

Research Article

Performance of a New Magnetic Chitosan Nanoparticle to Remove Arsenic and Its Separation from Water

Cheng Liu,^{1,2} Bin Wang,² Yang Deng,³ Biao Cui,¹ Jie Wang,¹ Wei Chen,^{1,2} and Si-yuan He²

¹Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, Hohai University, Nanjing 210098, China

²College of Environment, Hohai University, Nanjing 210098, China

³Department of Earth and Environmental Studies, Montclair State University, Montclair, NJ 07043, USA

Correspondence should be addressed to Wei Chen; cw5826@hhu.edu.cn

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Removal performance of arsenic in water by a novel magnetic chitosan nanoparticle (MCNP) with a diameter of about 10 nm, including adsorption kinetics, adsorption isotherm, main influencing factors, and regeneration effects, was investigated. In addition, the effective separation way for MCNP particles and the new application mode were developed to prompt the application of MCNP. The results showed that MCNP exhibited excellent ability to remove As(V) and As(III) from water in a wide range of initial concentrations, MCNP removed arsenic rapidly with more than 95% of arsenic adsorbed in initial 15 min, and the whole process fitted well to the pseudo-second-order model. The Langmuir model fits the equilibrium data better than the Freundlich isotherm model and the maximum adsorption capacities of As(V) and As(III) were 65.5 mg/g and 60.2 mg/g, respectively. The saturated MCNP could be easily regenerated and kept more than 95% of initial adsorption capacity stable after 10 regeneration cycles. A new magnetic material separation method was established to separate MCNP effectively. The continuous-operation instrument developed based on the MCNP could operate stably and guarantee that the concentration of arsenic meets the guideline limit of arsenic in drinking water regulated by the WHO.

1. Introduction

Arsenic has been found in the groundwater in many regions of the world such as Bangladesh [1], India [2], and other countries [3]. In China, approximately 20 million people are at risk of drinking As-contaminated water from tube wells which resulted in arsenic poisoning being the serious endemic disease [4–6]. The arsenic presence in drinking water is extremely detrimental to human health [7]; most countries are implementing the maximum permissible limit of arsenic in drinking water of 10 $\mu\text{g/L}$ recommended by the World Health Organization.

Several methods, just like precipitation [8], membrane separation, ion exchange, and adsorption [9–11], have been applied to remove excessive arsenic from water. Adsorption has received special attention due to its good removal effects and easy operation [12]. The characteristics of

absorbents played important role in their removal performance. Chitosan is a poly-N-glucosamine species obtained by the deacetylation of chitin, the most abundant amino-polysaccharide existing in the environment. It is highly hydrophilic and is characterized by a flexible polymer chain and by a large number of hydroxyl and amino groups that represent potential adsorption sites.

Chitosan derivatives, obtained through chemical and physical modifications, cross-linking, modifying its physical structure, immobilizing it on insoluble supports, or impregnating it with metals, are preferred. Chitosan and chitosan derivatives, as kinds of arsenic-removing agents, were receiving more and more attention. Nanochitosan [13], zero-valent iron encapsulated chitosan [14], mixed metal oxide impregnated chitosan beads (MICB) [15], TiO_2 -impregnated chitosan bead [16], aluminum and doping chitosan-Fe(III) hydrogel [17], and chitosan complexed with transition metal

ions [18] were used to remove arsenic from water in recent studies. The amino group existing in chitosan has been reported to be an efficient heavy metal scavenger [19]. Therefore, greater surface area and amine functions may cause better removal effects of arsenic. Two ways could be used to increase the surface area of the adsorbents; decreasing the particle size was one of the choices. However, smaller particle size may cause difficulty in the separation and influence the water quality of the effluent. In our recent research, a novel magnetic chitosan nanoparticle (MCNP) was prepared by one-step in situ coprecipitation at low temperature and normal atmosphere, which showed significant adsorption potential for the removal of humic acid (HA) from aqueous solution [20, 21], but the removal performance for arsenic and subsequent separation have not been examined.

Herein, the uptake capacity and adsorption kinetics for As(V) and As(III) by magnetic chitosan nanoparticle (MCNP) and its regeneration efficiency were investigated. New separation method of MCNP was explored in the meantime. Furthermore, removal of arsenic from real underground water by the adsorbent was also evaluated.

2. Material and Methods

2.1. Raw Water and Chemicals. As(III) and As(V) standard reference sodium arsenite (1000 mg/L) and chitosan with a deacetylation degree of 80–95% were purchased from Sinopharm Chemical Reagent Co. Ltd., China, and used without any further purification. All the other chemicals used were of analytical grade. Distilled water was used throughout the study.

Raw water sample was taken from Bayannur city in Inner Mongolia of China. The values of main water parameters for the raw water were shown in Table 1.

