Removal of As(III) and As(V) from Water Using Magnetic Core-Shell Nanomaterial Fe$_3$O$_4$@Polyaniline

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Abstract: Arsenic pollution is an important hot topic in environmental field, and it is of great value to develop new methods for removal of arsenic pollution. Present study reported a magnetic core-shell material, polyaniline coated Fe$_3$O$_4$ (Fe$_3$O$_4$@PANI) synthesized using a simple two-step polymerization method, which was characterized by transmission electron microscopy(TEM), scanning electron microscope(SEM), FT-IR, X-ray diffraction(XRD), and a vibrating sample magnetometer(VSM) to confirm microstructure and morphology of the hybrid materials. As(III) and As(V) were used as the model analytes and the various parameters such as pH, adsorbent dosage, contact time, coexisting ions and humic acid were investigated. Under optimal conditions, the adsorption of arsenic followed pseudo-second-order kinetics, and the adsorption isotherms conformed to Freundlich adsorption isotherm model. The adsorption capacity ($q_{max}$) of Fe$_3$O$_4$@PANI for arsenite and arsenate in terms of monolayer adsorption were 1.066 and 1.385 mg/g, respectively. The adsorption was spontaneous and exothermic process. These results indicated that present study provided a rapid, easy to separate, and low cost method for the removal of As(III) and As(V), and would have great prospect in the removal and remediation of pollutants.

Keywords: Fe$_3$O$_4$@polyaniline, magnetic core-shell material, arsenite, arsenate.

1. INTRODUCTION

Arsenic is a universal and highly toxic element around the world, especially in Southern and Southeastern Asia [1]. The increase of arsenic concentration in aquatic environment is attributed to two aspects, one is the natural process such as dissolution of arsenic-containing minerals by weathering, and the other is man-made process such as the release of effluent from exploiting and utilizing processes of arsenic-containing minerals, coal fired thermal power plants, industrial wastewater discharges, petroleum refining, and ceramic industries, and the degradation of the synthetic arsenic-containing compounds. Arsenic pollution will severely affect the drinking water sources which may influence beyond hundred of million people around the world by estimation [2-6]. Uptake of arsenic-contaminated water for a long interval will result in severe health diseases such as skin lesions, heart disorders as well as neurological, reproductive, and carcinogenic diseases [7-9]. Hence, international organizations and countries have put more attention on the arsenic pollution. The United States Environmental Protection Agency (EPA), the World Health Organization (WHO) and China have reduced the maximum permissible level of arsenic in drinking water from 50 to 10 µg/L [10-12].

Arsenic commonly exists as two inorganic forms of arsenite (AsO$_3^{3-}$) and arsenate (AsO$_4^{3-}$) which are the popular forms in water and referred to as As(III) and As(V). In general, As(V) is stable in aerobic environment and As(III) often exists in anaerobic environment. The toxicity of arsenic species is different, generally the toxicity of inorganic arsenic compounds is about 100 times higher than organic arsenic compounds, and the toxicity of organic As(III) compounds are approximately 60–80 times higher to humans than As(V) compounds [13-15]. So the world faces major threat to community health from the water supplies with contamination, which has been a clear common view, and stimulated many studies to develop new technologies for water purification. These new developed technologies for treating aqueous arsenic include coagulation, ion exchange, oxidation, membrane separation, and adsorption [16-20]. Among these technologies, adsorption has been widely studied because it is easy to operate and cost-effective. Many materials have been studied as the adsorbents for arsenic removal from aqueous solutions including magnetite-reduced graphene oxide, graphene oxide-MnFe$_2$O$_4$ magnetic nano-hybrids, granular activated carbon based adsorbents, iron based adsorbents, nanoscale zero valent iron, three-dimensional graphene-carbon nanotube-iron oxide nanostructures, DNA aptamers, Fe$_3$O$_4$ nanoparticles, chemically modified sawdust, metal (hydr) oxide coated sand, South African sands, aluminum hydroxide and zeolitic imidazolate framework-8 (ZIF-8) nanoparticles [21-34]. Up to date, the development of new materials
for arsenic removal still a hot topic in environmental field.

Polyaniline (PANI), a well-known conducting polymer, has become one of the most attractive subjects in the last few decades. Due to the unique properties such as electrical conductivity, environmental stability, mechanical strength etc., polyaniline has achieved wide applications including sensors [35], electromagnetic shielding devices [36], wave-absorbing [37] and anticorrosion coatings [38]. Because of large amounts of amine and imine functional groups in molecules, polyaniline is expected to have interactions with some metal ions, which have strong affinity to nitrogen atoms in the structure. For instance, polyaniline has been effectively used to preconcentrate and separate metal ions before instrumental analysis [39-40]. However, the separation of PANI powder absorbents is tedious and costly owing to its intrinsic hydrophilicity [41]. Therefore, it is favorable to develop outstanding absorbents with highly efficient adsorption and easy separation properties for arsenic removal. Combination with excellent magnetic separation property of Fe₃O₄ and good regeneration properties of PANI is a good topic worthing for further research. In fact, some work has been carried out for the preparation of Fe₃O₄@PANI nanomaterials. For example, Fe₃O₄@PANI core-shell microspheres with well-defined blackberry-like morphology were synthesized via an in situ surface polymerization method [42]. Deng et al. prepared conductive core-shell structured Fe₃O₄-polyaniline nanoparticles through an in situ polymerization method [43]. The coated PANI can not only prevent the oxidization and aggregation of pure Fe₃O₄ nanoparticles, but also endow the composite with high adsorption ability and high environmental stability.

