Role of Zn And Polyaniline In Magnetic Nanocomposites And Enhanced Arsenic Adsorption Capacity In Wastewater

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Research Article

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Abstract

Polyaniline/ $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ ($\text{PANI}/\text{Zn}_{0.10}\text{Fe}_{2.90}\text{O}_4$) nanocomposites were synthesized by a chemical method and an onsite polymerization method. XRD patterns showed that the $\text{Zn}_{0.10}\text{Fe}_{2.90}\text{O}_4$ grain size about 12 nm, while TEM image showed grain size from 10 to 20 nm. The results of Raman spectra and DTA analyses showed that PANI participated in part of the $\text{PANI}/\text{Zn}_{0.10}\text{Fe}_{2.90}\text{O}_4$ nanocomposite samples. The grain size of $\text{PANI}/\text{Zn}_{0.10}\text{Fe}_{2.90}\text{O}_4$ samples measured by SEM was about 35–50 nm. These results demonstrated the shell–core structures of the nanocomposite material. The magnetization measurements at room temperature showed that in 1250 Oe magnetic field, the saturation magnetic moment of $\text{PANI}/\text{Zn}_{0.10}\text{Fe}_{2.90}\text{O}_4$ samples decreased from 71.2 to 42.3 emu/g when the PANI concentration increased from 0 % to 15 %. The surface area and porous structure of nanoparticles were investigated by the BET method at 77 K and a relative pressure P/P_0 of about 1. The arsenic adsorption capacity of the $\text{PANI}/\text{Zn}_{0.10}\text{Fe}_{2.90}\text{O}_4$ sample with the PANI concentration of 5 % was better than that of Fe_3O_4 and $\text{Zn}_{0.10}\text{Fe}_{2.90}\text{O}_4$ in a solution of pH 7. In the solution with pH P14, the arsenic adsorption of magnetic nanoparticles was insignificant. Due to substitution of Fe ions by Zn transition metal and coating polyaniline, these materials could be reabsorbed and reused.

1. Introduction

Transition metal doped Fe_3O_4 magnetic nanomaterials attract attention of the scientists due to their wide applications, especially in water treatment or other environmental pollution monitoring [1–16]. Recently, Cd, Cr, As removals were observed using the metal oxide hetero-structures, as meso-porous MnO_2 , Al_2O_3 , TiO_2 , CuO , ZrO_2 [1, 17–23]. The major backwards of using these oxides are the difficulties in their recovery and thus leaving their residuals in the environment. In this circumstance, magnetic nanoporous materials are considered as potential candidates for heavy metal removal because it's simple and efficient to recover them from the solution by means of external magnetic field.

Due to the rapid oxidation of Fe_3O_4 into $\gamma\text{-Fe}_2\text{O}_3$ in air as well as its decreased magnetization, large numbers of studies have focused on improving the saturation magnetization and chemical stability of the magnetic nanomaterials for effective heavy metal ion adsorption [10, 19, 24–29]. Two research directions are being considered: (i) partial replacement of divalent metal ions for Fe^{2+} ions, and (ii) coating of magnetic nanoparticles by polymers.

The unit cell of Fe_3O_4 consists of two kinds of interstitial sites denoted as tetrahedral A-site (Fe^{3+}) and octahedral B-site (Fe^{2+} : $\text{Fe}^{3+}=1: 1$) [19, 25]. The divalent metal ions like Mn^{2+} , Cu^{2+} and Zn^{2+} are usually substituted into B-site to form inverse spinel ferrites such as $\text{Fe}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ (with $x = 0 \div 0.15$ or 0.5) [27, 30], $\text{Fe}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ (with $x = 0 \div 0.15$) [30], $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ sample system ($x = 0.04; 0.06; 0.11$) [25], or $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ sample system ($x = 0, 0.5$ and 1) [26]. However, $\text{Fe}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0; 0.2; 0.4; 0.5$) thin

films or nanopowders with pretty large magnetization were confirmed by the partial substitutions of Zn^{2+} ions into A-sites [19, 31].

Magnetic nanoparticles are studied to treat heavy metals, weak-acid oxyanion contaminants or dyes in the environment [32–35]. In particular, the coating of magnetic nanoparticles by polymers are also studied to protect the chemical physical properties of magnetic nanoparticles simultaneously ensuring the recovery and reuse of the adsorbent materials [35, 36].

Polyaniline (PANI) is well-known as a conductive polymer whose high electrical conductivity has been discovered and is expected to play an increasingly significant role in many fields due to its easy synthesis, physicochemical stability, and simple doping chemistry. In recent, the substitution of Mn, Cu, Zn elements for Fe ions and the coating of magnetic nanoparticles by poly(1-naphthylamine), polyvinyl pyrrolidone have been studied [30, 31, 36] in order to stabilize the physicochemical properties and enhance their applicability. In this work, we discuss the synthesis, magnetic properties, microstructure of PANI/ $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ nanocomposites with different mass ratios of PANI/ $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ and the Zn^{2+} substitution for Fe^{2+} . Besides, the effect of PANI content on the arsenic adsorption ability in aqueous at different pH values as well as the desorption/re-adsorption capacities of the magnetic nanomaterials are also discussed.

