Preparation of Iron Oxide Nanoparticles Mixed with Calcinated Laterite for Arsenic Removal

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Abstract-- This paper was studied about a simple and efficient method that is synthesis of Fe_3O_4 (Iron Oxide) nanoparticles mixed with calcinated laterite for arsenic removal from arsenic contaminated water. Ultrafine Fe_3O_4 powder synthesis firstly by a Novel Ageing process from a precursor $FeO(OH)$, which was the hydrolysate of $FeCl_3$ in the urea solution. Furthermore, the particle size of Fe_3O_4 nanoparticles was characterized by X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscope (SEM) to study the particle sizes, compositions, morphology, structure and surface of the adsorption materials. These iron oxide nanoparticles got with the mean diameter about 19-25 nanometer in processing of different heating time (2, 2.5, and 3 hr) and different ageing time (3, 4, and 5 hr) respectively. Optimum particle size of 19 nm can be found when 3 hr heating time and 5 hr ageing time processing. After preparing of these Fe_3O_4 powder, it was mixed with calcinated laterite grains to create more effective adsorption material. Next, adsorption experiments were conducted at room temperature for removing toxic arsenic. In this investigation, different adsorption parameters such as adsorbent dose of 0.03g, 0.05g, 0.07g and contact time period of 20min, 40min, 60min, 80min were determined. All of the arsenic contents both from raw and treated water were examined by using Atomic Absorption Spectrophotometer (AAS). The removal efficiency of this mixed adsorbent material is more than that of calcinated laterite (57%) or iron (61%) when the dosage amount of adsorbent is the same. The arsenic removal efficiencies of this mixed adsorbent are 75.5 % for 0.3 ppm initial arsenic concentration and 95% for initial arsenic concentration 0.03 ppm with very low dosage of 0.05g in 80min adsorption time. Initial arsenic concentration of 0.03 ppm is decreased below the limit of WHO drinking water standard (0.01 ppm) after treated with this mixed adsorbent.

Keywords-- Arsenic removal, novel ageing process, Fe_3O_4 (iron oxide nanoparticle), laterite, mixed adsorbent, adsorption, WHO drinking water standard

I. INTRODUCTION

ARSENIC contamination of drinking water has been reported from many parts of the world. Access to clean drinking water is an enormous problem faced by many people all over the world and lack of access to clean water is public health hazard [1].

Of all the naturally occurring groundwater contaminants, arsenic is by far the most toxic. It is known that arsenic is a human carcinogen in water over the wide ranges of pH values,

having harmful effects on both human health and environment, even at low concentration [2]. Because of arsenic threat to humans, the World Health Organization (WHO) and the US Environmental Protection Agency (USEPA) implemented a reduction of the Arsenic Maximum Contaminant (MCL) in drinking water from 50 to 10 μg/L in 2006. There is no effective treatment for arsenic toxicity. Only drinking of arsenic free water can prevent arsenic toxicity [3]. To save millions of people from being affected with arsenic toxicity, appropriate and sustainable treatment of contaminated water is necessary.

In areas where the drinking water supply contains unsafe levels of arsenic, the immediate concern is finding a safe source of drinking water. There were two main options: finding a new safe source, and removing arsenic from the contaminated source [4]. Arsenic in drinking water can be effectively removed by using a variety of conventional treatment processes. This study looks at adsorption of arsenic on nano-sized magnetite; Fe_3O_4 particles mixed with calcinated laterite is beginning to show many advantages, especially in environmental science.

Nowadays, Fe_3O_4 nanoparticles have been also widely used for magnetic materials, pigments, ferrofluids, and catalysts etc. [5]. Synthesis of nano size iron oxide (Fe_3O_4) can be made by various methods such as; co-precipitation, microemulsion, hydrothermal method, and some novel methods; sonochemical synthesis, arc discharge method, novel ageing method, microwave hydrothermal, and one-step hydrothermal process [6]. But in this study, Fe_3O_4 nanoparticles were synthesis via a Novel Ageing Process because of its simple procedure and pure Fe_3O_4 product. These prepared nanoparticles were then mixed with denaturized (calcinated) laterite to create new high performance adsorption materials because impregnation or coating with nanoparticles enhances the sorption capacity of adsorbents. Being iron oxide is the effective material for treating arsenic, laterite can be added the adsorption efficiency. Therefore, combination of these two effective materials can be obtained the best adsorbent material for arsenic removal.

