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CONTENTS

Study on the manufacture and application of nano Fe_3O_4 materials doped with manganese for treatment of water contaminated with Arsenic (III)

Nguyen Van Dung[1*], Nguyen Thi Thu Trang[2], Dao Dinh Thuan[1]
[1]Faculty of Environment, Hanoi University of Mining and Geology, Hanoi, Vietnam
[2]National Economics University, Hanoi, Vietnam
*Corresponding author: nguyenvandung@humg.edu.vn

***Abstract*: This article reports results of a research on manufacture and application of Fe_3O_4 nanomaterial doped with Mn (Fe_3O_4-x%Mn) for the treatment of water contaminated with As(III). The materials were synthesized by chemical method and it's particle size was studied by the XRD and TEM techniques. Experimental results showed that the materials were in crystallized form of cubic face centered structure with particles sizes ranging from 8 to 12 nm. The materials have paramagnetic property with values of magnetization (Ms) of 53 ÷ 65.8 emu/g at room temperature. The best adsorption property of the materials towards As was observed in neutral aquatic solutions.**

Keywords: Arsenic adsorption, Fe_3O_4 nanoparticles doped with Mn, Mangan, TEM technique, XRD technique.

I. INTRODUCTION

The transition metal-doped Fe_3O_4 magnetic nanomaterials are researched and manufactured because they are applied in many fields such as information storage, printing industry, soft magnetic magnets, cancer treatment, magnetic ultrasound, environmental treatment, etc [1-5]. Nanoparticles exhibit special properties because the ratio of their surface area to mass increases [1-3]. Nanoparticles exhibit special properties because the ratio of their surface area to mass increases [1-3]. As the ratio between surface area and particle mass increases, the electrical and magnetic properties change significantly due to the particle size quantum effect. At the same time, the particles tend to move to the minimum free energy levels through a number of forms such as phase transition, germinating, surface structure change [3, 4]. The important property of Fe_3O_4 iron oxide nanomaterials is that it is non-toxic to the environment and easy to separate adsorbed substances from the material. Therefore, scientists have been interested in research to improve the As adsorption capacity of iron oxide nanomaterials from Fe_3O_4 in aqueous environment [5, 6, 9, 10]. However, the publications have not fully mentioned the influence of Mn transition metal doping on the microstructure and magnetism of Fe_3O_4 ferromagnetic nanomaterials as well as the applicability of the material to treat As in the aquatic environment.

This paper reports the results of studying the microstructure, magnetic properties of Mn-doped Fe_3O_4 magnetic iron oxide nanomaterials and investigating the adsorption capacity of As in water with different pH.

II. EXPERIMENTAL

A. Chemistry

The chemicals used are $FeCl_3.6H_2O$, purity 99%; Na_2SO_3 purity 99%; $(CH_3COO)_2Mn.4H_2O$ purity 99% (Merck), acetone purity 99% (Merck). NH_3 solution 25%, As_2O_3 stock solution made from As_2O_3 with a concentration of l g/l (lg/l = 106 ppb, 105 times higher than the allowable As content) in domestic water [7]. Solution of NaOH (50%, purity 99%, Merck) and HCl (32%, purity 99%, Merck) were mixed in deionized water to adjust the pH in the study of As adsorption capacity of the materials.

B. Tool

A pH meter (TOA - Japan) is used to measure the pH of an aqueous solution containing As. The crystalline properties and grain sizes of the materials were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM) imaging techniques using the D5005 respectively (Bruker, Germany)) and the JEOL TEM 5410NV instrument (Bruker, Germany). XRD and TEM analysis were conducted at Analytical Chemistry Laboratory, Institute of Chemistry, Vietnam Academy of Science and Technology.

The magnetism of the materials was determined by a vibrating sample magnetometer (VSMVibrating Sample Magnetometer) on the MICROSENE EV11 (Japan).

The concentration of As in the solution was quantified by atomic absorption method using AAS Shimadzu 630 instrument of the Institute of Nuclear Science and Technology, Vietnam Institute of Atomic Energy.