In this work, core-shell structured Fe₃O₄@PANI magnetic microspheres were synthesized using a simple two-step polymerization method and its adsorption for arsenic removal from water was investigated. The whole procedure could be simply exhibited as Figure 1. The experimental parameters like pH, adsorbent dosage, contact time, coexisting ions and humic acid (HA) were evaluated.

**2. MATERIALS AND EXPERIMENTAL METHODS**

**2.1. Materials**

Ferric chloride hexahydrate (FeCl₃·6H₂O), sodium acetate (CH₃COONa), ethylene glycol (C₂H₆O₂), ethanol, ammonium peroxydisulfate ((NH₄)₂S₂O₈, APS), polyvinyl pyrrolidone (PVP, 30 kDa) were purchased from Sinopharm Co. (China). All chemicals were of analytical grade and used without further purification. NaAsO₂, Na₂HAsO₄·7H₂O, HCl, NaOH, and NaBH₄ were obtained from Aldrich Chemical Co. A stock standard solution at a concentration of 100 mg/L was purchased from the BHH Biotechnology Co. Ltd. Working solutions were obtained by step-wise dilution of standard solution with ultrapure water. 2.0 % (m/v) NaBH₄ solution was prepared by dissolving NaBH₄ in 0.5% (m/v) NaOH solution. HCl and NaOH were used to adjust the solution pH throughout the experiments. Ultrapure water was prepared by Milli-Q water purification system (Millipore, Bedford, MA, USA) and used throughout the experiments.

![Figure 1: The schematic diagram of Fe₃O₄@PANI preparation and adsorption of As(III) and As(V).](image-url)
2.2. Preparation of Fe₃O₄ and Fe₃O₄@PANI

A solvothermal method was employed for the synthesis of Fe₃O₄ microspheres [44-45]. In brief, FeCl₃·6H₂O (4.32 g) and sodium acetate (12.0 g) were dissolved in 80 mL ethylene glycol. The mixture was vigorously stirred for 30 min at room temperature. The homogeneous yellow solution was then transferred to a Teflon-lined stainless steel autoclave (100 mL). The autoclave was heated at 200 °C for 8 h and allowed to cool to room temperature, then the supernatant was discarded and the black precipitate was collected using a permanent magnet. The precipitate was washed with ethanol and distilled water several times, and finally dried in vacuum oven at 60°C for 12 h.

Magnetic core-shell Fe₃O₄@PANI nanomaterials were prepared using a self-assembly method in the presence of HCl as the method published previously described with modifications [22]. 0.1 g Fe₃O₄ was dissolved in 50 mL of deionized water containing 1 mL of 0.02 M HCl aqueous solution, and then the PVP and FeCl₃·6H₂O were added. Aniline monomer (0.2 mL) was added to the above mixture, and then the mixture was ultrasonically dispersed. Afterward, the mixture was mechanically stirred for 10 h in an ice bath for the primary polymerization. Further APS was slowly added to the suspension with constant stirring and this second oxidative polymerization was continued for 12 h. The obtained green precipitate of Fe₃O₄@PANI magnetic core-shell materials was washed several times with distilled water and ethanol and then dried in vacuum for 8 h at 60 °C.

2.3. Characterization of Fe₃O₄ and Fe₃O₄@PANI

The structures, magnetic characteristics and morphologies of Fe₃O₄ and Fe₃O₄@PANI were investigated using vibrating sample magnetometry (VSM, LakeShore7410, USA), scanning electron microscopy (SEM, Sirion 200 FEG), and transmission electron microscopy (TEM, JEOL-2100F). The surface functional groups were observed by X-ray photoelectron diffraction (XRD, Philips X'pert X-ray diffractometer) and Fourier transform infrared spectroscopy (FTIR, FT-IR-8400s, Shimadzu).

2.4. Batch Sorption Experiments

Batch adsorption experiments were carried out at room temperature (25±1°C), except for the thermodynamic experiments, in which additional temperatures of 35±1°C and 45±1°C were used. Batch adsorption experiments were conducted with 10 mg Fe₃O₄@PANI mixed with 10 mL 1 mg/L As(III) and As(V) solutions. The effect of pH, adsorbent dosage, coexisting ions and HA on the adsorption of As(III) and As(V) were investigated with related parameters changed. Adsorption kinetics and adsorption isotherms were carried out with designed experiments. The mixture was separated from the suspension using an external magnet, the supernatant concentration of arsenic with a hydride generation atomic fluorescence spectrometry (HG-AFS) (AFS-8220, Beijing Jitian Analytical Instrument Corp. Beijing, China), and the operating parameters of HG-AFS was listed in Table 1.