2.2. Preparation of MCNP. The MCNP was synthesized as the methods described in our former study [20], with the main steps as follows. Chitosan solution was prepared by dissolving 0.5 g of chitosan in 200 mL of 0.5% (v/v) acetic acid solution with continuous stirring. 4.7 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.4 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, which were dissolved in 22 mL of distilled water, respectively, were added to the chitosan solution by stirring at 1000 rpm for 20 min in a water bath at 40°C. After that, 40 mL of 28% (m/v) ammonia was added dropwise into the reaction system. After 20 min, the temperature of the reaction system was adjusted to 60°C, and then 6 mL of epichlorohydrin was added to the system with continuous stirring at 1000 rpm for 3 h. The resulting MCNP was separated by a magnet field. Finally, the obtained MCNP was washed by 0.5% (v/v) acetic acid, distilled water, and alcohol for three times, respectively, and dried in an oven at 60°C till reaching constant weight.

The main parameters of MCNP are shown in Table 2. As a comparison, the result of recent similar study is shown in the table either. The other important parameter, the total amount of amine groups, or the degree of deacetylation (DDA%) of MCNP can be determined with the carbon-to-nitrogen ratio (C/N ratio) [22] that resulted from XPS.

TABLE 1: Characteristics of the natural water sample from Inner Mongolia of China.

Items	Value
As (mg/L)	0.03–0.032
F (mg/L)	0.52–0.58
Cl (mg/L)	91.5–98.6
SO_4^{2-} (mg/L)	57.2–63.5
Hg (mg/L)	0.006
Pb (mg/L)	—
Mn (mg/L)	0.01–0.015
Fe (mg/L)	0.21–0.36
Cu (mg/L)	0.003–0.005
Na (mg/L)	43.5–51.3
Ca (mg/L)	88.9–95.4
Mg (mg/L)	0.0213
Total hardness (mg/LCaCO ₃)	432.5–465.8
UV ₂₅₄ (cm ⁻¹)	0.046
pH	7.3–7.5
DOC (mg/L)	0.57–0.86

TABLE 2: The main characterization of two kinds of magnetic chitosan.

Parameters	MCNP	MICB [19]
Diameter (nm)	6–10	2.5×10^6
Saturation magnetization (μg)	44.43	17.14
Specific gravity	1.002	—
Specific surface area (m ² /g)	108.32	50.20
Total pore volume (cm ³ /g)	0.40	0.052
Proportion of chitosan (%)	29.2	—
Point of zero	6.34	—
Magnetic powder category	Fe ₃ O ₄	Fe ₃ O ₄

2.3. Arsenic Adsorption Experiments. Similar experiment method as in former study [19] was used for contrast with other studies. Adsorption experiments were conducted in conical flasks containing 100 mL of As(III) and As(V) solution of variable initial concentrations from 0.2 to 50 mg/L and 0.05 g of MCNP at specified temperature. The flasks were shaken on a shaker equipped with thermostat at 150 rpm. After predetermined contact time, the aqueous sample was separated by a magnet, and the residual concentration of As(III) and As(V) in the supernatant was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, the detection limit of 0.001 mg/L, Intrepid II, Thermofisher, USA).

The adsorption capacity at equilibrium of the adsorbents for arsenic was calculated according to the following:

$$q_t = \frac{(C_0 - C_t)V}{m}, \quad (1)$$

where C_0 (mg/L) is the initial concentration of arsenic, C_t (mg/L) is the instant concentration of arsenic at any time t , V (L) is the volume of solution, and m (g) is the mass of MCNP.

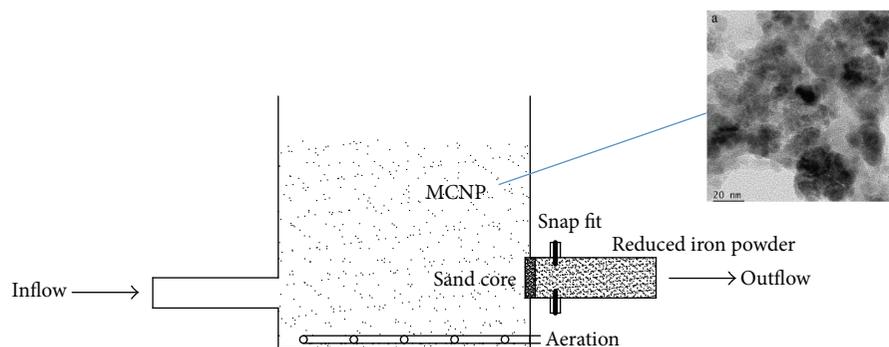


FIGURE 1: Diagram of continuous-operation instrument using MCNP as the arsenic removal agents.