2. Experimentals

2.1. Chemical and apparatus

All chemicals are at analytical grade: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Na_2SO_3 , 25% NH_3 , $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, NaOH , HCl , acetone 99%, isopropanol (IPA). As(III) solutions in which the As(III) content of 106 ppb, 10 times higher than allowed levels regulated by the World Health Organization (WHO) were prepared from As_2O_3 . Labconco Freeze Concentrator (USA) was used for material drying in vacuum. The structure and morphology of the samples were investigated by XRD patterns (D5005, Bruker), TEM (JEOL5410), SEM (S4800), IR Prestige -21 and thermal gravimetric analysis by DTG- 60H. Meanwhile the magnetization was measured by vibrating sample magnetometer (VSM 8600 S) and the mesopores structure of samples was observed by TriStar 3000 V6.07A with TriStar 3000 V6.08 software. The Flame-Atomic Absorption Spectrophotometer (F-AAS 6300 Shimadzu) was used to determine the arsenic content in the solutions before and after using adsorbent magnetic nanomaterials.

2.2. Synthesis of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ by chemical method

A detailed synthesis procedure was described in our previous paper [30, 31]. The chemical reactions occur during the synthesized process of Fe_3O_4 :

To get $\text{Fe}_{2.9}\text{Zn}_{0.10}\text{O}_4$ (signed $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$) nanoparticles, the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solutions containing Fe^{3+} and Zn^{2+} with nominal Zn atom content of 0.10 were mixed with a Na_2SO_3 solution. These mixed solutions were stirred until they turned to yellow in color. Then, the NH_3 solution was added dropwise until the pH was 10. The solution was kept stirring for 30 minutes until it turned to black. These magnetic grains were separated from the mixture solution using external magnets, and then filtered, washed with distilled water. Finally, these materials were desiccated at 50°C for 48 hours and finely grinded to obtain $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ nanoparticles.

2.3. Synthesis of PANI/ $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ nanocomposites

The synthesis of PANI/ $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ nanocomposite by *in-situ* polymerization method was briefly described as follow:

Step 1: a calculated amount of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ was added in 60 mL of distilled water, followed by 40 mL of IPA, aniline and well stirred for 60 minutes (mixture A).

Step 2: a stoichiometric amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution, with the monomer/oxidizing agent molar ratio of 1:1.5, was added dropwise into mixture A to obtain a black blue mixture (mixture B) which was allowed to stir for 2 hours with an exothermal reaction.

Step 3 : Filter the mixture using external magnet, then the obtained solid was dried by Labconco Freeze concentrator for 5 hours at 1 mPa and temperature of 40°C . The nanocomposites with 0%, 5%, 10% and 15% mass ratios of PANI/ $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ were coded by S_0 , S_1 , S_2 and S_3 as represented in Table 1.

Table 1
Mass ratios of PANI/ $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ in S_0 , S_1 , S_2 , S_3 samples

Sample	S_0	S_1	S_2	S_3
$\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$, (in g)	20	20	20	20
PANI (in g)	0	1.0	2.0	3.0

2.4. The evaluation of arsenic adsorption

The evaluation of arsenic adsorption capacity of the samples was performed at room temperature. The experiment was conducted by adding 0.01 g of samples (S_0 , S_1 , S_2 and S_3) into As(III) solutions of initial content of 106 ppb. Each mixture was then allowed to stir in 20 minutes for a complete adsorption. The arsenic contents before and after adsorption were analyzed by F-AAS.