The objectives of this study are; to synthesize Fe_3O_4 nanoparticles by Novel Ageing method, to prepare mixed adsorbent material by mixing Fe_3O_4 and calcinated laterite, to compare the adsorption capacities of pure calcinated laterite, Fe_3O_4 and mixed adsorbent and to study the arsenic removal efficiencies, adsorption isotherms and kinetics.

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II. EXPERIMENTAL METHOD

There were two main parts in this research. The first part was preparation of mixed adsorbent material and the second part was the arsenic removal by adsorption technique. And there were also three steps in this first part (preparation of mixed adsorbent material) roughly. Iron oxide (Fe_3O_4) nanoparticles were synthesized by novel ageing process firstly. Then calcination of laterite was carried on to mix with these iron oxide particles. Finally, creating of mixed adsorbent for arsenic removal was done by mixing these two adsorbent materials.

A. Synthesis of Iron Oxide Nanoparticles

The chemical reagents used in this preparation of iron oxide particles were Urea :$(NH_2)_2CO$, Ferric chloride: $FeCl_3.6H_2O$, Sodium hydroxide: NaOH, Ferrous Sulphate: $FeSO_4.7H_2O$, and Acetone.

A typical approach for this research work was given as follows. 5.41g $FeCl_3.6H_2O$ and 3.6g $(NH_2)_2CO$ were dissolved in 200ml distilled water in a container. After that, this solution was placed in a water bath at a constant temperature 90±3˚C. Various heating time parameters tested in this process were 2, 2.5 and 3 hr respectively. The solution turned into a kind of khaki slurry gradually and then it was cooled to room temperature. 1.99g $FeSO_4.7H_2O$ was dissolved in the above mixture with mechanical stirring at a speed of 546 rpm for 10 min. Then, NaOH solution (2mol/L) was dropped into the reaction mixture until the pH>10. Greenish precipitate could be observed at that time. The molar ratio of Fe(III) to Fe(II) in the observed system was nearly 2. When the pH reached greater than 10, the mixture was transferred into an ageing can with a cubage of 500 ml. Additional distilled water was added to make the ageing container full and then it was sealed by a capsule to prevent the air from entering. Finally, the container was aged at a room temperature with different ageing times such as 3hr, 4hr and 5hr. The black magnetic precipitate was separated by filtration, followed by washing with distilled water of 500 mL and acetone of 100 mL in order. Then, the obtained powders were oven-dried at 50˚C until to get constant weight. This chemical preparation route was shown in Fig. 1.

B. Laterite Calcination

After synthesized these nanoparticles, laterite calcination step was carried on. The collected iron rich raw laterite (collected from Mon State) was then calcinated at 400˚C for 4 hours. After calcination, the laterite was crashed and sieved to obtain powder laterite with a particle size less than 75µm. These laterite powders were washed with deionized water at least three times. If not washing like this it could not removed the laterite dust, as well as other undesired particle. It was dried at 110˚C for 12 hr; then it was stored in a desiccator for use in the next step of mixing experiments.

C. Preparation of Mixed Adsorbent

In the final step, prepared nanodimensional particles were mixed with denatured laterite in a grinder about thirty minutes to create new high performance adsorption materials. The mixing ratio of these two materials was 1:1 ratio (1g Laterite:1g Fe_3O_4). Finally, the prepared mixed adsorbent materials were stored in an airtight plastic bag and it was ready for removing arsenic. Due to its abilities, iron oxide nanoparticle is so famous for arsenic adsorption. On the other hand, iron rich laterite is very advantageous for removing arsenic because it is locally available adsorbent material. Therefore mixing of these two particles gets double benefits; effective adsorbent formation and process cost reduction.
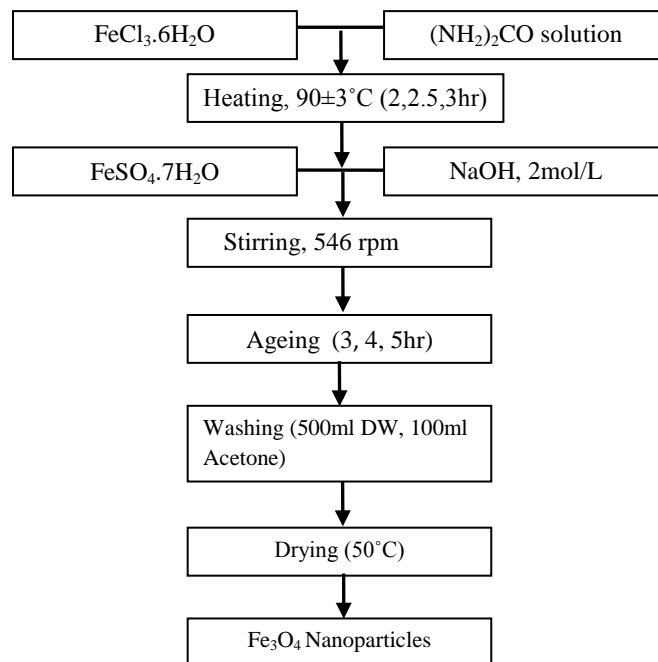