To estimate adsorption rate for the uptake of As(III) and As(V) by MCNP, time-dependent adsorption studies were conducted. The kinetics adsorption on both As(III) and As(V) was investigated using different initial arsenic concentrations of ~ 2.0 mg/L, ~ 5.0 mg/L, and ~ 10.0 mg/L, respectively, with 1.0 g/L of adsorbent and a total solution volume of 750 mL As(III) and As(V) solutions immersed in 1000 mL glass vessel. The pH of the solutions was chosen at 6.8 ± 0.2 for optimal adsorption. The mixtures were shaken at 140 rpm and approximately 5 mL aliquots were then removed periodically for measuring the corresponding arsenic concentration, in order to calculate their time-dependent adsorption capacity.

2.4. Regeneration of MCNP. Regeneration of arsenic saturated adsorbents was achieved using sodium hydroxide solution according to former study. As to the special characteristic of MCNP, regeneration conditions need to be optimized, especially for the proper concentration of sodium hydroxide solution and reaction time. The adsorption performance of the regenerated MCNP was evaluated with both adsorption capacity and removal efficiency for the initial arsenic concentration of 1 mg/L As(V) and As(III) solutions and adsorbent dose of 1 g/L at pH 6.8 ± 0.2 for 0.5 h.

2.5. Separation of MCNP. Magnetic field was one of the most popular ways to separate magnetic materials; however, it was limited in the practice of application, especially to the continuous operation. The down-flow filtration with iron powder was used to hold up the MCNP, during which the depth of iron powder was investigated for the influence of the separation effects. The diameter of powder used in the experiment was 1-2 mm. Turbidity, particle count of certain diameter, and particle size distribution were used to estimate the separation effect of the filtration. Turbidity meter (2010N, Hach), particle counting instrument (IBR), and Zetasizer Nano ZS90 instrument (Malvern Instruments Ltd., UK) were used to determine the above index.

2.6. Continuous Dynamic Adsorption Experiments. Continuous dynamic adsorption experiments were conducted in a Perspex device (as shown in Figure 1). The MCNP were added into the water as the concentration of 5 g/L and mixed

through the way of pulse aeration. The influent raw water blended with the water containing MCNP and flowed counterclockwise due to the heterogeneous intensity of aeration. The effluent was collected from the devices outlet at regular intervals of time and the concentrations of arsenic, turbidity, and metal ions in the effluent solution were measured immediately. The outlet was composed of sand core filter and iron powder filter consequently, and both could be exchanged if needed. The used MCNP were taken away for regeneration and the same dosages of regenerated particles were put back into the instrument at certain time. The exchanged iron powder filter was flushed with water and air; the backwash water was collected together to reclaim, regenerate, and reuse the MCNP accordingly. All the experiments were operated at room temperature.

3. Results and Discussion

3.1. Performance of MCNP to Remove Arsenic from Water

3.1.1. Adsorption Kinetics for Arsenic Removal from Synthetic Water. Figure 2 shows the change of adsorbed arsenic as a function of contact time.

As seen from Figure 2, MCNP adsorbs both As(V) and As(III) with a fast speed. More than 95% of the equilibrium adsorption capacity for As(V) and As(III) was achieved within 15 min, which was significantly less than that of MICB [19]. In addition, little difference existed for the As(V) and As(III) adsorption process. As shown from Table 2, the main differences between the MCNP and MICB were the particle size and surface area. MCNP has smaller particle diameter and larger surface area than MICB, which increased the contact area of MCNP and arsenic ion and shortened the migration distance of arsenic molecular. Pseudo-first-order and pseudo-second-order kinetic models were used to simulate the kinetics and quantify the changes of arsenic adsorption (Table 3). The pseudo-first-order model fitted the experimental data better than the pseudo-second-order one for both As(V) and As(III), which was different from that of MICB. Because the MCNP had little pores, the adsorption process may consist of two processes: (1) the transport of arsenic from bulk solution to the surface of MCNP and (2) the attachment of arsenic to MCNP. According to former

TABLE 3: Kinetics parameters for As(V) and As(III) adsorption on the MCNP and MICB with various initial arsenic concentrations.

Arsenic species	Initial concentration (mg/L)	Adsorbent category	First-order kinetics			Second-order kinetics		
			k_1 (1/min)	q_e	R^2	k_2 (1/min)	q_e	R^2
As(V)	2.02	MICB	0.00447	0.09829	0.923	0.0184	2.03	0.999
		MCNP	0.66894	2.0381	0.999	1.47387	2.05	0.988
	5.28	MICB	5.37×10^{-3}	2.762	0.786	6.985×10^{-3}	5.229	0.999
		MCNP	0.80321	5.07219	0.999	1.35289	5.09	0.989
	10.73	MICB	5.82×10^{-3}	3.549	0.648	5.80×10^{-3}	10.619	0.999
		MCNP	1.03997	10.1352	0.999	0.83557	10.21	0.98
As(III)	2.01	MICB	0.00937	0.6384	0.886	0.0152	2.03	0.999
		MCNP	0.67013	2.00007	0.999	2.0559	2.002	0.96
	5.19	MICB	0.00898	3.9759	0.927	6.659×10^{-3}	5.089	0.999
		MCNP	0.80656	4.99143	0.999	1.10786	5.01	0.985
	10.58	MICB	0.00963	7.9044	0.960	3.07×10^{-3}	9.859	0.999
		MCNP	1.19382	9.68389	0.999	1.00456	9.724	0.982

Note: the data of MICB is taken from the study of Wang et al. [19].