3. Results And Discussion

3.1. Structure, morphology and physical properties

In *Fig. 1*, the diffraction peaks of (220), (311), (400), (442), (511), (440) of the $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ (S_0) sample were completely fitted with the standard diffraction pattern of Fe_3O_4 as in our previous publication [31], and demonstrated the centered face cubic structure. Similarly, the XRD patterns of S_2 and S_3 samples showed the same diffraction peaks as that of Fe_3O_4 sample, which proved that the Zn^{2+} doping as well as the addition of polymer did not affect the crystal structure of materials. Thus, *Fig. 1* presented typical S_2 and S_3 samples of all samples with different PANI amount. From diffraction conditions, $2d\sin\theta = n\lambda$, the lattice constants of the nanoparticles in the $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$, S_2 and S_3 samples were the same with $a = 8.376 \text{ \AA}$ which was determined by the relation: $a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$; where d_{hkl} is the distance of the lattice planes of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$. Because PANI polymer is an amorphous material and does not affect the crystal structure of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$, thus the calculated particle size from XRD patterns is also the particle size for S_1 , S_2 and S_3 samples. Thus, the average crystal particle sizes of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ in all S_0 , S_1 , S_2 and S_3 samples were about 12 nm, calculated by the formula $D = 0.9\lambda/\beta\cos\theta$ ($\lambda = 1.5416 \text{ \AA}$; β : full width at half maximum of diffraction line). In *Fig. 2a*, the TEM image of S_0 sample shows the grain sizes of *ca.* 10 -18 nm, however, *Fig. 2b* show the agglomeration in S_1 sample with grain size of *ca.* 40 -50 nm. Meanwhile, in SEM images in *Fig. 2c* and *Fig. 2d*, the grain sizes in S_2 , S_3 samples were about 35 - 50 nm and 40 - 50 nm, respectively. This result proved that PANI prevented the agglomeration of the magnetic nanoparticles. Simultaneously, it also suggested that S_1 , S_2 and S_3 samples have the core-shell structures created by the polymerization of PANI at the surface of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ nanoparticles.

3.2. FTIR spectra analyses

Fig. 3a shows strong absorbed peaks of PANI in the region from 1149 to 1570 cm^{-1} with the highest intensity at 1149 cm^{-1} peak. These peaks were attributed to the absorption of the C = C (aromatic), C-N⁺, C = N groups of the PANI [37]. Meanwhile, *Fig. 3b* shows the strong adsorbed peak of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ at 570 cm^{-1} , and *Fig. 3c* shows some characteristic peaks of both samples.

The infrared spectrum of S_2 (*Fig. 3c*) showed the absorption peaks appeared in the range of 1134 to 1173 cm^{-1} with much stronger intensity than some peaks of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$. This suggests that PANI is present in the component of S_2 .

3.3. TGA and DTG analyses

TGA curve in *Fig. 4a* showed that at temperature range below 80°C , the volume reduction of PANI was due to the evaporation of water, corresponding to 13% with a sharp endothermic peak at 45°C in the DTG curve. From $80 - 210^\circ\text{C}$, the sample volume stays almost unchanged. However, from $210 - 320^\circ\text{C}$, the reduction of sample volume in TGA curve happened due to the decomposition of PANI to form monomers, oligomers, dimers and trimers corresponding to a sharp endothermic peak at 292°C in the

DTG curve. At temperature higher than 320 °C, the weight loss caused by the thermal decomposition of the oligomers, dimers, trimers. This led to a complete decomposition of PANI at above 600 °C.

TGA curve of typical S₂ sample (for S₁ and S₃) in *Fig. 4b* also showed that at temperature range below 80 °C, the 8.6% reduction of sample volume due to water evaporation corresponding to a sharp endothermic peak at 45.2 °C in the DTG curve. However, from 100 - 300 °C in the TGA curve, the 3.3% reduction of sample volume may be happened due to the decomposition of the residual monomers and oligomers in the sample. From 300 - 600 °C, the thermal decomposition of the oligomers, dimers, trimers caused a small and broad endothermic peak at 395 °C in the DTG curve. Thus, the sample mass remained only 30% at 600 °C. Because PANI is quite stable in the temperature range below 150 °C, it can be seen from above results that the S₁, S₂ and S₃ nanocomposites have been successfully synthesized and the presence of PANI in these samples has improved the thermal stability of PANI-coated Fe_{0.90}Zn_{0.10}Fe₂O₄ in temperature range below 150 °C.

3.4. Magnetization and chemical instability

In the air environment, Fe₃O₄ is easy to be oxidized to give γ-Fe₂O₃. Thus, the saturation magnetization of new synthesized Fe₃O₄ samples decreased from 63.13 emu/g to 56 emu/g after 2 months of synthesis [30]. This phenomenon related the oxidation of Fe₃O₄ into γ-Fe₂O₃ due to oxygen in air according to the equation:

The change of magnetization and chemical instability of the Fe₃O₄ sample led to a limitation of their application ability. Thus, the Zn²⁺ substitution for Fe²⁺ ions and the polymer coating outside nanoparticles are the optimal methods to stabilize chemical properties and magnetization of Fe_{0.90}Zn_{0.10}Fe₂O₄ material.