Fig. 1 Chemical preparation route of Fe_3O_4 nanoparticles

D. Arsenic Removal by Adsorption

The second part of this research was treating toxic arsenic from arsenic contaminated water by adsorption technique with the help of mixed adsorbent material. The adsorption technique is the best method among variety of conventional treatment processes for arsenic removal due to its obvious advantages. Moreover using of this mixed adsorbent was better than using some of the common adsorbents.

About 50ml of arsenic contaminated water was taken into a beaker and added the different adsorbent dosage for various batch on the magnetic stirrer. The used adsorption process parameters in this research were 0.03g, 0.05g, 0.07g adsorbent dosage and 20min, 40min, 60min, and 80min adsorption time for the initial arsenic concentration about 0.3ppm. Next testing with 0.05g dosage for initial arsenic concentration 0.03ppm was also examined in these adsorption times. Moreover comparison of adsorption capacities for calcinated laterite adsorbent and pure Fe_3O_4 nanoparticles adsorbent with this mixed adsorbent material was carried on.

III. RESULTS AND DISCUSSIONS

A. Effect of Heating and Ageing Time on Fe_3O_4 Preparation

The ultrafine Fe_3O_4 powders obtained from novel ageing process were characterized by X-ray Diffraction (XRD) analysis to examine their particle size in nanometer scale. The average particle sizes of prepared Fe_3O_4 particles were calculated by "Scherrer's Equation" using the XRD line broadening method.

$$D = K\lambda / Bcos\theta$$

where, D is crystal size, K is a shape factor (about 0.89 for magnetite), λ is the wavelength of X-ray (1.54056˚A), B is the full width at half maximum (FWHM) of the peak in radians, and θ is the diffraction angle (or) the Bragg angle of the peak, respectively [7]. All these required values could be obtained from their corresponding XRD peak search report.

The resultant sizes of iron oxide particle obtained from different processes are expressed in the following Table I.

TABLE I
RESULTS FOR PREPARED NANOPARTICLES

	Heating time (hr)	Ageing time (hr)	Size (nm)	Yield (%)
Process 1	2	5	25.81	97.62
Process 2	2.5	5	22.40	96.99
Process 3	3	5	19.27	92.53
Process 4	3	4	20.59	90.78
Process 5	3	3	24.17	90.60

According to Table I, it was found that varying on heating time significantly affects the particle size, but varying on ageing time slightly affects the particle size. Among these processes, the best conditions for the preparation of Fe_3O_4 nanoparticles were 3 hours heating time and 5 hours ageing time to get smaller particle size. So Novel Ageing process could be produced smaller particle size than other processes.

B. XRD and SEM Results of Fe_3O_4, Calcinated Laterite, Mixed Adsorbent

The X-ray diffraction spectrum of Fe_3O_4 particle prepared by process 3 is shown in Fig. 2(a). From the analysis of the peak width for process 3 using Scherrer's equation it was determined that Fe_3O_4 particle had an average grain size of 19nm. This process could be produced smaller particle size than other processes.

The chemical compositions of synthesized Fe_3O_4 particle were known in detail by XRF result. Fe, the best element for removing toxic arsenic, was the main composition in this prepared particle about 99 % and other minor compositions are Mn, Zn, and Cu. And Scanning Electron Microscopy (SEM) shows in the measurement range within 1µm and could be seen the morphology of this prepared iron oxide nanoparticle [Fig. 3(a)]. The prepared particle shapes were mainly in cubic shapes.

