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Arsenic removal from water by magnetic $Fe_{1-x}Co_xFe_2O_4$ and $Fe_{1-y}Ni_yFe_2O_4$ nanoparticles

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This article studies the effects of Co and Ni replacement in $Fe_{1-x}Co_xFe_2O_4$ and $Fe_{1-y}Ni_yFe_2O_4$ (x, $y = 0$, 0.05, 0.1, 0.2, 0.5) nanoparticles, pH, weight of nanoparticles/mL of water, and time of stirring on the arsenic removal ability. The results showed that a small amount ($0.25\,g\,L^{-1}$) of Fe_3O_4 nanoparticles after stirring time of 3 min can reduce the arsenic concentration from 0.1 to $0.01\,mg\,L^{-1}$. The removal was also affected by the pH of the water. Absorption of arsenic by nanoparticles was effective when pH was smaller than seven and reduced with the increase of pH. At pH of 13, there was a strong release of arsenic ions from arsenic-absorbed nanoparticles back to water. The time of stirring was studied from 1 min to 2 h and the optimal time was about few minutes. Co and Ni's presence was reported to keep saturation magnetisation stable under working conditions. For Co replacement, absorption does not change significantly when $x \leq 0.1$ and slightly reduces when $x > 0.1$. The presence of Ni improved the absorption in most cases.

Keywords: magnetic nanoparticles; ferrites; arsenic removal; water treatment

1. Introduction

Arsenic occurs naturally in rocks, soil, water, air, plants, and animals. It can be further released into the environment through natural activities such as volcanic action, erosion of rocks and forest fires, or through human actions. Higher levels of arsenic tend to be found in ground water sources than in surface water sources of drinking water. Arsenic-contaminated water has been a serious problem especially in Vietnam, Bangladesh and in some other areas in the world (http://www.epa.gov/safewater/arsenic) [1]. Human exposure to arsenic can cause both short- and long-term health effects. Short-term or acute effects can occur within hours or days of exposure. Long-term or chronic effects occur over many years. Long-term exposure to arsenic has been linked to cancer of the bladder, lungs, skin, kidneys, nasal passages, liver, and prostate. Short-term exposure to high doses of arsenic can cause other adverse health effects [2,3]. The World Health Organization (WHO) has set a maximum permissible concentration (MPC) value of

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$0.01\,\mathrm{mg\,L^{-1}}$ which has been applied in many countries. There are many arsenic-removal techniques which have been available such as co-precipitation, adsorption in fixed-bed filters, membrane filtration, anion exchange, electrocoagulation, and reverse osmosis [4,5]. Iron oxides have been reported to have a high affinity for the adsorption of arsenic and arsenate [6–8] due to their ability to form inner-sphere bidentate-binuclear complexes with iron oxides [9,10]. Iron oxide nanoparticles with large surface area are promising for arsenic removal. Some researchers have been paid to study the effects of environment on arsenic adsorption ability of magnetite Fe_3O_4 nanoparticles [8,11]. Magnetite nanoparticles have the highest saturation magnetisation of $90\,\mathrm{emu\,g^{-1}}$ among iron oxides. Therefore, magnetite nanoparticles can be used to adsorb arsenic ions followed by magnetic decantation. Other iron oxides and hydroxides have been reported to have arsenic ability. However, the magnetic properties of these compounds are much less than that of magnetite. Oxidation of magnetite which resulted in the reduction of the saturation magnetisation was found. Research by our group showed that the replacement of Fe^{2+} in Fe_3O_4 by a small amount of Co^{2+} or Ni^{2+} can improve the oxidation resistance of the compound [13]. Oxidation resistance is an important factor for arsenic removal under atmospheric conditions. In this article, we study arsenic adsorption ability of $Fe_{1-x}Co_xFe_2O_4$ (Co-ferrites) and $Fe_{1-y}Ni_yFe_2O_4$ (Ni-ferrites) (x, $y = 0$, 0.05, 0.1, 0.2, 0.5) nanoparticles.