For the Fe_{0.90}Zn_{0.10}Fe₂O₄ sample in *Fig. 5*, the saturation magnetization of 71.5 emu/g is higher than that of Fe₃O₄ [36] (*ca.* 63 emu/g). Unlike the replacement of transition metal elements Cu, Mn, Ni for Fe²⁺ into octahedral B-site [24, 25, 27], preferably the replacement of Zn²⁺ ions for Fe³⁺ at tetrahedron A-site occurs [19, 26], simultaneously Fe²⁺ amount at the octahedral B-site gives electrons to become Fe³⁺ in order to balance the charge of cell network [19, 26]. Since the ionic radius of the Fe³⁺ ion is 0.64 Å and the ionic radius of the Zn²⁺ ion is 0.74 Å, the substitution of Zn with content x = 0.10 caused a slight increasing of the lattice constant (a = 8.386 Å) in comparison with Fe₃O₄ (a = 8.3760 Å) [30, 36]. This was due to the Zn²⁺ size larger than Fe³⁺. This substitution and transformation caused a change in ions distribution of the network subdivisions to [Zn_x²⁺Fe_{1-x}³⁺]_A[Fe³⁺Fe_x³⁺Fe_{1-x}²⁺]_B.

The magnetic moment depends on the content of x that is considered due to the decision of spin direction of Fe_x³⁺ in B-site, but do not depends on the presence of non-magnetic Zn ions [19, 31]. This has

been clearly explained in our recent publication [31]. Therefore, the saturation magnetization of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ is higher than Fe_3O_4 [30, 31].

On the other hand, the saturation magnetizations of S_1 , S_2 and S_3 samples decreased from 65 emu/g to 43 emu/g when the non-magnetic PANI content increased from 5–15% (Table 2). However, due to the PANI coating, the magnetization of nanocomposite materials is more stable over time.

Table 2
Lattice constant, grain size, Ms of S_0 , S_1 , S_2 and S_3

	Lattice constant ($\text{\AA}$)	$D_{\text{x-ray}}$ (nm)	D_{TEM} (nm)	D_{SEM} (nm)	Ms (Oe)
S_0	8.385	11.81	10-18		71.5
S_1				40-50	65
S_2	8.386	11.80		35-50	53
S_3	8.386	11.81		40-50	43

3.5. Adsorption kinetic, porous properties and arsenic adsorption ability

The adsorption kinetic of S_0 , S_1 , S_2 and S_3 nanocomposites can be explained [30, 36] by the relation of adsorption ability based on the inelastic exchange interaction between specific surface area of nanoparticles and adsorbed materials. The surface and structure of nanoparticle mesopores were studied by the nitrogen adsorption-desorption isotherms of 0.54 g for S_0 , S_1 , S_2 and S_3 samples at 77 K [30, 36].

Collision of N_2 gas molecules with nanoparticles is considered to be inelastic, so that the N_2 gas molecules remain in contact with the nanoparticles for a time before returning to the gas phase. This time delay is taken as responsible for the phenomenon of adsorption that demonstrated by equation: $P/V_a(P_0 - P) = (1/V_m)(P/P_0)$ [38]. Here, V_a is the quantity of N_2 gas adsorbed at pressure P and V_m is the quantity of gas adsorbed when the entire surface is covered with a mono-molecular layer. The N_2 adsorption–desorption isotherm curves of S_0 and S_1 samples at 77 K were presented in Fig. 6. It can be clearly seen that the adsorption and desorption ability of S_1 sample is higher than that of S_0 . By the BET (Brunauer, Emmett, and Taller) theory [38], the pore size distribution at relative pressure $P/P_0 \approx 1$ and the specific surface area at low P/P_0 were calculated as shown in Table 3.

Table 3
Porous properties and maximum arsenic adsorption ability

Sample	BET pore size (nm) at $P/P_0 \approx 1$	BET specific surface area $\pm 0.02 \text{ (m}^2\text{/g)}$ at $P/P_0 = 0.294$	Maximum adsorption capacity $q_{\max} \text{ (mg/g)}$
S ₀	9.16 ± 0.02	$64.83 \text{ m}^2\text{/g}$	41.49 ± 0.02
S ₁	7.88 ± 0.05	$105.89 \text{ m}^2\text{/g}$	43.48 ± 0.03
S ₂	8.42 ± 0.03	$98.25 \text{ m}^2\text{/g}$	40.06 ± 0.02
S ₃	8.36 ± 0.04	$99.67 \text{ m}^2\text{/g}$	34.48 ± 0.03

3.5. Arsenic adsorption ability

In order to study As adsorption ability of the nanoparticles, the effects of pH in environment and As maximum adsorption capacity also investigate at room temperature.

Effects of pH to arsenic adsorption

To study the pH effect on the adsorption ability of the nanocomposites, the As(III) solutions with different pH in range of 1-14 were prepared. The As(III) adsorption results were presented in *Fig. 7*. It can be seen from *Fig. 7* that the remaining arsenic content was a function of the pH. For all nanocomposite samples, the arsenic adsorption capacity increased as the pH was increased from 1 to 7. Then, the adsorption capacity decreased as the pH was increased above 7. The highest adsorption capacities were obtained in the range of pH 5-9. In both strong acidic and basic solution, the adsorption capacity decreased.