Table 1: Operating Parameters of the HG-AFS

| Parameters                     | Settings |
|--------------------------------|----------|
| Negative high voltage of the PTM (V) | 270      |
| Atomizer height (mm)            | 8        |
| Lamp current (mA)               | 60       |
| Flow rate of carrier gas (mL/min) | 400      |
| Flow rate of shield gas (mL/min) | 800      |
| Concentration of NaBH₄ (m/v)    | 2.0%     |
| Concentration of HCl (V)        | 5%       |
| Read time (s)                   | 12       |
| Delay time (s)                  | 3        |
| Injection volume (mL)           | 1        |
| Read mode                       | Peak area|

Adsorption capacity (qₑ, mg/g) and removal rate (R, %) for arsenic by Fe₃O₄@PANI at equilibrium is calculated as follows:

\[
q_e = \frac{C_o - C_e \times V}{m},
\]

\[
R = \frac{C_o - C_e}{C_o} \times 100\%.
\]

Where qₑ is the equilibrium adsorption capacity of arsenic (mg/g), Cₒ is the initial concentration of arsenic (mg/L), Cₑ is the equilibrium concentration of arsenic (mg/L), V is the volume of the arsenic solution (L), and m is the adsorbent dosage (g), respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Fe₃O₄ and Fe₃O₄@PANI

The morphology of the prepared Fe₃O₄ and Fe₃O₄@PANI was characterized with transmission electron
microscopy and scanning electron microscopy. Figure 2 showed the TEM images of Fe$_3$O$_4$ and Fe$_3$O$_4$@PANI composites. From Figure 2 we can see that Fe$_3$O$_4$ particles are monodisperse and average size of the Fe$_3$O$_4$ particles is about 200 - 300 nm, as shown in Figure 2a. Figure 2b shows that a continuous layer is clearly observed on the outer shell of the Fe$_3$O$_4$ microsphere cores. Figure 2c shows the TEM image of a single Fe$_3$O$_4$@PANI particle with a typical core-shell structure. Moreover, the TEM images with higher resolutions (Figure 2d) reveal that the PANI coating is relatively rough with sizes of 40-70 nm. Figure 2A (a and b) depicts SEM images of Fe$_3$O$_4$ and core-shell Fe$_3$O$_4$@PANI, indicating that both of Fe$_3$O$_4$ and the core-shell Fe$_3$O$_4$@PANI products are well-dispersed with spherical morphology, which is similar to the results obtained from TEM. From Figure 3A (b), it can be seen that the surface of Fe$_3$O$_4$ is covered with PANI and some of them agglomerated due to magneto-dipole interactions between particles [46].

Figure 3B shows the XRD patterns of the Fe$_3$O$_4$ microsphere and Fe$_3$O$_4$@PANI composites. All detected diffraction peaks can be indexed with the standard XRD pattern of face centered cubic (fcc) Fe$_3$O$_4$ (JCPDS card No. 19-629) and no characteristic impurity peaks are observed, which indicates the high purity of Fe$_3$O$_4$. The main peaks of Fe$_3$O$_4$@PANI powder are at 2$\theta$ =30.09°, 35.42°, 43.05°, 56.94° and 62.51°, the diffraction peaks of the Fe$_3$O$_4$@PANI are similar to the pristine Fe$_3$O$_4$ particles, which reveals that the crystal structure of Fe$_3$O$_4$ is well-maintained after the coating process because PANI is thin layer and amorphous crystallinity [47-48].

Fourier transform infrared spectroscopy (FTIR) was used to confirm that aniline had been successfully polymerized onto the Fe$_3$O$_4$ nanoparticles. It can be seen from Figure 3C(a), the characteristic peaks of Fe$_3$O$_4$ microspheres appear at about 594 cm$^{-1}$, belonging to the Fe-O bond stretching [45,49-51], by contrast, the same of the peaks of Fe-O are appeared in Figure 3C(b). Figure 3C(b) shows the spectrum of Fe$_3$O$_4$@PANI, the adsorption peak at 1564 cm$^{-1}$ is attributed to the stretching vibration of the C=C group of the quinoid ring, and the peaks at 1481, 1166 and 1216 cm$^{-1}$ can be assigned to the C=C stretching mode of the benzenoid ring, C-H bending of the quinoid or benzenoid ring and C-N stretching mode, respectively. This indicates that the modification of Fe$_3$O$_4$ particles surface with
PANI is successfully performed. The FT-IR results confirmed the subsequent coating of PANI on Fe$_3$O$_4$ surfaces.

The magnetic behaviors of the Fe$_3$O$_4$ nanoparticles and Fe$_3$O$_4$@PANI composites are investigated at room temperature in the field range of -20 < H < +20 kOe, as shown in Figure 3D. The saturated magnetization (Ms) for Fe$_3$O$_4$ and Fe$_3$O$_4$@PANI is 71.4 and 40.4 emu/g, respectively. The remnant magnetization (Mr) values increased from 1.06 emu/g for Fe$_3$O$_4$ to 1.46 emu/g for Fe$_3$O$_4$@PANI samples. The decreased saturation magnetization values and increased remnant magnetization (Mr) after PANI coating of the Fe$_3$O$_4$ cores may be attributed to the polymer polyaniline coating. After adsorption, the complete magnetic separation of Fe$_3$O$_4$@PANI samples was easily achieved in 2 min by an external magnetic field.