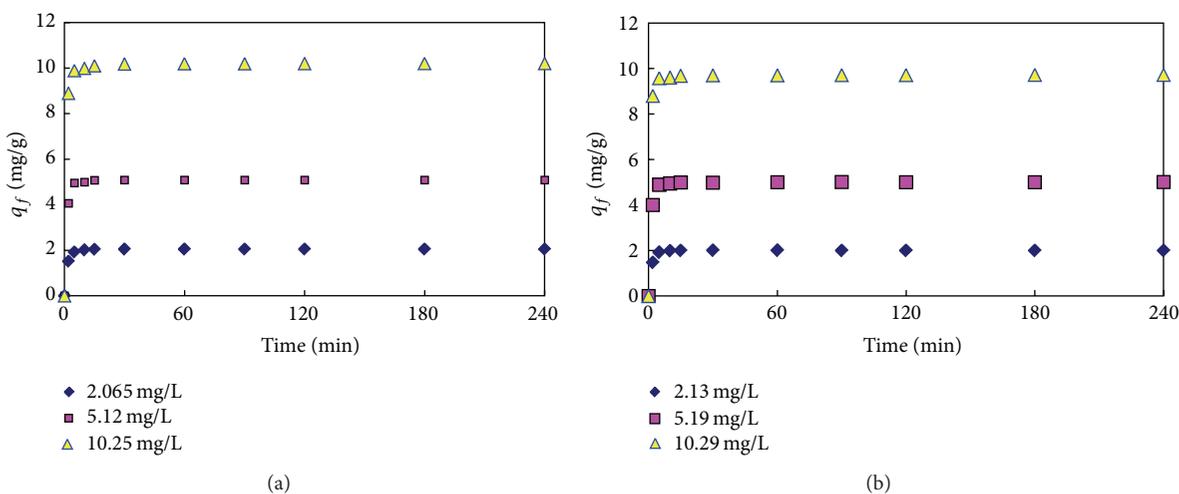


FIGURE 2: Kinetics of (a) As(V) and (b) As(III) removal by the MCNP at different initial concentrations: ~ 2 mg/L, ~ 5 mg/L, and ~ 10 mg/L, respectively. Adsorbent dose: 1 g/L, pH: 6.8 ± 0.2 , and temperature: 25°C .

studies, the attachment of arsenic molecules to the protonated amino groups ($-\text{NH}_3^+$) on the chitosan was quite instant. Due to higher surface area and shorter transport distance, the effects of mass transport were decreased significantly and the attachment of arsenic onto MCNP became the main limited step. Therefore, the removal process was found to follow the pseudo-first-order kinetic model. As seen in Table 3, the removal rate of MCNP was significantly higher than that of MICB (0.66894, 0.67013 versus 0.00447, 0.00937 for 2 mg/L of As(V) and As(III), resp.). In addition, proper agitation during the removal process was needed to further accelerate the removal rates of arsenic according to the analysis for removal process, for that proper agitation could thin the aqueous layer and shorten the migration distance from the water bulk to the particle surface.

As to the two kinds of arsenic, similar values of k_1 for As(V) and As(III) adsorption were found under the same experimental conditions, which is different from other studies. According to the adsorption process of arsenic

onto MCNP, the relatively shorter distance and abundance of accessible adsorption sites may cause the remarkable difference.

3.1.2. Adsorption Isotherms for Arsenic Removal from Synthetic Water. The isotherm points at different equilibrium concentration, the fitting curves, and adsorption parameters obtained from the isotherms are shown in Figure 3 and the maximum adsorption capacities of the adsorbents derived from chitosan in recent studies are shown in Table 4. The Langmuir model could be used to describe the adsorption behavior of both As(V) and As(III) on the MCNP. Maximum adsorption capacities were calculated from the Langmuir equation to be 65.5 mg/g for As(V) and 60.2 mg/g for As(III), respectively, which were about two times higher than those of MICB at the similar applied experimental conditions and higher than other chitosan adsorbents except for some impregnated chitosan derivation. The reason may lie in two aspects: one is the fact that the value of the specific area of

TABLE 4: Comparison of adsorption capacity with different granular adsorbents.