For creating mixed adsorbent, calcinated laterite should be analyzed firstly by XRD analysis which is shown in Fig. 2(b) and the particle size of this was found about 35 nm.

The chemical composition of calcinated laterite was determined by XRF analysis result and it was clear that iron was the main composition and other metal such as Ti and Zr were also contained in this laterite. Moreover the morphology of this laterite was also examined by SEM analysis [Fig. 3(b)]. According to this result, average particle size of calcinated laterite was larger than that of the prepared Fe_3O_4 particle.

Next for the particle size calculation of this mixed adsorbent, the required data of XRD analysis result is shown in Fig. 2(c). In this spectrum the highest peak of this material was peak number 104 and all the necessary data for Scherrer's Equation were taken from their peak results. After calculation, the size of particle was 27 nm.

After combination, all the chemical compositions (Fe, Ti, Mn, Cu and Zn) of pure Fe_3O_4 and calcinated laterite were found altogether in this mixed adsorbent by examining their XRF result. Moreover average particle size of which was also higher and that is shown in SEM photo [Fig. 3(c)].
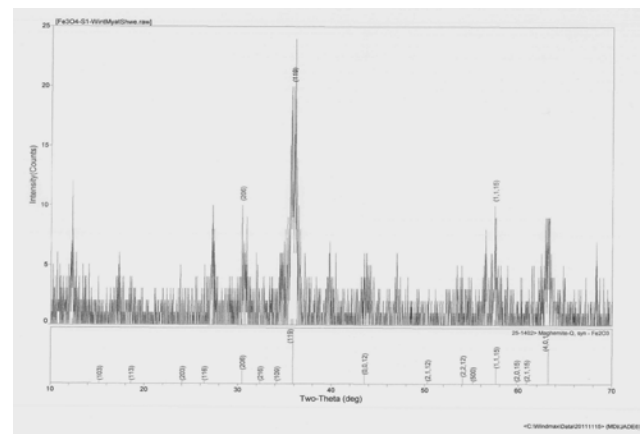

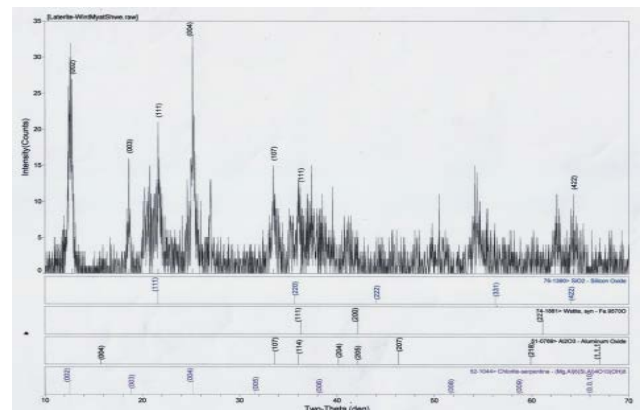Fig. 2 (a) XRD Spectrum of Fe_3O_4 Particles (Process 3)

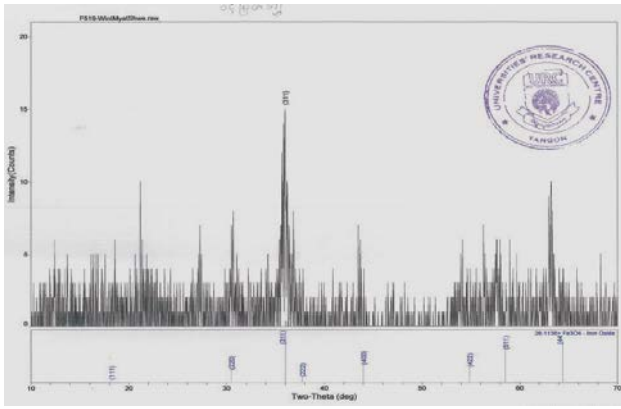Fig. 2 (b) XRD Spectrum of Calcinated Laterite
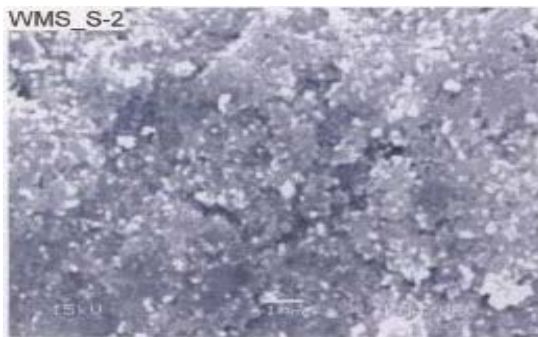
Fig. 2 (c) XRD Spectrum of Mixed Adsorbent