### 3.2. Optimization of Adsorption Parameters

The effect of pH on the adsorption of As(III) and As(V) by Fe$_3$O$_4$@PANI was studied in the range of pH 2.0-10.0 with the initial concentration of As(III) and...
As (V) both at 1 mg/L. The results were shown in Figure 4A. It was obvious that, for both the As(III) and As(V) system the adsorption efficiency was highly pH dependent. When the pH increased from pH 2 to pH 8, the adsorption amounts of As(III) and As(V) significantly increased and when the pH value was about pH 8, the adsorption capacity of the adsorbent almost reached a maximum value.

Dosage of adsorbent was an important parameter for the adsorption of pollutants. A series of experiments were carried out to investigate the effect of adsorbent dosage in the range of 1-30 mg (See Figure 4B). It was observed that the removal rates of the As(III) and As(V) increased as the Fe3O4@PANI dosage was increased over the range from 1 mg to 10 mg and then reached a plateau when the Fe3O4@PANI dosage was 10 mg. With further increase of the Fe3O4@PANI dosage, the removal rates of the As(III) and As(V) exhibited remarkable decrease. Therefore, in the following experiment, 10 mg Fe3O4@PANI sorbents was selected to assure adsorption of analytes.

The effect of competing ions on the adsorption behavior of As(III) and As(V) solution was studied. As can be seen from the Figure 4C, when the concentration of sodium, potassium, calcium, magnesium were 10 fold of As(III) and As(V), the concentration of iron copper, lead, cadmium, nickel and manganese were 1/10 fold of As(III) and As(V), the concentration of sulfate, bicarbonate, nitrate, chlorine were 20 fold of As(III) and As(V), they had no effect on As(III) and As(V) adsorption. When the concentration of HA was 1/10 fold of As(III) and As(V), it has no effect on As(III) and As(V) adsorption. The dependence from As(III) and As(V) adsorption on Fe3O4@PANI against contact time is shown in Figure 4D. It could be seen that the adsorption reached equilibrium at 60 min.

3.3. Adsorption Kinetics

In order to describe the adsorption rate, the pseudo-first-order kinetics model and the pseudo-second-order kinetics model were investigated in this study. The equations are as follows, respectively:

Figure 4: Optimization of experimental parameters for the removal of arsenic by Fe3O4@PANI. A. pH; B. adsorbent dosage; C. co-existing ions and HA; D. contact time.
\[
\ln(q_e - q_t) = \ln q_e - k_1 t \\
\frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{t}{q_e}
\]

(3) \hspace{1cm} (4)

Where \(q_e (\text{mg g}^{-1})\) and \(q_t (\text{mg g}^{-1})\) are the adsorption capacity at equilibrium time and at time \(t\) (min), \(k_1 (\text{min}^{-1})\) and \(k_2 (\text{g mg}^{-1} \text{min}^{-1})\) are the pseudo-first-order adsorption rate constant and the pseudo-second-order adsorption rate constant.

A series of experiments were designed to investigate the adsorption kinetics of Fe\(_3\)O\(_4@\)PANI for As(III) and As(V). The fitting results of the adsorption kinetics were listed in Figure 4D and Table 2. From Figure 4D, the adsorption process was rapid within the first 60 min, and then slowly down. The equilibrium time was found within 60 min for both As(III) and As(V) solutions. From Table 2, it was found that the pseudo-first-order kinetic model did not satisfactorily fit to the experimental data. The calculated equilibrium adsorption capacities \((q_e)\) had great difference with the experimental \((q_e)\) value. The difference between the \(q_e\) values could be due to a time lag, possibly as a result of formation of boundary layer on the surface of the polymer or by the external resistance controlling the adsorption process. On the other hand, from Figure 5 and Table 2, it can be seen that the pseudo-second-order kinetic model was better fit to the experimental data than the pseudo-first-order kinetic model, and the coefficients of \((R^2)\) were much higher than that of pseudo-first-order kinetic model. The calculated equilibrium adsorption capacities \((q_e)\) were similar with the experimental \((q_e)\) value. These results of adsorption kinetics indicated that the adsorption of As(III) and As(V) on Fe\(_3\)O\(_4@\)PANI followed the pseudo-second-order kinetic model. These results were similar to the results in some reports about the adsorption of the As(III) and As(V) on zirconia nanoparticles and the NZVI/AC [52-53].

3.4. ADSORPTION ISOTHERMS

Adsorption isotherms were to explain the relationship between adsorbate and adsorbent. The Langmuir and Freundlich isotherm models were most commonly used. Langmuir model assumes monolayer coverage on adsorbent [54], and the monolayer adsorption occurred without interaction between sorption sites. Freundlich model was an empirical model allowing for multilayer adsorption on adsorbent [55]. In our study both of the two models were applied to simulate the adsorption of As(III) and As(V) on Fe\(_3\)O\(_4@\)PANI. The Langmuir linear model can be expressed as:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}
\]