Granular adsorbent	C_{initial} (mg/L)	$q_{e,\text{max}}$ (mg/g)		pH	Ref.
		As(V)	As(III)		
Iron-impregnated chitosan granular	10	22.5	16.1	7.0	[22]
TiO ₂ -impregnated chitosan bead	10	2.05 ^a	2.10 ^b	9.2 ^a , 7.7 ^b	[16]
Iron oxide coated sponge	5	4.5	3.85	6.5–7.3	[23, 24]
MICB	50	35.7	35.3	6.8	[19]
MCNP	50	65.5	60.2	6.8	Our work

The labels “a” and “b” only denote the corresponding relationship. C_{initial} is the initial concentration of arsenic (mg/L); $q_{e,\text{max}}$ represents the maximum adsorption capacity of arsenic (mg/g).

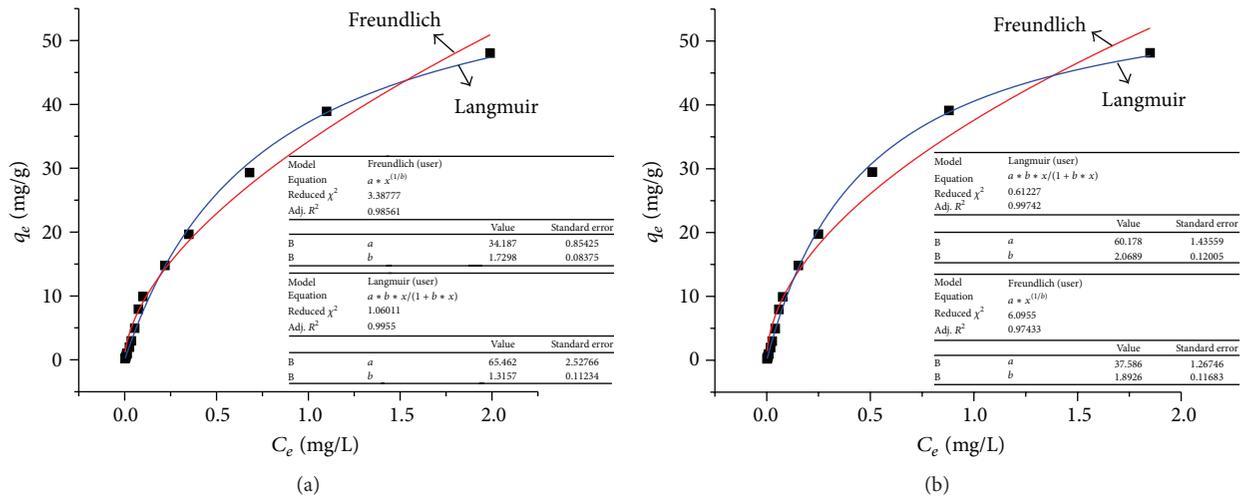


FIGURE 3: Adsorption isotherms of (a) As(V) and (b) As(III) by the MCNP with adsorbent dose of 1 g/L at pH 6.8 ± 0.2 and room temperature. Blue solid lines represent the Langmuir model and red solid lines represent the Freundlich model.

the MCNP was $108.32 \text{ m}^2/\text{g}$, higher than other adsorbents; the second is the fact that the quantity of amino groups may be another influencing factor for the adsorption capacity due to the removal mechanism of chitosan. It is well known that the removal mechanism of chitosan for the arsenic mainly lies in the electrostatic attraction between the positive surface charges of the protonated chitosan amine functions and the negative charges of the arsenate ions [19, 25]. The total amount of amino groups on MCNP was determined at about 1.93 mmol/g using the nitrogen-carbon ratio (N/C ratio) of 0.252. Since the amine groups were involved in the hydrogen bonding of the chitosan and have been considered as the main group to remove the heavy metals, the maximum possible adsorption capacity of MCNP may attain about 144.75 mg/g (multiplication of atomic weight of As and the quantity of amino group).

These results demonstrated that the MCNP was effective for both As(V) and As(III) removal. In particular, it showed good adsorption performance for As(III), as most adsorbents reported previously were effective for As(V) adsorption, but not for the case of As(III) due to its uncharged form at most pHs [15, 26]. This is the advantage of the adsorbent since As(III) was more toxic and more difficult to remove from water than As(V), for the MCNP showed better conditions for the removal of As (just as relatively shorter immigration

distance and abundance of accessible adsorption sites), which weakened the influence of arsenic charge to some extent. The detailed reasons need further investigation.

3.2. Regeneration of MCNP. Sodium hydroxide solution was generally used to regenerate the chitosan and its derivations [19]. The regeneration conditions were optimized as 0.15 mol/L sodium hydroxide solution and 30 min regeneration time. Figure 4 shows the adsorption efficiency of the regenerated MCNP for As(V) and As(III) with initial arsenic concentration of 1 mg/L and adsorbent dose of 1 g/L at pH 6.8 ± 0.2 for 10 times.