C. Experiment

Mix the Fe^{3+} solution into the Mn^{2+} solution so that the doping ratio is 0, 5, 10, 15, 20 and 30%. Pour the mixture of Fe^{3+} and Mn^{2+} solutions with different doping ratios into 200 ml of Na_2SO_3 solution and stir until the solution turns yellow. Then, slowly add NH_3 solution until pH = 10, stir the solution for 30 minutes, get a black solution. Use magnets to deposit particles of magnetic material. Then decant the solution. Incubated at 50ºC under low pressure (less than 0.1 atm) for 2 days, obtained nanomaterials from Fe_3O_4-Mn with different Mn doping concentrations, denoted as Fe_3O_4, Fe_3O_4-5 %Mn, Fe_3O_4-10%Mn, Fe_3O_4-15%Mn, Fe_3O_4-20%Mn and Fe_3O_4-30%Mn. Put a certain amount of material with the above-mentioned Mn doped content into an aqueous solution containing As(III) with a concentration 10 times higher than the allowable level for domestic water and stir the solution for 20 minutes at room temperature. Previous experiments showed that with 20 minutes of stirring, As adsorption on the material will reach equilibrium. Use a magnet to separate the material from the solution. Quantitative As concentration in the solution after adsorption to determine the As adsorption capacity of the material.

III. RESULTS AND DISCUSSION

A. Microstructure of Mn doped Fe_3O_4 nanostructures

Figure 1 presents the X-ray diffraction spectrum of Fe_3O_4 and Fe_3O_4-5% Mn samples. From Figure 1, it can be seen that the diffraction peaks of the material coincide with the standard spectrum of the NaCl lattice showing that the samples of the material are single-phase and have a face-centered cubic structure. The lattice constant d of the Fe_3O_4 nanosample is calculated according to Bragg's formula:

$$2d\sin\theta = n\lambda \quad (1)$$

In which θ is the diffraction angle (also known as the Bragg angle), n is an integer, and λ is the wavelength of the X-ray beam hitting the sample.

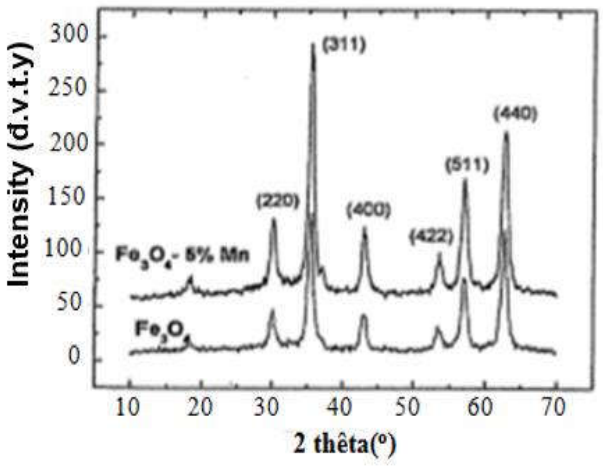

Figure 1. X-ray diffraction spectrum of Fe_3O_4 and Fe_3O_4-5%Mn samples compared with standard diffraction spectrum of NaCl crystal lattice with face-centered cubic structure.

The lattice constant value d was determined to be 0.8389 nm, quite similar to the standard lattice constant of NaCl crystals of 0.8396 nm.

The size of the material crystals is calculated using the Debuy - Scherrer formula:

$$D = \frac{0{,}9\lambda}{\beta\cos\theta} \quad (2)$$

In which β is the width at half height of the intensity peak (FWHM) of the diffracted beam in the XRD analysis, in radians. The symbols λ and θ are the same as in expression (1).

Experimental results show that the Fe_3O_4 crystals have a size of D = 8.8 nm.

Figure 2 is a TEM image of the Fe_3O_4 sample showing the clustering of particles. However, many particles with sizes between 8.4 and 12.7 nm can be seen. Similar to the Fe_3O_4 sample, the XRD analysis results (Figure 1) allow the lattice constant (d) of the Fe_3O_4-5%Mn sample to be calculated as 0.8377 nm. Compared with the lattice constant of Fe_3O_4 crystals, the d-value of Fe_3O_4-5%Mn lattice is narrower, but the difference is very small. This is explained because the Mn^{2+} ion radius is smaller than the Fe^{2+} ion radius, so when the Mn^{2+} ion replaces the Fe^{2+} ion in the lattice, the distance between the crystal faces narrows.