(5)

where \(q_m (\text{mg/g})\) is the maximum adsorption capacity; \(q_e (\text{mg/g})\) is the equilibrium adsorption capacity of

| Ions    | \(q_{\text{equat}} (\mu\text{g/g})\) | Pseudo-First-Order Kinetic Model | Pseudo-Second-Order Kinetic Model |
|---------|------------------------------------|----------------------------------|-----------------------------------|
|         | \(k_1 (\text{min}^{-1})\) | \(q_{\text{calat}} (\mu\text{g/g})\) | \(R^2\) | \(k_2 (\text{g/(mg.min)})\) | \(q_{\text{calat}} (\mu\text{g/g})\) | \(R^2\) |
| As(III) | 476.2                             | 0.0015                           | 14.61                             | 0.023 | 1.073                             | 477.15 | 0.9996 |
| As(V)   | 476.1                             | 0.0032                           | 22.55                             | 0.284 | 0.585                             | 478.05 | 0.9993 |

Figure 5: The pseudo-second-order kinetic models. (a) As(III); (b) As(V).
adsorbent; Ce is the equilibrium concentration of the adsorbate and $K_L$ (L/mg) is the Langmuir adsorption equilibrium constant, which is related to the adsorption energy.

Furthermore, the type of the Langmuir isotherm can be used to predict whether the adsorption is favorable or unfavorable in term of dimensionless constant separation factor $R_L$.

$$R_L = \frac{1}{1 + K_L C_0}$$

Here $C_0$ (mg/L) represents the initial concentration of As(III) and As(V). The values of separation factor constant ($R_L$) are used to indicate that the possibility of the adsorption process to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The $R_L$ values for As(III) and As(V) were calculated as 0.038 and 0.171, which were all between 0 and 1, and indicated that the adsorption were favorable.

The Freundlich isotherm linear model is depicted by the following formula:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K$$

where $K$ and $n$ are the empirical constants.

The results for Langmuir and Freundlich isotherms were listed in Table 3. The correlation coefficients ($R^2$) for Freundlich isotherm model was higher than that for Langmuir isotherm model, and $n$ values were greater than one, which indicated that the adsorption of arsenic onto Fe$_3$O$_4$@PANI was favorable and obeyed the Freundlich isotherm model. The results also indicated that the adsorption was heterogeneous and multilayer. The maximum adsorption capacities for As (III) and As(V) were 1.066 and 1.385 mg/g, respectively.

3.5. Thermodynamic Studies

It is necessary to conclude whether the adsorption process is spontaneous or not. Free energy of adsorption ($\Delta G^o$), enthalpy ($\Delta H^o$), and entropy ($\Delta S^o$) changes are often calculated to predict the nature of adsorption. The relationship between the equilibrium constant ($K^o$) and Gibbs free energy change ($\Delta G^o$, kJ/mol) of the adsorption process can be obtained from the equation as below,

$$\Delta G^o = -R T \ln K^o$$

Where $R$ is the universal gas constant (8.314 J/mol K) and $T$ is the absolute temperature (K). Values of $K^o$ can be calculated according to the method by plotting $\ln(q_e/C_e)$ versus $q_e$ and extrapolating $q_e$ to zero under different temperatures.

Enthalpy ($\Delta H^o$, kJ/mol) and entropy ($\Delta S^o$, J/mol K) changes can be estimated by the following equations, where $\Delta H^o$ and $\Delta S^o$ values can be calculated from the slope and intercept of the plot of $\ln K^o$ versus $1/T$.

$$\ln K^o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

$$\Delta H^o = \Delta G^o + T \Delta S^o$$

The thermodynamic parameters for the adsorption process of As(III) As(V) were shown in Table 4. The negative values of $\Delta G$ at different temperatures confirmed the spontaneous nature of the adsorption pro-

| Ions   | $K_L$  | $q_{max}$(mg/g) | $R_L$  | $R^2$  | $K_F$ | $1/n$ | $R^2$  |
|--------|--------|-----------------|-------|--------|-------|-------|--------|
| As(III)| 25.09  | 1.066           | 0.038 | 0.721  | 4.89  | 0.684 | 0.985  |
| As(V)  | 4.84   | 1.385           | 0.171 | 0.847  | 2.80  | 0.794 | 0.997  |

| Ions   | 298K   | 308K   | 318K   |
|--------|--------|--------|--------|
| As(III)| -12.56 | -9.79  | -8.93  |
| As(V)  | -10.53 | -8.93  | -4.88  |

| Ions   | 298K   | 308K   | 318K   |
|--------|--------|--------|--------|
| As(III)| -67.08 | -67.08 | -8.93  |
| As(V)  | -95.18 | -95.18 | -4.88  |
cess. The negative standard enthalpy change suggested that the interaction of arsenic adsorbed by Fe₃O₄@PANI was exothermic. The -ΔG° values decreased with increasing temperature, which indicated that elevated temperature was unfavorable to the adsorption of arsenic, and which was identical with the exothermic nature of the adsorption.

3.6. Desorption and Regeneration

In order to evaluate the reusability of the Fe₃O₄@PANI, adsorption-desorption experiments were performed. In this experiment, 0.1 M HCl was used to elute the arsenic adsorbed on the surface of Fe₃O₄@PANI. The same Fe₃O₄@PANI nanoparticles were used for adsorption and then desorbed with 10 mL 0.1 M HCl for 10 min by ultrasonication, after that, washed by water, repeated for five times and the results were shown in Figure 6. It could be seen that Fe₃O₄@PANI could maintain high adsorption capacity during the fifth sorption-desorption cycles.