This trend can be explained by the speciation of arsenic (III) at different pH media and the surface charge status of the nanocomposites [39] in strong acidic environment. The surface of nanocomposites will be negatively charged at pH higher than pH_{pzc} (~ 7). Meanwhile, in neutral media, the un-charge in surface of nanocomposites and As(III) occurs mostly in neutral state (H_3AsO_3 at pH below 9.2) [40], so at pH 7, the highest As(III) adsorption occurred, due to the electrostatic interaction is not feasible under this condition. Therefore, the As(III) adsorption was controlled by the surface complexation rather than the electrostatic interactions. Similar results were observed with other magnetic nanocomposites as reported earlier [39, 40].

When the pH elevates, As(III) exists mainly in form of $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} anions while the surface charge of the nanoparticles is negative. Thus, the sharp decrease in the arsenic adsorption capacity at pH range of 11-14 is likely due to the electrostatic repulsion between the negatively charged surface of the nanocomposites and the deprotonated anionic arsenic. At extreme high pH 14, due to strong electrostatic repulsive force, the material has depicted no arsenic adsorption ability.

Moreover, at very low pH levels (1-2), a decomposition of the $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ nanocomposites was observed proving by the presence of iron and zinc in the solution. In neutral and alkaline media, the nanocomposites were stable with no iron and zinc ions detected in the solution. Thus, it's suggested that the de-adsorption process of S_0 , S_1 , S_2 and S_3 should be conducted in solution at pH 14.

As above analyzed results, the best As adsorption occurs in a neutral environment (pH7), where the inelastic exchange interaction takes place, which has the source of the Van der Waal interaction between the magnetic nanoparticles and adsorbent. Thus, maximum arsenic adsorption capacity was investigated by the Langmuir isotherm mode at 300 K in environment with pH 7.

Maximum arsenic adsorption capacity

Equilibrium time of As(III) adsorption was analyzed by measuring the remaining arsenic content in solution pH 7. As shown in *Fig. 8*, the arsenic contents remain in the equilibrium state when the adsorption time is 20 minutes at room temperature. The maximum arsenic adsorption capacity $q_{\max}$ of unit volume of adsorbent (mg/g) is calculated by the Langmuir isotherm equation at pH 7 and 300 K [6, 10, 17] with the first order linear relation:

$$\frac{C_f}{q} = \frac{1}{q_{\max}} C_f + \frac{1}{b \cdot q_{\max}}$$

where C_f : the remaining arsenic content (mg/L) at equilibrium; q : the arsenic adsorption ability at equilibrium for a unit volume of adsorbent (mg/g); b : constants attributed to the interaction of the adsorbent and adsorbed compounds.

The calculated values of $q_{\max}$ for S_0 , S_1 , S_2 and S_3 are presented in Table 3.

As in Table 3, the arsenic adsorption capability of the materials, $q_{\max}$ of S_1 was better than that of S_0 ($\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$) sample and Fe_3O_4 , that reported in [36] with the same condition. The results in Table 2 also are in good agreement with those discussed in *Fig. 8*.

Conclusion

The PANI/ $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$ nanocomposite materials were successfully synthesized with different mass ratios. These nanocomposite materials with core-shell structure have high saturated magnetic moments and high specific surface area that contribute to its high capability of adsorbing arsenic (III) in aqueous solutions. The pH 7 and 20-minute adsorption time are suitable factors for an effective adsorption process. The sample S_1 (PANI 5% mass ratio) with As adsorption capacity ($q_{\max} = 43.48$ mg/g) is highest than that of S_0 , S_2 , S_3 samples and Fe_3O_4 nanoparticles. Due to the improving of saturation magnetization and chemical stability of nanomaterials, this work suggests the ability for heavy metal ion adsorption and the desorption in strong alkaline solution, then the materials could reabsorb for further trials.

Declarations

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AUTHOR STATEMENT

No conflict of interest exists in the submission of this manuscript and manuscript is approved by all authors for publication.

AUTHOR CONTRIBUTIONS

Tran Minh Thi: Conceptualization, Writing - review & editing; **Nguyen Mau Lam:** Formal analysis; **Do Khanh Tung:** Investigation, Methodology; **Nguyen Manh Nghia:** Validation; **Duong Quoc Van:** Formal analysis; **Vu Quoc Manh:** Writing - original draft; **Nguyen Thi Bich Viet:** Writing - original draft; **Duong Khanh Linh:** Data curation, Formal analysis; **Nguyen Thuy Chinh:** Investigation, Methodology; **Thai Hoang:** Writing - review & editing and **Vu Quoc Trung:** Conceptualization; Writing - review & editing, Project administration.

