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

Nguyen Hoang Hai*, Nguyen Dang Phu

Center for Materials Science, Faculty of Physics, College of Science, VNU
334 Nguyen Trai, Hanoi, Vietnam

Absrtact. This paper studied the effects of Co, Ni replacement in the $Fe_{1-x}Co_xFe_2O_4$ 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 small amount of 0.25 g/l of Fe_3O_4 nanoparticles after stirring time of 3 minutes can reduce the arsenic concentration from 0.1 mg/l to 0.01 mg/l. The removal was also affected by the pH of the water. Absorption of arsenic by nanoparticles was effective when pH was smaller than 7 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 minute to 2 hours, the optimal time was about few minutes. Co and Ni presence was reported to maintain saturation magnetization 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 more 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 some areas in the world [1, 2]. Human exposure to arsenic can cause both short and long term health effects. Short or acute effects can occur within hours or days of exposure. Long 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 [3, 4]. The World Health Organization (WHO) maximum permissible concentration (MPC) value was set as 0.01 mg/l which has been applied in many countries. There are many arsenic-removal techniques which have been available such as coprecipitation, adsorption in fixed-bed filters, membrane filtration, anion exchange,

---

* Corresponding author. Tel.: (84-4) 35582216
E-mail: nhhai@vnu.vn

electrocoagulation, and reverse osmosis [5, 6]. Iron oxides have been reported to have a high affinity for the adsorption of arsenic and arsenate [7-9] due to the ability to form inner-sphere bidentate-binuclear complexes with iron oxides [10-11]. Iron oxide nanoparticles with large surface area are promising for arsenic removal. Some researches have been paid to study the effects of environment on arsenic adsorption ability of magnetite Fe_3O_4 nanoparticles [9, 12]. Magnetite nanoparticles have highest saturation magnetization of 90 emu/g 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, magnetic properties of these compounds are much less than that of magnetite. Oxidation of magnetite which resulted to the reduce of the saturation magnetization was found. In a research of our group reported that 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 [14]. Oxidation resistance is an important factor for arsenic removal under atmospheric conditions. In this paper, we studied 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 coprecipitation of Fe^{3+} and Fe^{2+} ions by OH^- at room temperature. In a typical synthesis, 4.17 g of $FeCl_3.6H_2O$ and 1.52 g of $FeCl_2.4H_2O$ (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 with the rate of 1 drop per second at room temperature during constant stirring. Black precipitates of Fe_3O_4 ($FeO.Fe_2O_3$) were formed and isolated from the solvent by magnetic decantation. Water washing and decantation process were repeated four times to remove excess solution. By a similar way, $Fe_{1-x}Ni_xO.Fe_2O_3$ and $Fe_{1-y}Co_y.Fe_2O_3$ 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 $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$, respectively. All procedures were conducted under N_2 atmosphere. Electron Transmission Microscope (TEM) JEM1010-JEOL was used to determine particle size. The structure was examined by X-ray diffractometer (XRD) D5005, Bruker, using Cu K_α radiation. Magnetic properties were measured by Vibrating Sample Magnetometer DMS 880-CTS. Arsenic solution (0.1 mg/l of As^{3+}) was obtained by dissolving As_2O_3 in doubly distilled improve the oxidation resistance of the compound [16]. Oxidation resistance is an important factor for arsenic removal under atmospheric conditions. In this paper, we studied 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.

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 low size dispersity. The mean particle size was estimated to be 13.3 ± 3.1 nm. The surface area of 77.9 m^2/g was calculated for magnetite sample from the mean particle and magnetite density (5.18 g/cm^3). XRD patterns of magnetite, Co-ferrites (Fig. 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 magnetization showed that all samples were superparamagnetic at room temperature. In inverse spinel magnetite, a half of Fe^{3+} ions locate at A sites and the half of

tthem together with the divalent Fe^{2+} ions locate at B sites. The Co^{2+} and Ni^{2+} ions prefer to replace at B3 sites. Therefore, the orientation of spins is as followings:

$$\overrightarrow{Fe^{3+}}\left(\overleftarrow{Co_x^{2+}\ Fe_{1-x}^{2+}\ Fe^{3+}}\right)O_4^{2-}$$

$$\overrightarrow{Fe^{3+}}\left(\overleftarrow{Ni_y^{2+}\ Fe_{1-y}^{2+}\ Fe^{3+}}\right)O_4^{2-}$$
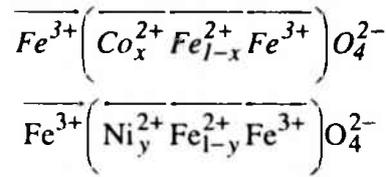
According to Neel theory [15] saturation magnetization for a formula unit of the Co- and Ni-ferrites ccan be determined by:

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

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

Magnetic moment of Ni^{2+} and Co^{2+} ions is $2\,\mu_B$ and $3\,\mu_B$, respectively. As a result, the saturation cof magnetization of the Co- and Ni-ferrites linearly reduces with x and y. Figure 3 presents the ssaturation magnetization as a function of Co and Ni content. A linear dependence was found in the ssamples with the Co and Ni content lower than 0.5. At the higher content (x, y = 0.5), the Co and Ni aatoms can also place at A sites which resulted in the deviation from the linear dependence.
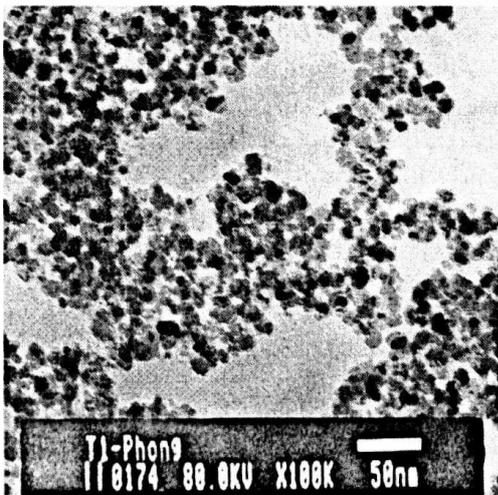
Fig. 1. TEM image of the Fe_3O_4 nanoparticles.
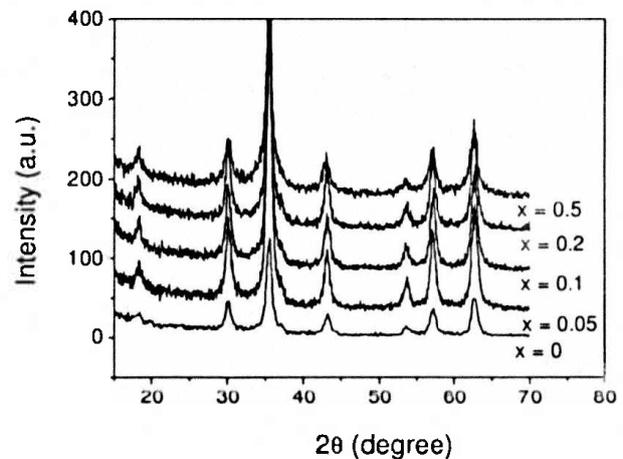
Fig. 2. XRD patterns of the magnetite nanoparticles.

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 g/l of Co-ferrites at neutral pH. The starting concentration of 0.1 mg/l was reduced about 10 times down to the MPC value of 10 µg/l after stirring time of 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 few minutes of stirring and the removal did not 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 minutes and the weight of samples was changed from 0.25 g/l to 1.5 g/l with step of 0.25 g/l. The results showed that, after 3 minutes, the optimal weight to reduce arsenic concentration down to the value lower than the MPC was 0.25 g/l for magnetite and 0.5 g/l for Co- and Ni-ferrites.
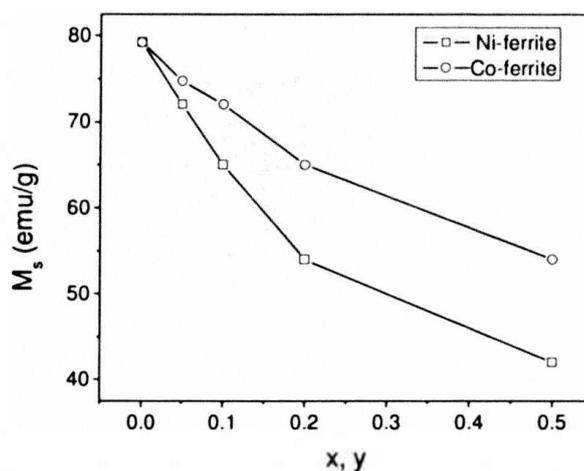
Fig. 3. Saturation magnetization of the Co- and Ni-ferrite as a function of Co^{2+} (x) and Ni^{2+} (y) content.