![Figure 6: Recycling of Fe₃O₄@PANI in the removal of As(III) at T= 298 K.](image)

4. CONCLUSIONS

A core-shell structured polyaniline coated Fe₃O₄@PANI material was successfully prepared and used as magnetic sorbents to remove the arsenic from environmental water. Adsorption of arsenic followed pseudo-second-order kinetics, and Freundlich isotherm model was suitable for describing the adsorption of As(III) and As(V) by Fe₃O₄@PANI. The adsorption capacity (q_max) of Fe₃O₄@PANI for As(III) and As(V) were 1.066 and 1.385 mg/g, respectively. The results indicated that the prepared core-shell Fe₃O₄@PANI material could be used as an effective sorbent for the simple and rapid removal of arsenic from water samples. Core-shell Fe₃O₄@PANI material exhibited good adsorption ability and had excellent potential prospect in the removal of pollutants.

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REFERENCES

[1] Winkel LHE, Pham TKT, Vi ML, Stengela C, Aminia M, Hac NT, et al. Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century, Proc Natl Acad Sci USA. 2011; 108: 1246-1251. http://dx.doi.org/10.1073/pnas.1011915108

[2] Kleinert S, Muehe EM, Posth NR, Dippon U, Daus B, Kappler A. Biogenic Fe(III) minerals lower the efficiency of iron-mineral-based commercial filter systems for arsenic removal, Environ Sci Technol. 2011; 45: 7533-7541. http://dx.doi.org/10.1021/es102552n

[3] Budinova T, Petrov N, Razvigorova M, Parra J, Galiatsatou P. Removal of arsenic(III) from aqueous solution by activated carbons prepared from solvent extracted olive pulp and olive stones, Ind Eng Chem Res. 2006; 45: 1896-1901. http://dx.doi.org/10.1021/ie050127a

[4] Dhar R, Biswas B, Samanta G, Mandal B, Chakraborti D, Roy S, et al. Groundwater arsenic calamity in Bangladesh. Curr Sci. 1997; 73: 48-59.

[5] Chakraborti D, Rahman MM, Das B, Murrill M, Dey S, Mukherjee SC, et al. Status of groundwater arsenic contamination in Bangladesh: A 14-year study report. Water Res. 2010; 44: 5789-5802. http://dx.doi.org/10.1016/j.watres.2010.06.051

[6] Ng JC, Wang J, Shraim A. A global health problem caused by arsenic from natural sources. Chemosphere 2003; 52: 1353-1359. http://dx.doi.org/10.1016/S0045-6535(03)00470-3

[7] Awual MASM, Yaita T, Shiwaku H, Jyo A. Efficient arsenic (V) removal from water by ligand exchange fibrous adsorbent, Water Res. 2012; 46: 5541-5550. http://dx.doi.org/10.1016/j.watres.2012.07.038

[8] Nguyen VA, Bang S, Viet PH, Kim KW. Contamination of groundwater and risk assessment for arsenic exposure in Ha Nam province. Vietnam Environ Int. 2009; 35: 466-472. http://dx.doi.org/10.1016/j.envint.2008.07.014

[9] Bhattacharjee P, Banerjee M, Giri AK. Role of genomic instability in arsenic-induced carcinogenicity, A review. Environ Int 2013; 53: 29-40. http://dx.doi.org/10.1016/j.envint.2012.12.004

[10] Who, Guidelines for drinking-water quality, second ed., vol. 1. Recommendations, WHO (a), Geneva, Switzerland, 1993.

[11] USEPA, Arsenic treatment technologies for soil, waste and water, Tech Report No. EPA-542-R-02-004, 2002.

[12] CMOH, China Ministry of Health (CMOH), Standards for Drinking Water Quality-GB5749-2006, 2006 (in Chinese).

[13] Ferguson JF, Gavis J. A review of the arsenic cycle in natural water, Water Res. 1972; 6: 1259-1274. http://dx.doi.org/10.1016/0043-1354(72)90052-8

[14] Villaescusa I, Bollinger JC, Arsenic in drinking water: sources, occurrence and health effects (a review). Rev Environ Sci Biotechnol. 2008; 7: 307-323. http://dx.doi.org/10.1007/s11157-008-9138-7
[15] Bhandari N, Reeder RJ, Strongin DR. Photoinduced oxidation of arsenite to arsenate in the presence of goethite. Environ Sci Technol. 2012; 46: 8044-8051. http://dx.doi.org/10.1021/es300988p

[16] Baskan MB, Pala A. A statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate. Desalination 2010; 254: 42-48. http://dx.doi.org/10.1016/j.desal.2009.12.016

[17] Hristovski K, Westerhoff P, Möller T, Sylvester P, Condit W, Mashe H. Simultaneous removal of perchlorate and arsenate by ion-exchange media modified with nanostructured iron (hydr)oxide. J Hazard Mater. 2008; 152: 397-406. http://dx.doi.org/10.1016/j.jhazmat.2007.07.016

[18] Sorlini S, Gialdini F. Conventional oxidation treatments for arsenic from contaminated groundwater by membrane-integrated hybrid treatment system. J Membrane Sci. 2010; 354: 108-113. http://dx.doi.org/10.1016/j.memsci.2010.02.063