References

1. S. Prasanna, S. Mitsugu, K. Kenji, Y. Iwao, Growth conditions, structural and magnetic properties of M/Fe₃O₄/I (M = Al, Ag and I = Al₂O₃, MgO) multilayers. *Journal of Magnetic and Materials* **247**, 1–5 (2002)
2. L. Jun, B. Yuezhen, M. Masaru, Magnetic behavior of Zn-doped Fe₃O₄ nanoparticles estimated in terms of crystal domain size. *J. Phys. Chem. C* **116**, 134–143 (2012). <https://doi.org/10.1021/jp207354s>
3. J.F. Bertone, J. Cizeron, R.K. Wahi, J.K. Bosworth, V.L. Colvin, Hydrothermal synthesis of quartz nanocrystal. *Nano Lett.* **3**, 655–659 (2003). <https://doi.org/10.1021/nl025854r>
4. A.I. Rusanov, Surface thermodynamic revisited. *Surf. Sci. Rep.* **58**, 111 (2005). <https://doi.org/10.1016/j.surfrep.2005.08.002>
5. G. Hongbo, H. Yudong, Z. Xi, W. Qiang, Z. Jiahua, S. Lu, H. Neel, P.Y. David, W. Suying, G. Zhanhu, Magnetoresistive polyaniline-magnetite nanocomposites with negative dielectrical properties. *Polymer* **53**, 801–809 (2012). <https://doi.org/10.1016/j.polymer.2011.12.033>
6. A. Khodabakhshi, M.M. Amin, M. Mozaffari, Synthesis of magnetic nanoparticles and evaluation of its efficiency for arsenic removal from simulated industrial wastewater. *Iran J. Environ. Health. Sci. Eng* **8**, 189–200 (2011)

7. A. Melanie, P. Jerome, P. Olivier, B. Daniel, Enhanced adsorption of arsenic onto magnetic nanoparticles: As(III) as a probe of surface structure and heterogeneity. *Langmuir* **24**, 3215–3222 (2008). 10.1021/la702998x
8. I.Z. Anastasios, A.K. Ioannis, Recent arsenic-contaminated ground waters. *Environ. Int.* **31**, 213–219 (2005)
9. R.C. Ganga, S. Priya, K. Arun, S.K. Mehta, M. Suman, U. Ahmad, Adsorption studies of cationic, anionic and azo-dyes via monodispersed Fe₃O₄ nanoparticles. *J. Nanosci. Nanotechnol.* **13**, 3240–3245 (2013). 10.1166/jnn.2013.7152
10. L. Ruijiang, L. Yi, S. Xiangqian, Y. Xinchun, C. Xuewen, G. Yingying, Adsorption Kinetics and isotherms of arsenic(V) from aqueous solution on to Ni_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles. *J. Nanosci. Nanotechnol.* **13**, 2835–2841 (2013). 10.1166/jnn.2013.7392
11. X.B. Fang, Z.Q. Fang, P.K.E. Tsang, W. Cheng, X.M. Yan, L.C. Zheng, Selective adsorption of Cr(VI) from aqueous solution by EDA-Fe₃O₄ nanoparticles prepared from steel pickling waste liquor. *Appl. Surf. Sci.* **314**, 655–662 (2014). 10.1016/j.apsusc.2014.06.191
12. H. Tao, Y. Chao, W. Jide, N. Chung, S. Xintai, R. Xuehui, Facile additive-free synthesis of iron oxide nanoparticles for efficient adsorptive removal of Congo red and Cr(VI). *Appl. Surf. Sci.* **292**, 174–180 (2014). <https://doi.org/10.1016/j.apsusc.2013.11.108>
13. Y. Guide, T. Lin, L. Xiaoxia, Z. Guangming, C. Ye, W. Xue, Z. Yaoyu, L. Sisi, F. Yan, Z. Yi, Cd(II) removal from aqueous solution by adsorption on α -ketoglutaric acid-modified magnetic chitosan. *Appl. Surf. Sci.* **292**, 710–716 (2014). 10.1016/j.apsusc.2013.12.038
14. C. Qi, H. Qinqin, L. Mengmeng, L. Xueting, W. Jin, L. Jianping, The vital role of PANI for the enhanced photocatalytic activity of magnetically recyclable N–K₂Ti₄O₉/MnFe₂O₄/PANI composites. *Appl. Surf. Sci.* **311**, 230–238 (2014). <https://doi.org/10.1016/j.apsusc.2014.05.046>
15. Q.L. Jiang, S.W. Zheng, R.Y. Hong, S.M. Deng, L. Guo, R.L. Hu, B. Gao, M. Huang, L.F. Cheng, G.H. Liu, Y.Q. Wang, Folic acid-conjugated Fe₃O₄ magnetic nanoparticles for hyperthermia and MRI *in vitro* and *in vivo*. *Appl. Surf. Sci.* **307**, 224–233 (2014). <https://doi.org/10.1016/j.apsusc.2014.04.018>
16. M.J. Chen, H. Shen, X. Li, H.F. Liu, Facile synthesis of oil-soluble Fe₃O₄ nanoparticles based on a phase transfer mechanism. *Appl. Surf. Sci.* **307**, 306–310 (2014). <https://doi.org/10.1016/j.apsusc.2014.04.031>
17. C.M. Babu, B. Palanisamy, B. Sundaravel, M. Palanichamy, V. Murugesan, A Novel Magnetic Fe₃O₄/SiO₂ core–shell nanorods for the removal of arsenic. *J. Nanosci. Nanotechnol.* **13**, 2517–2527 (2013). 10.1166/jnn.2013.7376
18. C. Lei, X. Hongchuan, F. Yuan, Z. Cong, Z. Feng, C. Xing, Z. Chunhui, L. Xuebing, Application of metal oxide heterostructures in arsenic removal from contaminated water. *Journal of Nanomaterials* **2014**, 793610 (2014). <https://doi.org/10.1155/2014/793610>. 10 pages.
19. J.W. Park, A.N. Jang, J.H. Song, C.Y. Park, Y.S. Lee, Electronic structure of Zn doped Fe₃O₄ thin films. *J. Nanosci. Nanotechnol.* **13**, 1895–1898 (2013). 10.1166/jnn.2013.6996