In the recycle study, The MCNP maintained 98.1% for As(V) and 95.6% for As(III) after one adsorption-desorption cycle, respectively. And after 10 cycles of reuse, the regenerated MCNP still retained about 97.5% and 95.3% for As(V) and As(III), respectively, which indicated that the MCNP could be readily regenerated by the sodium hydroxide solution and seldom adsorption capacity decreases during the regeneration. Similar results were gained for the regeneration of magnetic ion exchange resins (MIEX) [27]. Comparing the characteristics of the MIEX and MCNP, we could see that a similar feature existed between them, that is to say, the nonpore structure, which could avoid the block of pore inside the adsorbents; therefore, the regeneration effects could keep

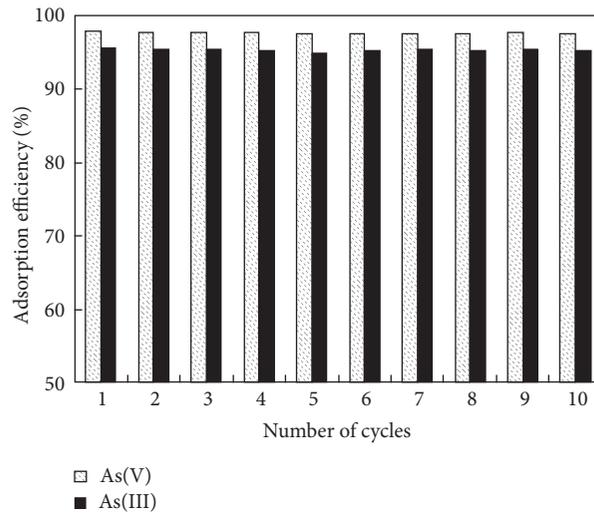


FIGURE 4: Adsorption efficiency of the regenerated MCNP for As(V) and As(III) with initial arsenic concentration of 1 mg/L and adsorbent dose of 1 g/L at pH 6.8 ± 0.2 for 10 times.

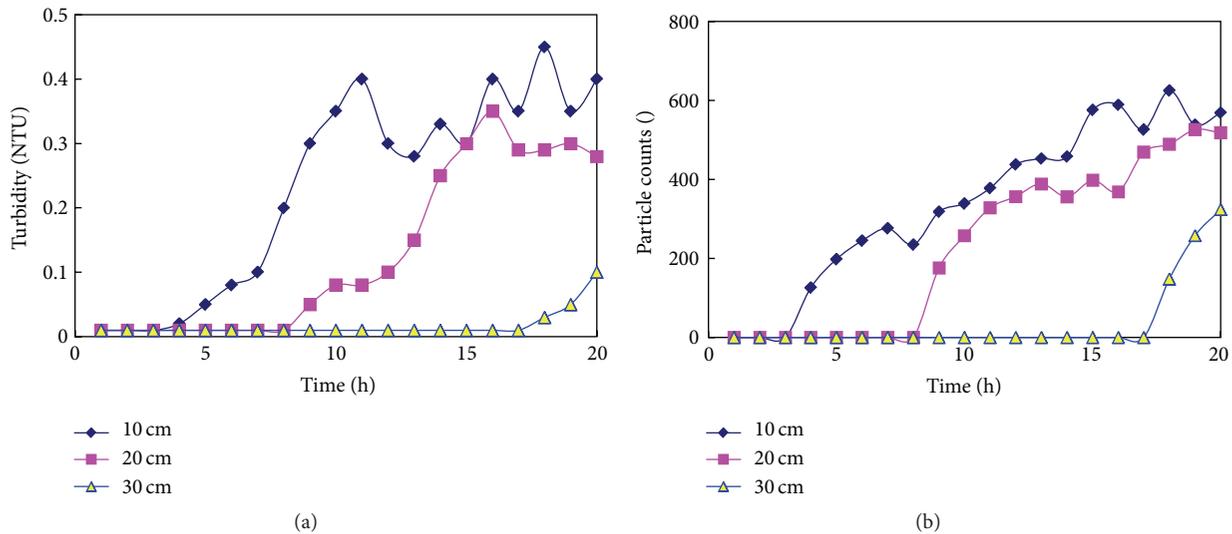


FIGURE 5: (a) Influence of iron powder depth on the turbidity of outlet. (b) Influence of iron powder depth on the total particle count of the outlet.

at a high degree. In all, MCNP showed better reusability for arsenic removal than former studies.

3.3. Separation of MCNP. Due to the typical characteristics of the particle, MCNP showed superior advantages to the other chitosan and derivations, including higher adsorption capacity and rate and better regeneration effect. However, one fatal demerit existing in the application of engineering was the difficult isolation with the product water. Due to smaller size and relatively low density, the MCNP could exist with water harmoniously, while the biological toxicity of nanoparticles had raised much concern [28, 29]. Although the external and induced magnetic field could strengthen the separation process and the nanoparticles could be nearly entirely separated from water at the magnetic field for its relatively higher saturation magnetization, it was limited to

use in the continuous operation [30]. Therefore, new method to separate the MCNP effectively was needed. Filtration was one of effective ways to remove particles from water, so filter with specific diameter of iron powder may be one of better choices with the consideration of the particles' magnetism. However, seldom successful experience was found in the former studies, so the influences of diameter and depth of iron powder on the separation effects are discussed (Figures 5(a) and 5(b)).

