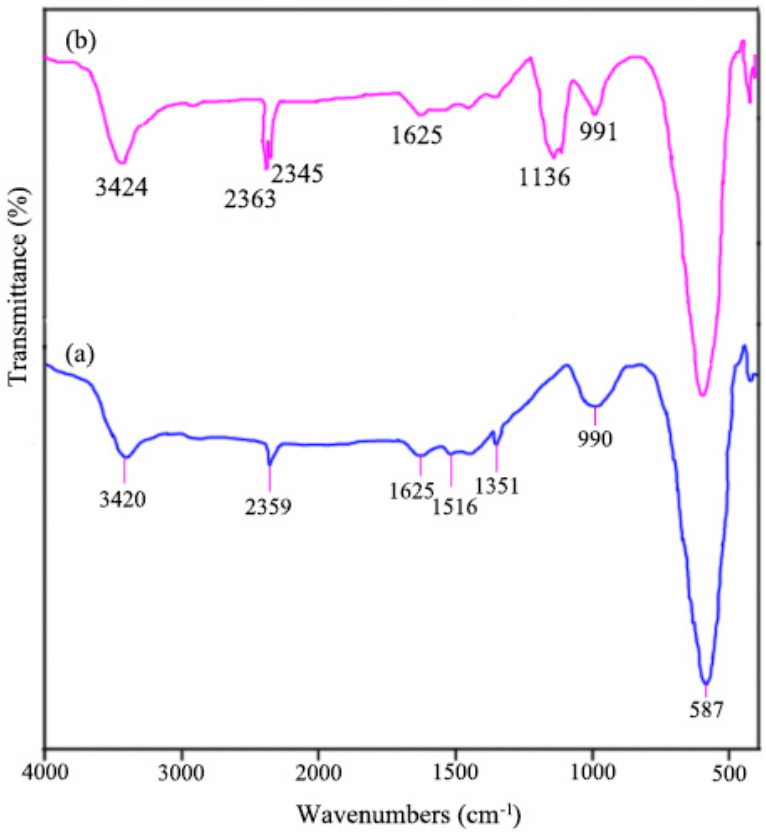

Fig. 2. FT-IR spectra: a) $NiFe_2O_4$ nanoparticles and b) activated carbon/$NiFe_2O_4$ nanocomposite

the long bond length of oxygen metal ions in the octahedral sites and shorter bond length of oxygen metal ions in the tetrahedral sites in the spinel structure, respectively [23]. The band of 1135 cm^{-1} in Fig. 2b shows the connection of $NiFe_2O_4$ to surface of activated carbon. The morphology of the as-prepared nanocomposite was investigated by TEM image. As shown in Fig. 3. It could be seen that $NiFe_2O_4$ particles deposited on the surface of activated carbon in the composite are uniform with the particle size in the range of 20–30 nm.

The effect of adsorption of nickel ferrite ($NiFe_2O_4$) nanoparticles and activated carbon/$NiFe_2O_4$ nanocomposite on heavy cations were investigated in different conditions. The removal of Ag^+, Cu^{2+}, Zn^{2+}, and Cd^{2+} ions from wastewater was evaluated in this study. Table 1 reports the results of the studies. According to Table 1, it could be said that the absorption of copper by both nanoparticles and nanocomposite is higher than others, which

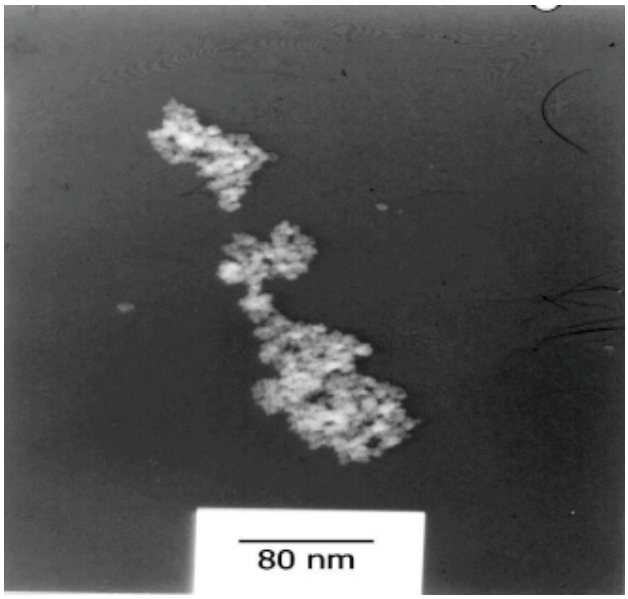

Fig. 3. TEM image of the as-prepared activated carbon/$NiFe_2O_4$ nanocomposite

Table 1. Results of adsorption of 12.5 mg of heavy cations by 1 g of adsorbent

Adsorbent	*Heavy Cations and amounts of adsorbation*					
	Cd^{2+}	Cd^{2+}(NaCl 0.001 M)	Cd^{2+}(NaCl 0.1 M)	Cu^{2+}	Zn^{2+}	Ag^+
Nanocomposite	10.33	10.25	1.43	12.34	11.88	8.7
	82.64%	82%	11.44 %	98.72 %	95.04 %	69.60 %
Nanoparticles	11.75	11.50	3.17	12.481	11.91	9.05
	94%	92%	25.36%	99.85%	95.28%	72.40%

Table 2. Properties of heavy cations

Cations / *Pr property*	Cd^{2+}	Cu^{2+}	Zn^{2+}	Ag^+
Density(g/cm^3)	8.65	8.96	7.14	10.49
Ionic radius (pm)	95	73	74	115
Boiling Point(K)	1040	3200	1180	2435
Melting Point(K)	592.22	1357.77	692.68	1234.93
Superconducting temperature(K)	0.517	-	0.85	-
Seawater : Pacific surface(ppm)	$1.1 * 10^{-6}$	$8 * 10^{-5}$	$5 * 10^{-5}$	10^{-7}

may be caused by a smaller ionic radius of copper. According to Table 2, the size of ion radii is as follows:

$Cu^{2+} < Zn^{2+} < Cd^{2+} < Ag^{+}$

More surface absorption can be expected with a smaller ionic radius. Another important point is that the empty nanoparticles have better efficiencies than composite and this could be attributed to the reduction of the hydroxyl group on the surface of the composite. The presence of hydroxyl groups is crucial for the absorption of cations. These groups are reduced by compositing. Hence, the reduction of efficiency can be attributed to this. NaCl molestation was also studied in the presence of heavy cations. As can be seen, the absorption of Cd^{2+} ions in the presence of sodium ion has declined sharply and this may be caused by the occupation of the surface of the nanoparticles with sodium ions.

CONCLUSION

In short, nickel ferrite and activated carbon/$NiFe_2O_4$ nanocomposite were synthesized by a simple co-precipitation method. The structure and morphology of the as-prepared composite were characterized by XRD, TEM, and FT-IR spectroscopy. Absorption of heavy ions of these synthetic materials was then investigated. According to the results, the nickel ferrite has a better absorption than its composite with active charcoal. The size of the ions affects the absorption rate and smaller ions are more absorbed. The presence of inhibitory ions is also important, and sodium ion strongly reduces the absorption of cadmium cations.

ACKNOWLEDGEMENTS

This research work was supported by Semnan University, Semnan, Iran.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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