

## Supplementary Materials

*for*

A property-performance correlation and mass transfer study of  
As(V) adsorption on three mesoporous aluminas

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This file contains,

- a) 3 experimental procedures and 1 discussion (S1 - S4).
- b) 6 figures (Fig. S1-Fig. S6)
- c) 3 tables (Table S1 - Table S3)

**S1 Preparation of three mesoporous aluminas.** MA1 was prepared following a modified procedure of Tokudome *et al.*<sup>1,2</sup> Poly(ethylene oxide) (0.08 g) was dissolved in a mixture of 5.5 ml absolute ethyl alcohol and 4.0 ml deionized water until completely dissolved. After that, AlCl<sub>3</sub>·6H<sub>2</sub>O (4.32 g) was added under vigorous stirring. The mixture was placed in a thermostated water bath at 25 °C for complete dissolution. Then propylene oxide (PO) (3.8 ml) was quickly added. The beaker was

sealed and allowed to gel at 40 °C for 48 h. After aging, the gel was washed several times by isopropanol (four-fold volume) at room temperature before slowly drying at 100 °C.

MA2 was prepared using another modified Hartmann *et al.* procedure.<sup>3</sup> An aqueous dodecylamine (DDA) (0.3707 g) solution was added into 2-BuOEt (55.71 ml) under vigorous stirring at room temperature. After mixing, deionized water (4.74 ml) was added and this solution was re-stirred. This was called solution A. Solution B was prepared by adding 12.70 ml Al(OsecBu)<sub>3</sub> into 55.71 ml of 2-BuOEt. Then solution A was slowly added into solution B (over 20 min) under vigorous stirring, and a precipitate was formed. It was aged for 24 h at 33 °C. After aging, the precipitate was washed with secBuOH three times and subsequently dried at 80 °C for 24 h. The product obtained was ground for further characterization.

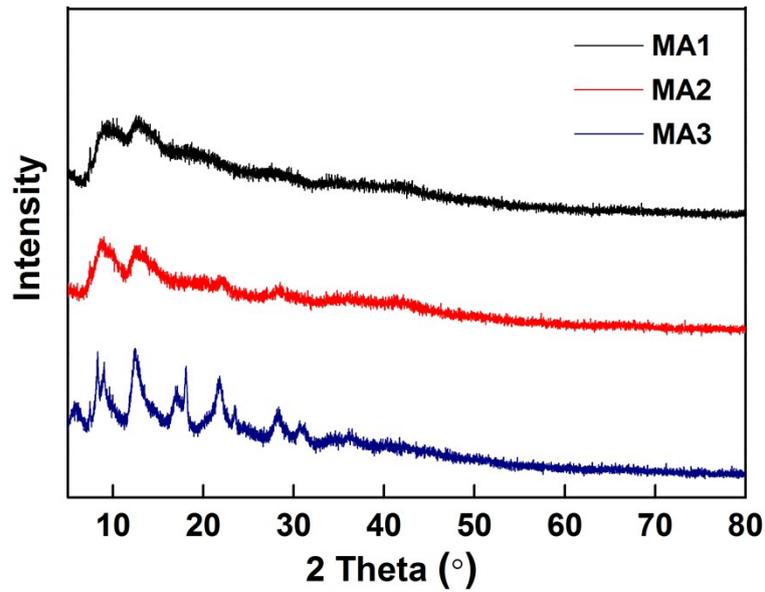
MA3 was prepared by modifying a procedure reported by Cabrera.<sup>4</sup> NaAlO<sub>2</sub> (4.92 g) and cetyl trimethyl ammonium bromide (CTAB) (2.19 g) were dissolved in a solution of 30 g hot water and 23 g absolute ethyl alcohol, until a transparent solution was obtained (solution A). Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (7.50 g) and sodium dodecyl sulfate (SDS) (0.54 g) were added into a mixture of 6 g deionized water and 23 g absolute ethyl alcohol (solution B). Then solution A was added into solution B under vigorous stirring, and a precipitate was formed. The mixture was aged for 24 h at 60 °C. The aged mixture was filtered several times and the filtered solid was washed with deionized water and dried at 60 °C. The solid obtained was ground for further use.