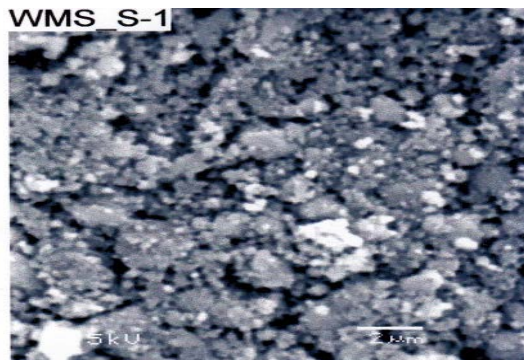Fig. 3 (a) SEM Image of Fe_3O_4

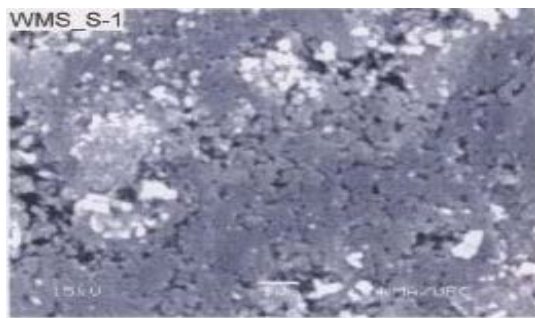Fig. 3 (b) SEM Image of Calcinated Laterite

Fig. 3 (c) SEM Image of Mixed Adsorbent

C. Studies of Arsenic Removal

Furthermore studies on the effect of adsorbent dose and adsorption time were conducted for initial arsenic concentration of 0.3 ppm. Fig. 4 illustrates that the aqueous arsenic concentration decrease with the increasing adsorbent dose as well as with adsorption time. This is due to more availability of the surface-adsorbent sites and more contact time. By comparing these two adsorbent, it could be said that the removal efficiency of pure Fe_3O_4 nanoparticle adsorbent was higher than that of calcinated laterite adsorbent in the same conditions.
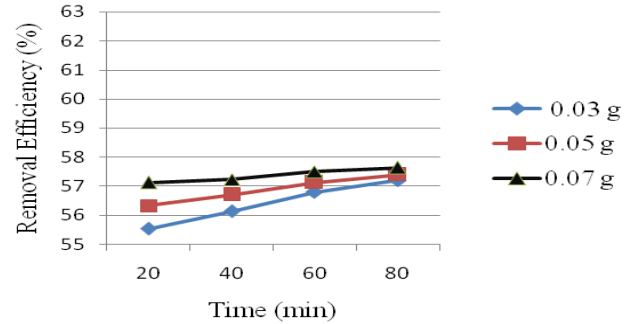

Fig. 4 (a) Arsenic Removal by Different Adsrobent Dose via Different Adsorption Time using Calcinated Laterite
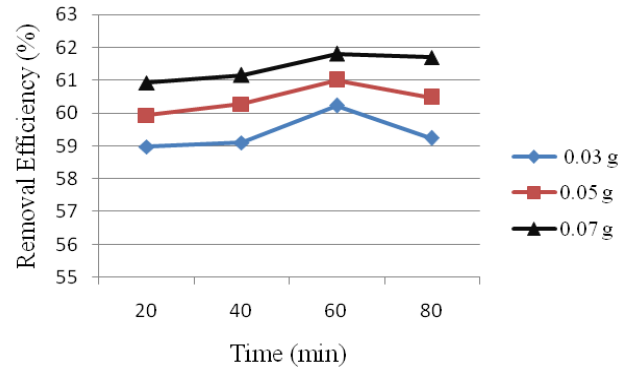