The iron powder could intercept the particle of MCNP effectively and the effect was proportional to the depth of filter. Due to relatively higher saturation magnetization, the MCNP could adsorb onto the surface of iron powder immediately and accumulate together as the powder was the center. The pore size became smaller as the aggregation gets bigger, and the velocity of water grew higher accordingly.

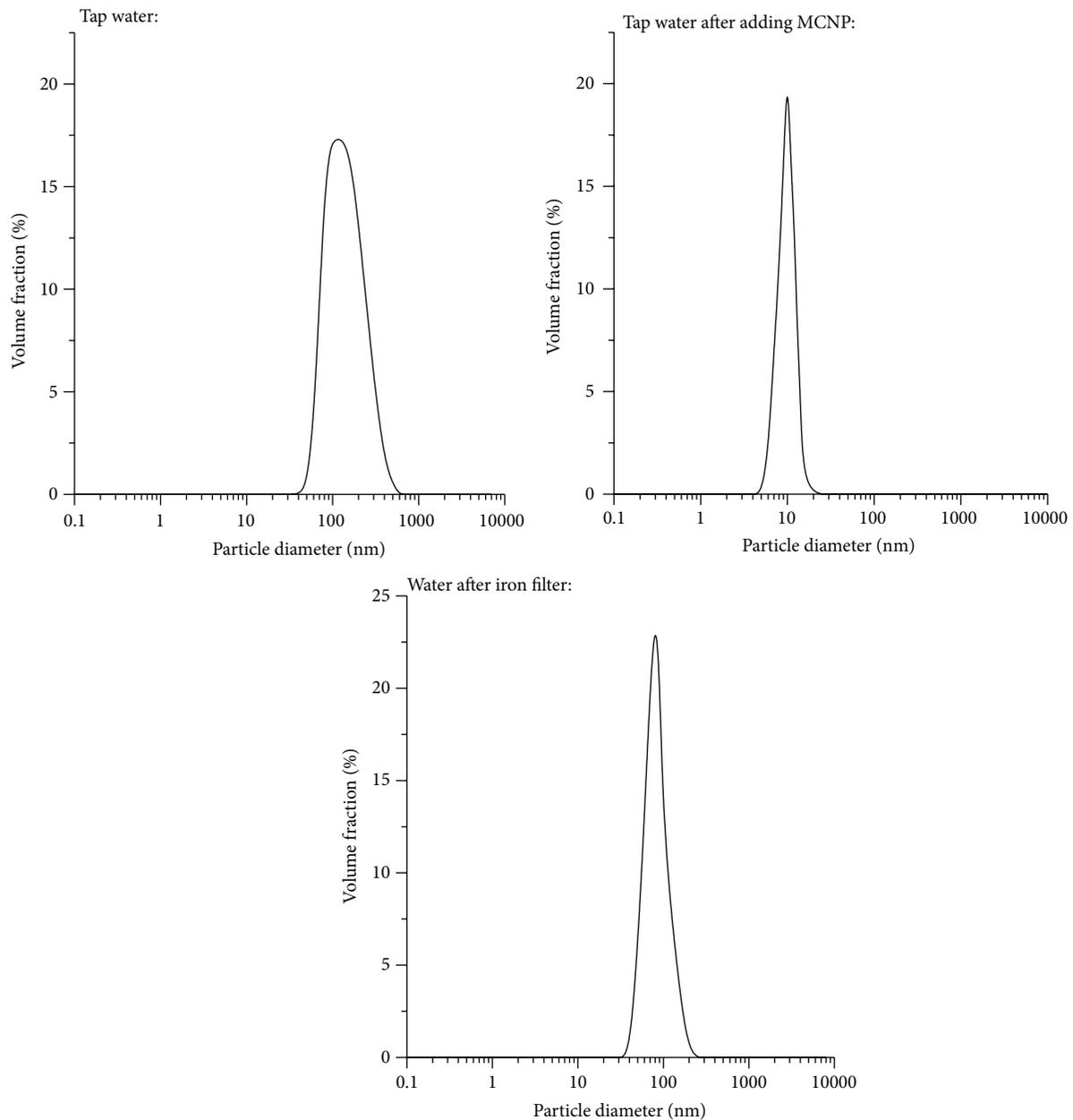


FIGURE 6: The size distribution of tap water, water adding MCNP, and water after iron filter.

