

## Supplementary Information

*For*

### **Size-controlled synthesis of uniform akaganeite nanorods and their encapsulation in alginate microbeads for arsenic removal**

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## Experimental Section

**Materials.** Iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , Sigma Aldrich), sodium oleate ( $\text{C}_{18}\text{H}_{33}\text{NaO}_2$ , TCI), sodium arsenate diacid heptahydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , Sigma Aldrich), barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , Kanto), sodium chloride ( $\text{NaCl}$ , Samchun), alginic acid sodium salt from brown algae (sodium alginate, medium viscosity, Sigma Aldrich), ethanol, hexane, and acetone (Samchun) were purchased and used without further purification.

**Synthesis of uniform akaganeite nanorods.** Akaganeite nanorods were synthesized via hydrolysis of ferric ions in the presence of sodium oleate using a two-phase system. Typically, 20 mmol of iron chloride and sodium oleate with different molar ratios were added to a mixture of 70 mL of hexane, 40 mL of ethanol, and 30 mL of distilled water. The solution was stirred at 60 °C for 4 hours. After reaction, the solution was allowed to separate into two phases. The oil phase was discarded, and the water phase containing akaganeite nanorods was retrieved and centrifuged to obtain akaganeite nanorods as a brown precipitate. The nanorods were washed with acetone twice and finally re-dispersed in water. The size of akaganeite nanorods could be controlled by varying the molar ratio of  $\text{Fe}^{3+}$ :oleate.

**Fabrication of alginate microbeads embedded with akaganeite nanorods.** Ionically cross-linked alginate beads were prepared using an electrostatic droplet method.<sup>16</sup> 2 wt% alginate solution in distilled water was mixed with an aqueous solution of akaganeite nanorods to prepare 1.5 wt% akaganeite-alginate solution. The akaganeite/alginate mixture solution was passed through a blunt needle using a syringe pump (Harvard Apparatus)

under high voltage. The alginate droplets were then ionically cross-linked as spheres in a 100 mM barium chloride bath. Alginate microbeads were rinsed several times with excess deionized water and stored in deionized water until use. The alginate bead diameter was controlled by the applied voltage, flow rate, needle size, or dropping height. For example, 650- $\mu\text{m}$ -sized alginate microbeads were prepared under a voltage of 12 kV, a flow rate of 0.4 ml/min, and a dropping height of 8 cm.

#### **Fabrication of magnetically separable core-shell alginate microbeads.**

Magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ) were synthesized via co-precipitation from a mixture of  $\text{FeCl}_3$  and  $\text{FeCl}_2$  in aqueous conditions.<sup>17</sup> Using magnetic nanoparticles as core materials, core-shell alginate microbeads were prepared by electrostatic droplet methods. Core-shell alginate microbeads were also fabricated in the same conditions.

**Arsenic removal from contaminated water mimicking the arsenic contaminated drinking water in Bangladesh.** Alginate beads encapsulating akaganeite nanorods were added to 10 ml of 10-ppb arsenic (V) solution in a 50-ml tube and rotated for 10 min. After separation of the microbeads, the remaining arsenic solution was analyzed using ICP-MS to measure the residual concentration of arsenic.

**Isotherm.** Alginate beads encapsulating akaganeite nanorods were added to 10 ml of 10-ppm arsenic (V) solution in a 50-ml tube and rotated for 3 h. After separation of the microbeads, the remaining arsenic solution was analyzed using ICP-MS to measure the residual concentration of arsenic. In order to investigate the adsorption results, the Langmuir and Freundlich isotherm models were tested. The Langmuir isotherm model for dilute As(V) solution can be expressed as below:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e}$$

where  $C_e$  (mg/L) is the equilibrium concentration of As(V) in solution,  $q_e$  (mg/g) is the equilibrium maximum adsorption capacity,  $q_m$  (mg/g) is the theoretical maximum adsorption capacity of As(V), and  $K_L$  is the Langmuir constant. The Freundlich isotherm model for dilute solution can be expressed as:

$$q_e = K_F C_e^{1/n}$$

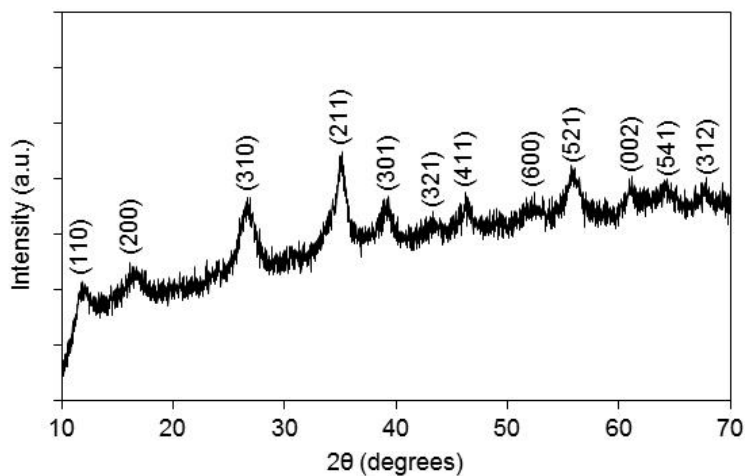
where  $C_e$  (mg/L) is the equilibrium concentration of As(V) in solution,  $q_e$  (mg/g) is the equilibrium maximum adsorption capacity, and  $K_F$  (mg/g) and  $n$  are Freundlich constants.