[19] Sen M, Manna A, Pal P. Removal of arsenic from contaminated groundwater by membrane-integrated hybrid treatment system. J Membrane Sci. 2010; 354: 108-113. http://dx.doi.org/10.1016/j.memsci.2010.02.063

[20] Maji SK, Pal A, Pal T. Arsenic removal from real-life groundwater by adsorption on laterite soil. J Hazard Mater. 2008; 151: 811-820. http://dx.doi.org/10.1016/j.jhazmat.2007.06.060

[21] Chandra V, Park J, Chun Y, Lee JW, Hwang IC, Kim KS. Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal. ACS Nano 2010; 4: 3979-3986. http://dx.doi.org/10.1021/nn1008897

[22] Kumar S, Nair RR, Pillai PB, Gupta SN, Iyengar MAR, Sood AK. Graphene oxide-MnFe2O4 Magnetic nanohybrids for efficient removal of lead and arsenic from water. ACS Appl Mater Interfaces 2014; 6: 17426-17436. http://dx.doi.org/10.1021/am504826q

[23] Gu Z, Fang J, Deng B. Preparation and evaluation of gac-based iron-containing adsorbents for arsenic removal. Environ Sci Technol. 2005; 39: 3833-3843. http://dx.doi.org/10.1021/es048179r

[24] Kanel SR, Manning B, Charlet L, Choi H. Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. Environ Sci Technol. 2005; 39: 1291-1298. http://dx.doi.org/10.1021/es048991u

[25] Vadahanamibi S, Lee SH, Kim WJ, Oh IK. Arsenic removal from contaminated water using three-dimensional graphene-carbon nanotube-iron oxide nanostuctures. Environ Sci Technol. 2013; 47: 10510-10517. http://dx.doi.org/10.1021/es401389g

[26] Kim M, Um HJ, Bang S, Lee SH, Oh SJ, Han JH, et al. Arsenic removal from Vietnamese groundwater using the arsenic-binding DNA aptamer. Environ Sci Technol. 2009; 43: 9335-9340. http://dx.doi.org/10.1021/es902407g

[27] Luo T, Cui J, Hu S, Huang Y, Jing C. Arsenic removal and recovery from copper smelting wastewater using TiO2. Environ Sci Technol. 2010; 44: 9094-9098. http://dx.doi.org/10.1021/es1024355

[28] Lunge S, Singh S, Sinha A. Magnetic iron oxide(Fe3O4) nanoparticles from tea waste for arsenic removal. J Magn Magn Mater. 2014; 356: 21-31. http://dx.doi.org/10.1016/j.jmmm.2013.12.008

[29] Li CH, Xu W, Jia DM, Liu XW. Removal of arsenic from drinking water by using the Zr-loaded resin. J Chem Eng Data 2013; 58: 427-435. http://dx.doi.org/10.1021/je301148t

[30] Huang YX, Yang JK, Keller AA. Removal of arsenic and phosphate from aqueous solution by metal (hydr)oxide coated sand. ACS Sustainable Chem Eng. 2014; 2: 1128-1138. http://dx.doi.org/10.1021/sc400484s

[31] Setyono D, Vallyaveettil S. Chemically modified sawdust as renewable adsorbent for arsenic removal from water. ACS Sustainable Chem Eng. 2014; 2: 2722-2729. http://dx.doi.org/10.1021/sc500458x

[32] Trois C, Cibati A. South African sands as a low cost alternative solution for arsenic removal from industrial effluents in permeable reactive barriers: Column tests. Chem Eng J. 2015; 259: 981-989. http://dx.doi.org/10.1016/j.cej.2014.08.063

[33] Jian MP, Liu B, Zhang GS, Liu RP, Zhang XW. Adsorptive removal of arsenic from aqueous solution by zeolitic imidazolate framework-8 (ZIF-8) nanoparticles. Colloids and Surfaces A: Physicochem Eng Aspects 2015; 465: 65-76. http://dx.doi.org/10.1016/j.colsurfa.2014.10.023

[34] Liu RP, Zhu LJ, He Z, Lan H, Liu H, Jiuhui Qu J. Simultaneous removal of arsenic and fluoride by freshly-prepared aluminum hydroxide, Colloids and Surfaces A: Physicochem Eng Aspects 2015; 466: 147-153. http://dx.doi.org/10.1016/j.colsurfa.2014.10.007

[35] Huang JX, Virji S, Weiller BH, Kaner RB. Polyaniline nanofibers: facile synthesis and chemical sensors. J Am Chem Soc. 2003; 125: 314-315. http://dx.doi.org/10.1021/ja028371y

[36] Saini P, Choudhary V, Singh BP, Mathur RB, Dhawan SK. Polyaniline-MWNCNT nanocomposites for microwave absorption and EMI shielding. Mater Chem Phys. 2009; 113: 919-926. http://dx.doi.org/10.1016/j.matchemphys.2008.08.065

[37] Li Q, Zhang C, Li J. Photocatalysis and wave-absorbing properties of polyaniline/TiO2 microbelts composite by in situ polymerization method. Appl Surf Sci. 2010; 257: 944-948. http://dx.doi.org/10.1016/j.apsusc.2010.07.098