The arsenic adsorption was reported to be independent of pH in the range of 4 to 10. However, at high pH value, the adsorption reduced significantly. Arsenic was desorbed from the adsorbent at alkaline pH [9]. 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 arsenic concentration in the solution was determined by AAS. Results showed that 90% of 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 4 times, which proved that the nanoparticles can be reused for arsenic removal.

Table 1. Arsenic concentration ($\mu g/l$) remained in water after removal by 1 g/l 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

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 significantly arsenic adsorption ability. With small amount of the materials, simple preparation, we could reduce arsenic concentration to the value lower than MPC.

References

[1] http://www.epa.gov/safewater/arsenic

[2] M. Bissen, F.H. Frimmel, Arsenic–A review. Part I: Occurrence, toxicity, speciation, mobility, *Acta Hydroch. Hydrob.* 31 (2003) 9.

[3] L.C.D. Anderson, K.W. Bruland, Biogeochemistry of arsenic in natural waters: The importance of methylated species, *Environ. Sci. Technol.* 25 (1991) 420.

[4] W.P. Tseng, H.M. Chu, S.W. How, J M. Fong, C.S. Lin, S. Yeh, Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan, *J. Nat. Cancer Inst.* 40 (1968) 453.

[5] L.G. Twidwell, J. McCloskey, P. Miranda, M. Gale, Technologies and potential technologies for removing arsenic from process and mine wastewater, *in Proceedings global symposium on recycling, waste treatment and clean technology*, Ed. I. Gaballah, J. Hager, R. Solozabal, Warrendale, PA. (1999) 1715.

[6] M. Bissen, F.H. Frimmel, Arsenic–A review. Part II: Oxidation of arsenic and its removal in water treatment, *Acta Hydroch. Hydrob.* 31 (2003) 97.

[7] M.L. Pierce and C.B. Moore, Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.* 15 (1982) 1247.

[8] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.* 32 (1998) 344.

[9] S. Yean, L. Cong, C.T. Yavuz, J.T. Mayo, W.W. Yu, A.T. Kan, V.L. Colvin, M.B. Tomson, Effect of magnetite particle size on adsorption and desorption of arsenite and arsenate, *J. Mater. Res.*, 20 (2005) 3255.

[10] S. Fendorf, M.J. Eick, P. Grossl, Arsenate and chromate retention mechanisms on goethite Surface structure, *Environ. Sci. Technol.* 31 (1997) 315.

[11] A. Manceau, The mechanism of anion adsorption on ironoxides-Evidence for the bonding of arsenate tetrahedra on free Fe(O,OH)(6) edges, Geochim. Cosmochim, *Acta* 59 (1995) 3647.

[12] X.H. Sun, H.E. Doner, An investigation of arsenate and arsenite bonding structure on goethite by FTIR, *Soil Sci.* 161 (1996) 865.

[13] G.A. Waychunas, B.A. Rea, C.C. Fuller, J.A. Davis, Surface chemistry of ferrihydrite, Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. Geochim. Cosmochim, *Acta* 57 (1993) 2251.

[14] N.H. Hai, N.D. Phu, N. Chau, H.D. Chinh, L.H. Hoang, D.L. Leslie-Pelecky, Mechanism for Sustainable Magnetic Nanoparticles under Ambient Conditions, *J. Korean Phys. Soc.* 52 (2007) 1327.

[15] L. Neel, *Ann. de Phys.* 3 (1948) 137.