Fig. 4 (b) Arsenic Removal by Different Adsrobent Dose via Different Adsorption Time using Fe_3O_4 Adsorbent
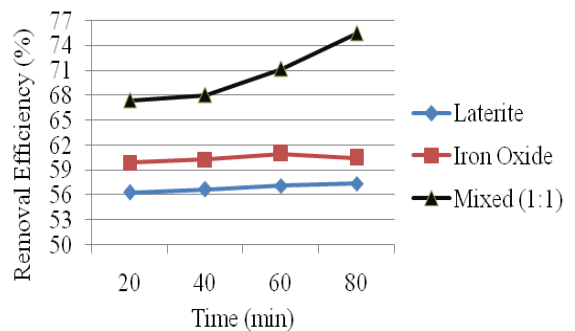

Fig. 5 Arsenic Removal of Different Adsorbents

Then Fig. 5 expresses the comparison of three type of adsorbent (Calcinated Laterite, Fe_3O_4, and Mixed Adsorbent) and their removal efficiency in the same conditions of 0.05 g adsorbent dosage and 20, 40, 60, and 80 min adsorption time. In which the removal efficiency of mixed adsorbent is the best in the same parameters. Although other adsorbent dose parameter such as 0.03 g

and 0.07 g adsorbent dosage were not identified, mixed adsorbent could also be removed more than the other two adsorbents in these dosages. The best removal efficiency of this mixed adsorbent from initial arsenic concentration about 0.3 ppm was over 75.5 % within the short adsorption time of 80 min using the adsorbent amount of 0.05g. Finally, it could be noted that although in the same parameter, the removal percent of the mixed adsorbent was the best in these three adsorbents.
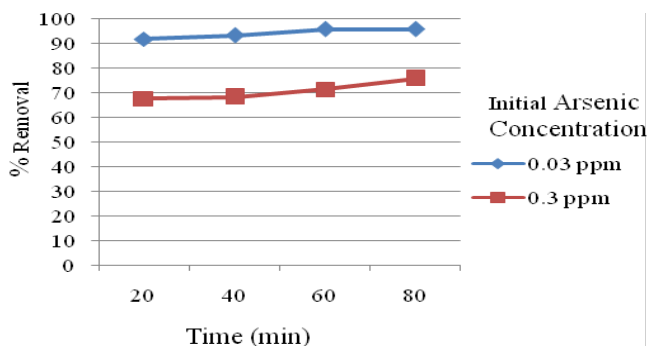

Fig. 6 Arsenic Removal of Different Concentrations for Mixed Adsorbent (1:1)

However when we used the initial concentration 0.03ppm, its removal efficiency was increased to 95% at the same adsorption parameters (0.05g adsorbent dosage, 80min adsorption time). Therefore the effect of initial arsenic concentration was significantly affected on arsenic adsorption and Fig. 6 shows the comparison of these two concentrations with their removal efficiencies. Although in the same adsorption parameters, the removal efficiencies of arsenic decrease at high initial arsenic concentration (0.3 ppm). It is the same with one of the U.S. EPA report. This report said that the arsenic adsorption efficiency of iron-based methods is strongly depending on both initial arsenic concentrations and iron concentrations.

IV. CONCLUSION

Iron oxide (Fe_3O_4) nanoparticles were prepared by novel ageing process with various parameters for examining which process can produce the smaller particle size. After checking the particle sizes with the XRD results, the best parameter was coming out with the size of 19 nm. That was process number three (process 3) and its conditions were 3 hr heating time and 5 hr ageing time. That is why we could say that changing the heating time was more important to the process than changing the ageing time.

The arsenic removal efficiency of calcinated laterite was over 57% when the small amount of 0.05 g within 80 min adsorption time was used. In the same condition, like calcinated laterite, Iron oxide (Fe_3O_4) nanoparticles can removed about 61% toxic arsenic from aqueous solution. However the removal efficiency of the mixed adsorbent is 75% (at 0.3 ppm initial concentration) or 95% (at 0.03 ppm initial concentration). Therefore, its removal efficiency is obviously higher than that of the two adsorbents in these

conditions (0.05 g dosage and 80 min adsorption time). Because both laterite and iron were very effective materials for arsenic removal, the combination of these two materials was the best for arsenic removal. Therefore, it was obvious that the removal efficiency of this mixed adsorbent was greater than that of the other two adsorbents. Finally this mixed adsorbent could successfully remove naturally existing arsenic (about 0.03 ppm) from groundwater.

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