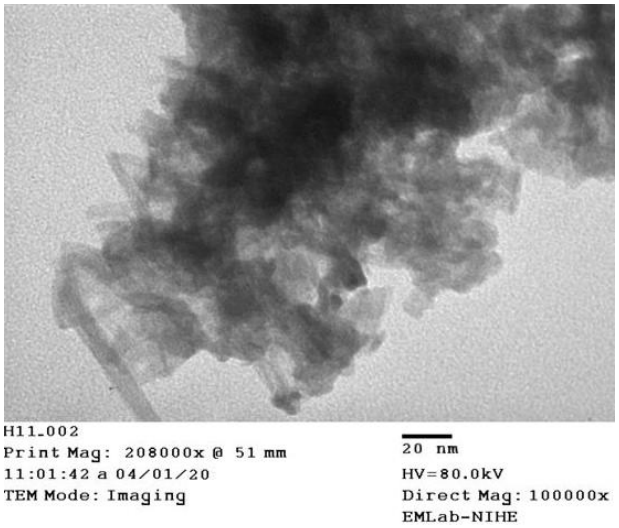

Figure 2. TEM image of the Fe3O4 nanocrystal sample

B. Magnetic properties of samples

Figure 3 presents the magnetic moment (Ms) of ferromagnetic oxide nanomaterials with different Mn doped content. From Figure 3, it can be seen that, at room temperature, Fe_3O_4, Fe_3O_4-5%Mn, Fe_3O_4-10%Mn, Fe_3O_4-15%Mn, Fe_3O_4-20%Mn and Fe_3O_4-30%Mn materials exhibit superparamagnetic properties with the saturation magnetic moment is about 65.8 emu/g. This is evidence that Mn has replaced Fe in the lattice of the material because Mn has paramagnetic properties.

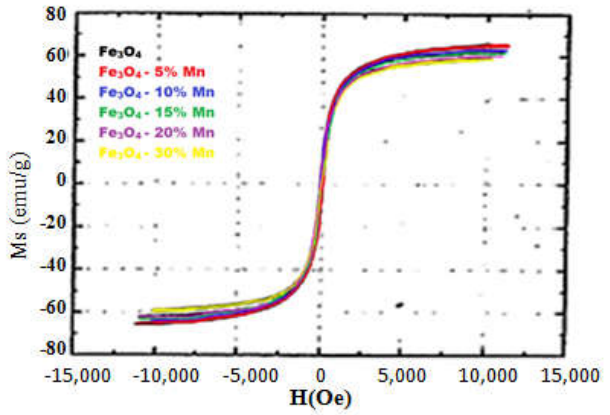

Figure 3. Magnetic moment (Ms) of ferromagnetic oxide nano samples with different Mn doped content

The saturation magnetic moment values of Fe_3O_4 and Fe_3O_4 in Mn phase with different contents are presented in Table 1. The results presented in Table 1 show that the saturation magnetic moment of the material decreases as the Mn impurity concentration increases, but the fluctuation of magnetic moment in the range of Mn doping content of 20-30% is not significant. The decrease in the saturation magnetic moment when the Mn content in the material increases is explained by the fact that Mn has a weaker magnetism than Fe, so when Mn^{2+} replaces Fe^{2+} in the crystal lattice, the magnetism of the material will decrease.

Table 1. Magnetic saturation moment (Ms) of Mn doped Fe_3O_4 and Fe_3O_4 samples

Sample	Ms, emu/g
Fe_3O_4	65.8
Fe_3O_4-5%Mn	65.3
Fe_3O_4-10%Mn	62.9
Fe_3O_4-15%Mn	61.9
Fe_3O_4-20%Mn	59.3
Fe_3O_4-30%Mn	59.5

C. Asen adsorption capacity of Fe3O4-x%Mn nanomaterials (x = 0, 5, 10, 15)

Table 2 presents the As adsorption capacity in water of Mn-doped Fe_3O_4 and Fe_3O_4 nanomaterials with different concentrations. In Table 2, columns from No. 2 to No. 5 are the concentration of As remaining in the solution after stirring time for 20 minutes with different amounts (column 1) and type of adsorbent.