2. Materials and methods

Magnetite particles with size of 15 nm were prepared by conventional co-precipitation of Fe^{3+} and Fe^{2+} ions by OH^- at room temperature. In a typical synthesis, 4.17 g of $FeCl_3 \cdot 6H_2O$ and 1.52 g of $FeCl_2 \cdot 4H_2O$ (such that $Fe^{3+}/Fe^{2+} = 2$) were dissolved in 80 mL water (concentration of Fe^{2+} is 0.1 M) with vigorous stirring. A solution of 6 ml NH_4OH 35% was added at the rate of one drop per second at room temperature during constant stirring. Black precipitates of Fe_3O_4 ($FeO \cdot Fe_2O_3$) were formed and isolated from the solvent by magnetic decantation. Water washing and decantation process were repeated four times to remove excess solution. In a similar way, $Fe_{1-x}Ni_xO \cdot Fe_2O_3$ and $Fe_{1-y}Co_y \cdot Fe_2O_3$ with $x = 0.05$, 0.1, 0.2, 0.5 and $y = 0.2$, 0.4 nanoparticles were made by replacing Fe^{2+} by Ni^{2+} and Co^{2+} using $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$, respectively. All procedures were conducted under N_2 atmosphere. A Transmission Electron Microscope (TEM) JEM1010-JEOL was used to determine particle size. The structure was examined by X-ray diffractometer (XRD) D5005, Bruker, using Cu-Kα radiation. Magnetic properties were measured by Vibrating Sample Magnetometer DMS 880-CTS. Arsenic solution ($0.1\,\mathrm{mg\,L^{-1}}$ of As^{3+}) was obtained by dissolving As_2O_3 in doubly distilled water. The adsorption process occurred when 0.25–1.5 g of nanoparticles was stirred in 1 L of arsenic solution for the time of 1–60 min. Then the nanoparticles were collected by an external magnet. The remaining solution was subjected for arsenic concentration by Atomic Absorption Spectroscopy (AAS).

3. Results and discussion

Figure 1 presents the TEM image of the Fe_3O_4 nanoparticles with particle size of 10–16 nm. The particles were almost spherical and had low size dispersity. The mean

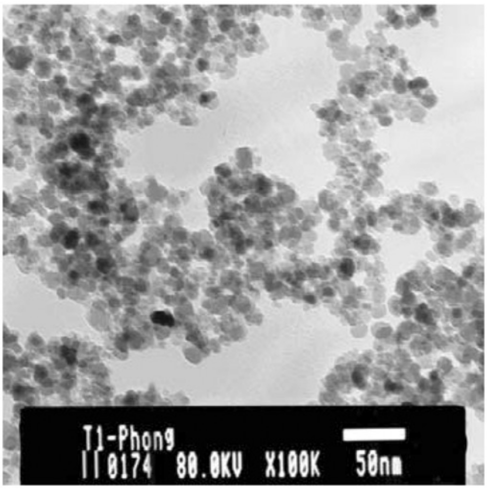

Figure 1. TEM image of the Fe_3O_4 nanoparticles.

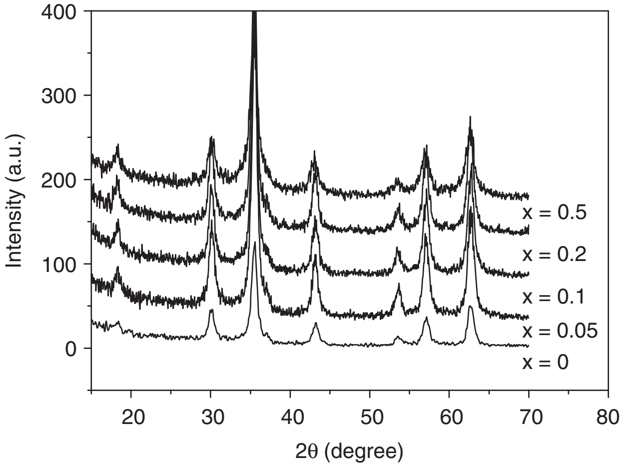

Figure 2. XRD patterns of the magnetite nanoparticles.

particle size was estimated to be 13.3 ± 3.1 nm. The surface area of $77.9\,m^2\,g^{-1}$ was calculated for magnetite sample from the mean particle and magnetite density ($5.18\,g\,cm^{-3}$). XRD patterns of magnetite, Co-ferrites (Figure 2), and Ni-ferrites (not shown) revealed that the particles have the invert spinel crystalline structure as in the bulk phase. The presence of Co^{2+} and Ni^{2+} ions did not change the particle size and reflection peaks significantly. The field dependence of magnetisation showed that all samples were superparamagnetic at room temperature. In an inverse spinel magnetite, half the Fe^{3+} ions were located at A sites and the other half of them, together with the divalent Fe^{2+} ions, were located at B sites. The Co^{2+} and Ni^{2+} ions preferred to replace at B sites.

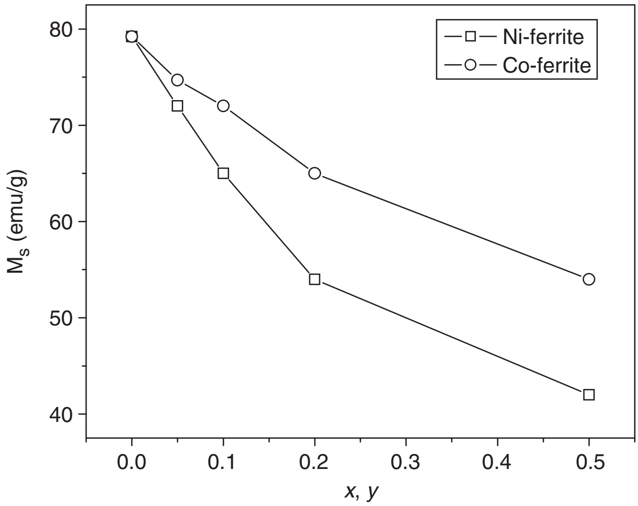

Figure 3. Saturation magnetisation of the Co- and Ni-ferrite as a function of Co^{2+} (x) and Ni^{2+} (y) content.