20. L. Xiaolong, Z. Fengqin, M. Chao, S. Elingarami, H. Nongyue, Green Synthesis of Uniform Magnetite (Fe_3O_4) Nanoparticles and Micron Cubes. *J. Nanosci. Nanotechnol.* **12**, 2939–2942 (2012). 10.1166/jnn.2012.5684
21. B. Zapotoczny, M.R. Dudek, N. Guskos, J.J. Koziol, B.V. Padlyak, M. Kośmider, E. Rysiakiewicz-Pasek, FMR Study of the Porous Silicate Glasses with Fe_3O_4 Magnetic Nanoparticles Fillers. *Journal of Nanomaterials* **2012**, 341073 (2012). <https://doi.org/10.1155/2012/341073>
22. L. Méndez-Rodríguez, T. Zenteno-Savín, B. Acosta-Vargas, J. Wurl, M. Imaz-Lamadrid, Differences in arsenic, molybdenum, barium, and other physicochemical relationships in groundwater between sites with and without mining activities. *Natural Science* **5**, 238–243 (2013). 10.4236/ns.2013.52A035
23. L. Kuen-Song, D. Khalilallahman, L. Yeu-Jye, K. Hua, H. Pei-Ju, Synthesis and Characterization of Porous Zero-Valent Iron Nanoparticles for Remediation of Chromium-Contaminated Wastewater. *J. Nanosci. Nanotechnol.* **13**, 2675–2681 (2013). 10.1166/jnn.2013.7381
24. H.M. Zaki, S. Al-Heniti, U. Ahmad, F. Al-Marzouki, A. Abdel-Daiem, T.A. Elmosalami, H.A. Dawoud, F.S. Al-Hazmi, S.S. Ata-Allah, Magnesium-Zinc Ferrite Nanoparticles: Effect of Copper Doping on the Structural, Electrical and Magnetic Properties. *J. Nanosci. Nanotechnol.* **13**, 4056–4065 (2013). 10.1166/jnn.2013.7434
25. S. Larumbe, C. Gómez-Polo, J.I. Pérez-Landazábal, A. García-Prieto, J. Alonso, M.L. Fdez-Gubieda, D. Cordero, J. Gómez, Ni Doped Fe_3O_4 Magnetic Nanoparticles. *J. Nanosci. Nanotechnol.* **12**, 2652–2660 (2012). 10.1166/jnn.2012.5769
26. R. Deepshikha, K. Rajnish, R.K. Pandey, Structural, Magnetic and Dielectric Properties of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0, 0.5$ and 1) Nanoparticles Synthesized by Chemical Co-Precipitation Method. *J. Nanosci. Nanotechnol.* **13**, 812–1819 (2013). 10.1166/jnn.2013.7120
27. I. Mizue, T. Hidekazu, K. Tomoji, Preparation of highly conductive Mn-doped Fe_3O_4 thin films with spin polarization at room temperature using a pulsed-laser deposition technique. *Appl. Phys. Lett.* **86**, 222504 (2005). <https://doi.org/10.1063/1.1942640>
28. D. Tripathy, A.O. Adeyeye, Microstructure and magnetotransport properties of Cu doped Fe_3O_4 films. *J. Appl. Phys.* **103**, 07F701 (2008). 10.1063/1.2828504
29. F. Genç, E. Turhan, H. Kavas, U. Topal, A. Baykal, H. Sözeri, Magnetic and Microwave Absorption Properties of $\text{Ni}_x\text{Zn}_{0.9-x}\text{Mn}_{0.1}\text{Fe}_2\text{O}_4$ Prepared by Boron Addition. *J. Supercond. Novel Magn.* **28**, 1047–1050 (2015)
30. T.M. Thi, N.T.H. Trang, N.T.V. Anh, Effects of Mn, Cu doping concentration to the properties of magnetic nanoparticles and arsenic adsorption capability in wastewater. *Appl. Surf. Sci.* **340**, 166–172 (2015). <https://doi.org/10.1016/j.apsusc.2015.02.132>
31. T.M. Thi, V.Q. Trung, D.K. Tung, P.T. Thanh, N.H. Yen, N.M. Lam, Effect of Zn nonmagnetic element doping and a polyvinyl pyrrolidone shell layer on the superparamagnetism and stability properties of magnetic nanoparticles. *Jpn. J. Appl. Phys.* **60**, 025001 (2021). doi.org/10.35848/1347-4065/abd86d