Table 2. Test results of As adsorption capacity in water of Fe_3O_4-x%Mn nanomaterials after 20 minutes of adsorption time at room temperature

Amount of adsorption (g/l)	Concentration of As remaining in solution (ppb). Material: Fe_3O_4	Concentration of As remaining in solution (ppb). Material: Fe_3O_4-5%Mn	Concentration of As remaining in solution (ppb). Material: Fe_3O_4-10%Mn	Concentration of As remaining in solution (ppb). Material: Fe_3O_4-15%Mn
0	113	113	113	113
0.6	30.3460	31.6188	27.0847	37.0277
0.8	19.0508	27.2011	21.3576	29.5506
1.0	17.1020	24.2212	22.1530	26.1700
1.2	12.0111	21.9144	16.7012	25.6530
1.4	8.5510	16.9429	14.1588	13.4827
1.6	8.1135	17.1020	9.1078	17.7648
1.8	6.2417	9.5453	12.5680	15.6702
2.0	8.5510	5.1204	9.2271	12.8464
2.2	6.5823	9.5453	7.5965	16.1872

The results of Table 2 show that, in the case of ferromagnetic oxide nanomaterials with 10% Mn replacing iron in the crystal lattice and the amount of material (adsorbent) is 1.6 g/l, after 20 minutes of high concentration As level in water has decreased from 113 ppb, which is 10 times higher than the allowable standard [7], to below the standard level of 10 ppb (Table 2). The more Mn-doped samples have the higher the impurity content, the lower the As adsorption capacity. Fe_3O_4-5%Mn and Fe_3O_4-10%Mn materials showed the best adsorption: with the amount of 2 g/l, this material was able to reduce the concentration of As in water from 113 ppb to less than 10 ppb, ie reduce tens of times compared to the original concentration.

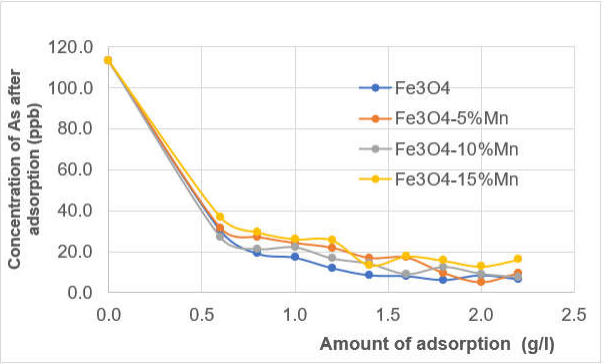

Figure 4. Effect of manganese (Mn) on arsenic (As) adsorption.

The test results show that the material has a good ability to adsorption As in water with a pH from neutral to weakly alkaline (pH = 5-8). In alkaline environment, pH > 10, the material exhibits poor adsorption for As.

IV. CONCLUSION

Fe_3O_4-x%Mn nanomaterials (x = 0; 5; 10; 15; 20 and 30) were synthesized by chemical methods and studied the structure and magnetic properties by XRD, TEM analysis techniques. The studied materials have particle sizes ranging from 8.42 to 12.7 nm, exhibit superparamagnetic properties at room temperature and have a saturation magnetic moment in the range of 53 ÷ 65.8 emu/g. Materials with < 10% Mn content replacing Fe in the crystal lattice have the ability to reduce As(III) concentration in water from a high level of hundreds of ppb to a level lower than 10 ppb, if the pH of the medium is neutral.

The limitation of this study is that the adsorption mechanism has not been determined as well as thermodynamic parameters such as maximum adsorption capacity, adsorption equilibrium constant, Gibb free energy (ΔG^0), enthalpy (ΔH^0), entropy (ΔS^0) of the As adsorption process in water of the material. These studies will be implemented in the near future.

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