When the velocity can overcome the attraction of the particles, some MCNP will come into the water and cause the higher turbidity. Figure 5(b) also testified the similar process. According to the demand of water treatment, 30 cm was the proper depth of the iron powder, for it needs not only to retain the particle effectively during the filtration but also to be stripped off entirely during the back-flush. Table 2 shows that the saturation magnetization of MCNP is 44.43 meu/g, that is, weakly magnetic, which may cause poor separation through the way of iron powder. However, the separation effect was excellent even with a relatively short depth of iron powder filter. The reason may lie in that the particles of MCNP have evident tendency to aggregation due to their

nanosize and most of the particles could be excluded by the iron powder filter with a depth of more than 30 cm.

Figure 6 shows the particle size distribution of tap water and outflow of the iron filter. As the size distribution of pure water cannot be determined by the Zetasizer Nano ZS90 instrument, the tap water was used to investigate the removal effect of iron filter for the MCNP.

As seen from Figure 6, the size of particle in tap water was mainly focused in about 100 nm and converted to about 10 nm after addition of MCNP, which indicated that the size of MCNP was mainly focused on diameter of 10 nm and dominates in the all particles. However, the particles size distribution before and after the iron filter adding MCNP was

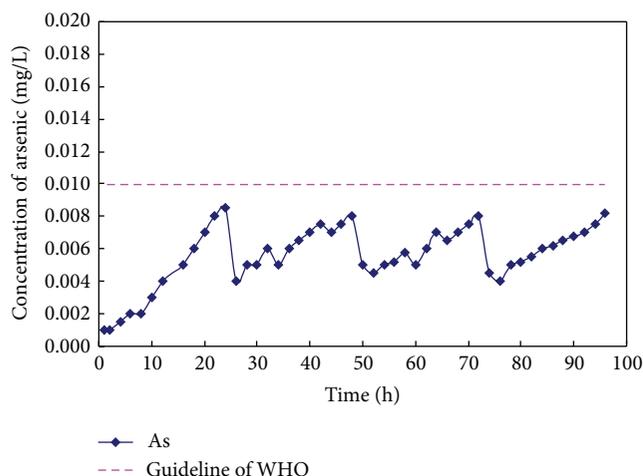


FIGURE 7: Removal efficiency of the new continuous-operation instrument to treat the underground water sample from Inner Mongolia.

similar, that is to say the MCNP were separated entirely. It is regretful that the ZS90 instrument could not determine the nanoparticles counts directly, but the determination results also verified the perfect separation performance for the MCNP.

3.4. Continuous Operation to Remove Arsenic from Raw Water. To verify the removal effects of MCNP for the arsenic in the raw water and the separation effect of MCNP, continuous dynamic adsorption experiment is used to treat the raw water taken from the water plant in Bayannur city. The concentration of arsenic in the outlet water was shown in Figure 7. As shown in Figure 7, the concentration of arsenic in the outlet water was about 5–8 $\mu\text{g/L}$ at 800 BV, which met the guideline limit of arsenic in drinking water regulated by the WHO (10 $\mu\text{g/L}$). Some other advantages were found in the operation of instrument. Firstly, the hydraulic retention time (HRT) was relatively short and could decrease the volume of the reactor; second, the regeneration method was simple so as to guarantee the continuous operation of the instrument; third, the MCNP can be separated effectively by the filter with iron powder and can be recycled through the way of backwashing. In addition, one particular phenomenon was found in the continuous operation. Although the pore size of sand core filter (G2) was about 10–15 μm , it can intercept most of the nanometer MCNP, which may be caused by the aggregation of magnetic particles and pulse aeration to put the aggregator back to the main solution. The backwash period of the iron powder filter was extended to about 25 h due to the primary exclusion of sand core filter. The wavy removal curve was mainly caused by the regeneration of the MCNP intercepted in the filter after one backwash period.

In all, although the diameter of MCNP was about 10 nm, it can be easily isolated from water due to its higher saturation magnetization and can be used to remove arsenic effectively in the real operation.

4. Conclusion

This study demonstrated that MCNP could be used as an effective adsorbent for arsenic removal. MCNP presented better arsenic adsorption performance within relatively short time than other adsorbents and the adsorption kinetics followed pseudo-second-order kinetic model. The adsorption isotherm could be described well by the Langmuir model, and the maximum capacity was calculated to be 65.5 mg/g for As(V) and 60.2 mg/g for As(III) at pH 6.8, respectively, which was reasonably good compared with that of other granular adsorbents reported previously. And the MCNP could retain more than 95% of the original adsorption capacity for both As(V) and As(III) after 10 cycles of reuse. A new style iron powder filter was established to effectively separate MCNP from water. A field application of the adsorbent for removal of arsenic in groundwater demonstrated that it could be promising for practical drinking water treatment.

Highlights

- (i) Magnetic chitosan nanoparticle showed better removal performance for the arsenic.
- (ii) A new separation method for magnetic nanoparticles was first established.
- (iii) A new continuous-operation instrument was used to remove arsenic from raw water.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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