32. V. Uwamariya, B. Petrusevski, Y.M. Slokar, C. Aubry, P.N.L. Lens, G.L. Amy, Effect of Fulvic Acid on Adsorptive Removal of Cr(VI) and As(V) from Groundwater by Iron Oxide-Based Adsorbents. *Water Air Soil Pollut.* **226**, 184 (2015). [10.1007/s11270-014-2193-5](https://doi.org/10.1007/s11270-014-2193-5)
33. F. Huda, P. Yi-Fong, L. Tsair-Fuh, Effect of Humic Acid on Arsenic Adsorption and Pore. Blockage on Iron-Based Adsorbent. *Water Air Soil Pollut.* **226**, 14 (2015). <https://doi.org/10.1007/s11270-014-2224-2>
34. D.H. Kiril, M. Jasmina, Engineering metal (hydr)oxide sorbents for removal of arsenate and similar weak-acid oxyanion contaminants: A critical review with emphasis on factors governing sorption processes. *Science of The Total Environment* **598**, 258–271 (2017). [10.1016/j.scitotenv.2017.04.108](https://doi.org/10.1016/j.scitotenv.2017.04.108)
35. A. Sadia, M.S. Akhtar, Y.S. Kim, O.B. Yang, S. Hyung-Shik, Synthesis and characterization of novel poly(1-naphthylamine)/zinc oxide nanocomposites: Application in catalytic degradation of methylene blue dye. *Colloid Polym. Sci.* **288**, 633–1638 (2010). <https://doi.org/10.1007/s00396-010-2284-9>
36. T.M. Thi, N.T.H. Trang, V.Q. Trung, N.M. Vuong, Properties of poly(1-naphthylamine)/Fe₃O₄ composites and arsenic adsorption capability in wastewater. *Front. Mater. Sci.* **10**, 56–65 (2016). <https://doi.org/10.1007/s11706-016-0320-5>
37. B. Bogdan, G. Andreea, D. Paul, B. Adriana, B. Valentin, Morphological and Structural Analysis of Polyaniline and Poly(*o*-anisidine) Layers Generated in a DC Glow Discharge Plasma by Using an Oblique Angle Electrode Deposition Configuration. *Polymers* **9**, 732 (2017). [doi:10.3390/polym9120732](https://doi.org/10.3390/polym9120732)
38. A.W. Paul, O. Clyde, contributors: W.C. Ronnie, P.O. James, Y.S. Yunes (1997) Analytical methods in fine particle technology, Micromeritics Instrument Corporation, Norcross, GA USA, 60-62
39. A.I.A. Sherlala, A.A.A. Raman, M.M. Bello, A. Buthiyappan, Adsorption of arsenic using chitosan magnetic graphene oxide nanocomposite. *J. Environ. Manage.* **246**, 547–556 (2019). <https://doi.org/10.1016/j.jenvman.2019.05.117>
40. H. Su, Z. Ye, N. Hmidi, High-performance iron oxide-graphene oxide nanocomposite adsorbents for arsenic removal. *Colloids Surfaces A Physicochem. Eng. Asp.* **522**, 161–172 (2017). <https://doi.org/10.1016/j.colsurfa.2017.02.065>

Figures

Figure 1

XRD patterns of $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$, S_2 and S_3

Figure 2

TEM image of S_0 (a), SEM images of S_1 (b), S_2 (c) and S_3 (d)

PANI structure

Figure 3

FTIR spectra of samples: a-PANI, b- $\text{Fe}_{0.90}\text{Zn}_{0.10}\text{Fe}_2\text{O}_4$, and c- nanocomposite S_2

Figure 4

TGA and DTG Analyses of samples: a). PANI, b). S₂

Figure 5

Magnetization curves of S₀, S₁, S₂ and S₃

Figure 6

N₂ adsorption-desorption isotherm curves of samples

Figure 7

Figure 8

The C_f/q dependence on C_f using adsorbents with different PANI ratios in PANI/Fe_{0.90}Zn_{0.10}Fe₂O₄