[38] Shimano JY, MacDiamid AG. Polyaniline, a dynamic block copolymer: Key to attaining its intrinsic conductivity. Synth Metal. 2001; 123: 251-262. http://dx.doi.org/10.1016/S0379-6779(01)00293-4

[39] Chandrasekaran K, Krishna MVB, Karunasagar D. On-line speciation of inorganic arsenic in natural waters using polyaniline(PANI) with determination by flow injection-hydride generation-inductively coupled plasma mass spectrometry at ultra-trace levels. J Anal At Spectrom. 2010; 25: 1348-1353. http://dx.doi.org/10.1039/c002330b

[40] Wang J, Deng BL, Chen H, Wang XR, Zheng JZ. Removal of Aqueous Hg(II) by Polyaniline: Sorption Characteristics and Mechanisms. Environ Sci Technol. 2009; 43: 5223-5228. http://dx.doi.org/10.1021/es803710k

[41] Guo X, Fei GT, Su H, Zhang LD. Synthesis of polyaniline micro/nanospheres by a copper(II)-catalyzed self-assembly method with superior adsorption capacity of organic dye from aqueous solution. J Mater Chem. 2011; 21: 8618-8625. http://dx.doi.org/10.1039/c004489j

[42] Xuan SH, Wang YXJ, Leung KCF, Shu KY. Synthesis of Fe3O4@Polyaniline Core/Shell Microspheres with Well-Defined Blackberry-Like Morphology. J Phys Chem C. 2008; 112: 18804-18809. http://dx.doi.org/10.1021/jp807124z

[43] Deng JG, He CL, Peng YX, Wang J, Long X, Li P, et al. Magnetic and conductive Fe3O4-polyaniline nanoparticles with core-shell structure. Synth Metal. 2003; 139: 295-301. http://dx.doi.org/10.1016/S0379-6779(03)00166-8
[44] Baykal A, Senel M, Unal B, Karaoğlu E, Sözeri H, Toprak MS. Acid Functionalized multiwall carbon nanotube/magnetite (MWCNT)-COOH/Fe₃O₄ hybrid: synthesis, characterization and conductivity evaluation. J Inorgan Organometal Polym Mater. 2013; 23: 726-735. http://dx.doi.org/10.1007/s10904-013-9839-4

[45] Xuan S, Wang YX, Yu JC, Leung KC. Preparation, characterization, and catalytic activity of core/shell Fe₃O₄@polyaniline@Au nanocomposites. Langmuir 2009; 25: 11835-43. http://dx.doi.org/10.1021/la901462t

[46] Zhao DL, Zhang HL, Zeng XW, Xia QS, Tang JT. Inductive heat property of Fe₃O₄/polymer composite nanoparticles in an ac magnetic field for localized hyperthermia. Biomed Mater. 2006; 1: 198-201. http://dx.doi.org/10.1088/1748-6041/1/4/004

[47] Li Q, Zhang C, Li J. Photocatalysis and wave-absorbing properties of polyaniline/TiO₂ microbelts composite by in situ polymerization method. Appl Surf Sci. 2010; 257: 944-948. http://dx.doi.org/10.1016/j.apsusc.2010.07.098

[48] Ma J, Wang Y, Niu J, Shen X. Synthesis and Characterization of La-doped Fe₃O₄-polyaniline magnetic response nanocomposites. J Macromol Sci, Part B. 2006; 45: 533-540. http://dx.doi.org/10.1080/00222340600769972

[49] Liu JF, Zhao ZS, Jiang GB. Coating Fe₃O₄ Magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. Environ Sci Technol. 2008; 42: 6949-6954. http://dx.doi.org/10.1021/es080924c

[50] Yao W, Shen C, Lu Y. Fe₃O₄@C@polyaniline trilaminar core-shell composite microspheres as separable adsorbent for organic dye. Comp Sci Technol. 2013; 87: 8-13. http://dx.doi.org/10.1016/j.compscitech.2013.07.023

[51] Zheng YM, Yu L, Wu D, Che JP. Removal of arsenite from aqueous solution by a zirconia nanoparticle. Chem Eng J. 2012; 188: 15-22. http://dx.doi.org/10.1016/j.cej.2011.12.054

[52] Zhu HJ, Jia YF, Wu X, Wang H. Removal of arsenic from water by supported nano zero-valent iron on activated carbon. J Hazard Mater. 2009; 172: 1591-1596. http://dx.doi.org/10.1016/j.jhazmat.2009.08.031

[53] Deng X, Lu L, Li H, Luo F. The adsorption properties of Pb(II) and Cd(II) on functionalized graphene prepared by electrolysis method. J Hazard Mater. 2010; 183: 923-30. http://dx.doi.org/10.1016/j.jhazmat.2010.07.117

[54] Chilton N, Jack NL, Wayne EM, Ramu MR. Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin-water system. Bioresource Technol. 2002; 85: 131-135. http://dx.doi.org/10.1016/S0960-8524(02)00093-7

[55] Guo XJ, Chen FH. Removal of arsenic by bead cellulose loaded with Iron oxyhydroxide from groundwater. Environ Sci Technol. 2005; 39: 6808-6818. http://dx.doi.org/10.1021/es048080k