**Adsorption study in different pH solution.** Alginate beads encapsulating akaganeite nanorods were added to 10 ml of 10-ppm arsenic (V) solution with different pH. pH was adjusted by adding HCl or NaOH solution. The mixture was rotated for 3 h. After separation of the microbeads, the remaining arsenic solution was analyzed using ICP-MS to measure the residual concentration of arsenic.

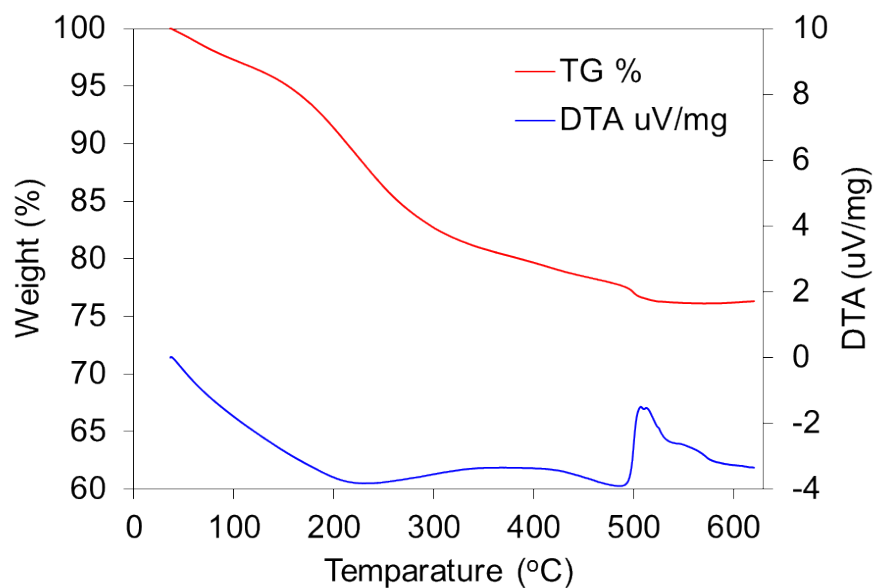
**Comparison of adsorption of As(III) and As(V).** Alginate beads encapsulating akaganeite nanorods were added to 10 ml of 3, 10, or 30 ppm of As(V) or As(III) solution in pH 7. The mixture was rotated for 3 h. After separation of the microbeads, the remaining arsenic solution was analyzed using ICP-MS to measure the residual concentration of arsenic.

**Characterization.** TEM images of akaganeite nanoparticles were obtained using a JEM-3010 (JEOL). Thermogravimetric analysis data were collected using a TG/DTA7300

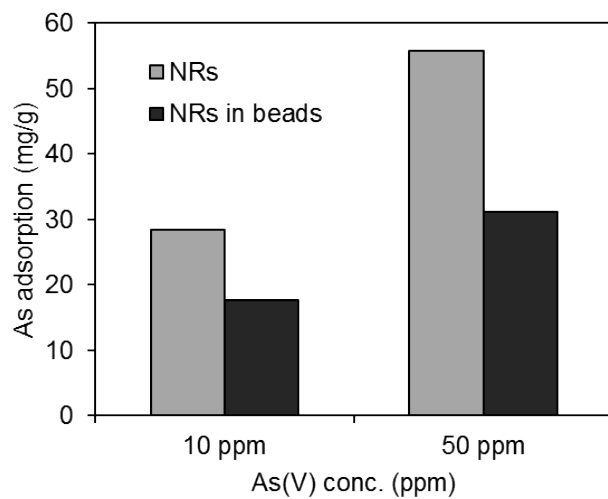
(SEICO INST) under N<sub>2</sub> atmosphere. Elemental analysis data collected under O<sub>2</sub> atmosphere using an Elementar Vario EL cube (Elementar Analysensysteme, GmbH). A D8 ADVANCE (Bruker Corporation) was employed using a Cu K $\alpha$  source to obtain XRD spectra. The angle was extended from 10° to 80° with a step size of 0.019657°. The residual arsenic concentration was analyzed using an ICP-MS (Agilent 7500, Agilent Technologies Inc.). Microscope images were obtained with a Carl Zeiss Microimaging system (GmbH).



**Fig. S1.** XRD pattern of the akaganeite nanoparticles.



**Fig. S2.** TGA data of synthesized akaganeite nanoparticles.



**Fig. S3.** The arsenic adsorption using bare (NRs) and alginate-encapsulated (NR in beads) akaganeite nanorods.

Langmuir isotherm			Freundlich isotherm		
$K_L$	$q_m$ (mg/g)	$R^2$	$K_F$	$n$	$R^2$
0.995	25.19	0.9923	11.18	3.61	0.9862

**Table R1.** The isotherm parameters of the Langmuir and Freundlich models for the adsorption of As(V) on the alginate microbeads encapsulating akaganeite nanorods.