Therefore, the orientation of spins is as follows:

$$\overrightarrow{\mathrm{Fe}^{3+}}\left(\overleftarrow{\mathrm{Co}_x^{2+}}\,\overleftarrow{\mathrm{Fe}_{1-x}^{2+}}\,\overleftarrow{\mathrm{Fe}^{3+}}\right)\mathrm{O}_4^{2-}$$

$$\overrightarrow{\mathrm{Fe}^{3+}}\left(\overleftarrow{\mathrm{Ni}_y^{2+}}\,\overleftarrow{\mathrm{Fe}_{1-y}^{2+}}\,\overleftarrow{\mathrm{Fe}^{3+}}\right)\mathrm{O}_4^{2-}.$$

According to Neel's theory [14], saturation magnetisation for a formula unit of the Co- and Ni-ferrites can be determined by:

$$M_s^{\text{Co-ferrite}} = (4 - 2x)\mu_B$$

$$M_s^{\text{Ni-ferrite}} = (4 - y)\mu_B.$$

The magnetic moment of Ni^{2+} and Co^{2+} ions is 2 μ_B and 3 μ_B, respectively. As a result, the saturation magnetisation of the Co- and Ni-ferrites linearly reduces with x and y. Figure 3 presents the saturation magnetisation as a function of Co and Ni content. A linear dependence was found in the samples with Co and Ni content lower than 0.5. At the higher content (x, $y = 0.5$), the Co and Ni atoms can also place at A sites which resulted in the deviation from the linear dependence. Arsenic-adsorption ability of magnetite, Co-, and Ni-ferrites was studied with different conditions of stirring time, concentration of nanoparticles, and pH. Table 1 shows the stirring time dependence of arsenic removal of $1\,\mathrm{g\,L^{-1}}$ of Co-ferrites at neutral pH. The starting concentration of $0.1\,\mathrm{mg\,L^{-1}}$ was reduced about 10 times down to the MPC value of $10\,\mu\mathrm{g\,L^{-1}}$ after stirring for few minutes. The removal process did not seem to depend significantly on the concentration of x in the Co-ferrites. Similar results were found for the Ni-ferrites, in which arsenic concentration was reduced to the MPC value after a few minutes of stirring and the removal did not

Table 1. Arsenic concentration ($\mu g\, L^{-1}$) remained in water after removal by $1\, g\, L^{-1}$ of the Co-ferrites as a function of the stirring time.

Time (min)	$x = 0.05$	$x = 0.1$	$x = 0.2$	$x = 0.5$
1	10	11	6	6.5
3	6	5	8.5	7
7	10	9	4.2	7.8
15	9	12	5	6.9
30	12	4.5	5	11.2
60	4.5	5	8	9.8

change significantly with y. We also studied the effects of the weight of nanoparticles on the removal process. The stirring time was fixed to be 3 min and the weight of samples was changed from 0.25 to $1.5\, g\, L^{-1}$ with a step of $0.25\, g\, L^{-1}$. The results showed that, after 3 min, the optimal weight to reduce arsenic concentration down to the value lower than the MPC was $0.25\, g\, L^{-1}$ for magnetite and $0.5\, g\, L^{-1}$ for Co- and Ni-ferrites.

The arsenic adsorption was reported to be independent of pH in the range of 4–10. However, at high pH values, the adsorption reduced significantly. Arsenic was desorbed from the adsorbent at alkaline pH [8]. Our reported results were conducted at pH of 7. After arsenic adsorption, the nanoparticles were stirred under pH of 13 to study the desorption process. Nanoparticles were collected by a magnet and the arsenic concentration in the solution was determined by AAS. Results showed that 90% of the arsenic was desorbed from nanoparticles. The nanoparticles after desorption did not show any difference in arsenic re-adsorption ability. The adsorption–desorption process was repeated four times, which proved that the nanoparticles can be reused for arsenic removal.

4. Conclusion

The presence of Co^{2+} and Ni^{2+} in $Fe_{1-x}Co_xFe_2O_4$ and $Fe_{1-y}Ni_yFe_2O_4$ with oxidation resistance did not change the arsenic-adsorption ability significantly. With a small amount of materials and simple preparation, we could reduce arsenic concentration to a value lower than the MPC.

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