**S2 Selective chemical extraction.** Mesoporous alumina (0.5000 g) was put into 1 L of a 0.0010 mol/L (COOH)<sub>2</sub>·2H<sub>2</sub>O - 0.0010 mol/L(COONH<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O mixture solution. Then the sample were shaken at 150 rpm with the temperature maintained at 50 °C. Approximately 4 mL aliquots were taken from the suspension at predetermined time

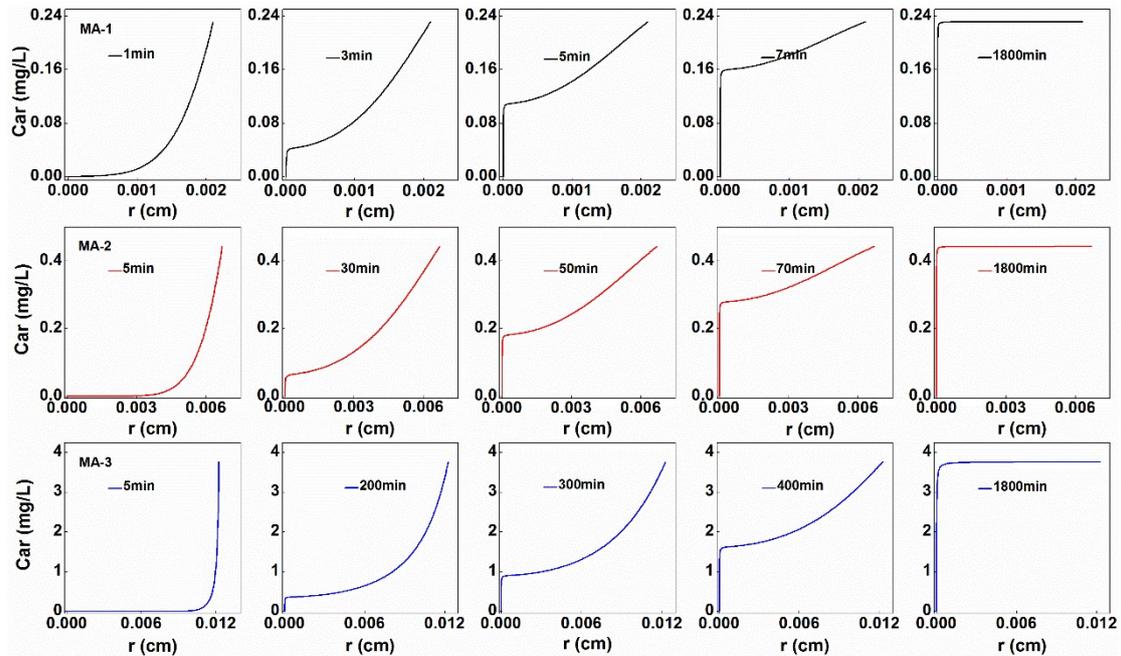
intervals. These aliquots were immediately filtered through a 0.45  $\mu\text{m}$  membrane, and the concentration of the dissolved Al in the solution was measured using an Optima 2000 ICP-OES (PerkinElmer, USA) equipment.

**S3 Determination of hydroxyl group density.** The densities of surface hydroxyl sites were measured by a surface titration method. Mesoporous alumina (0.3000 g) was added into 50 ml of ca. 0.05 mol/L NaOH solution. Its accurate molar concentration was titrated using a 0.0500 mol/L  $\text{Na}_2\text{CO}_3$  solution-calibrated HCl solution (0.0502 mol/L). After 4 h shaking at 130 rpm with the temperature maintained at 25  $^\circ\text{C}$ , the mixture solution was passed through a 0.45  $\mu\text{m}$  membrane. The filtrate was titrated using the HCl solution and residual NaOH in it was neutralized until pH up to 7.0, then the amount of surface hydroxyl can be calculated based on the amount of NaOH consumed.

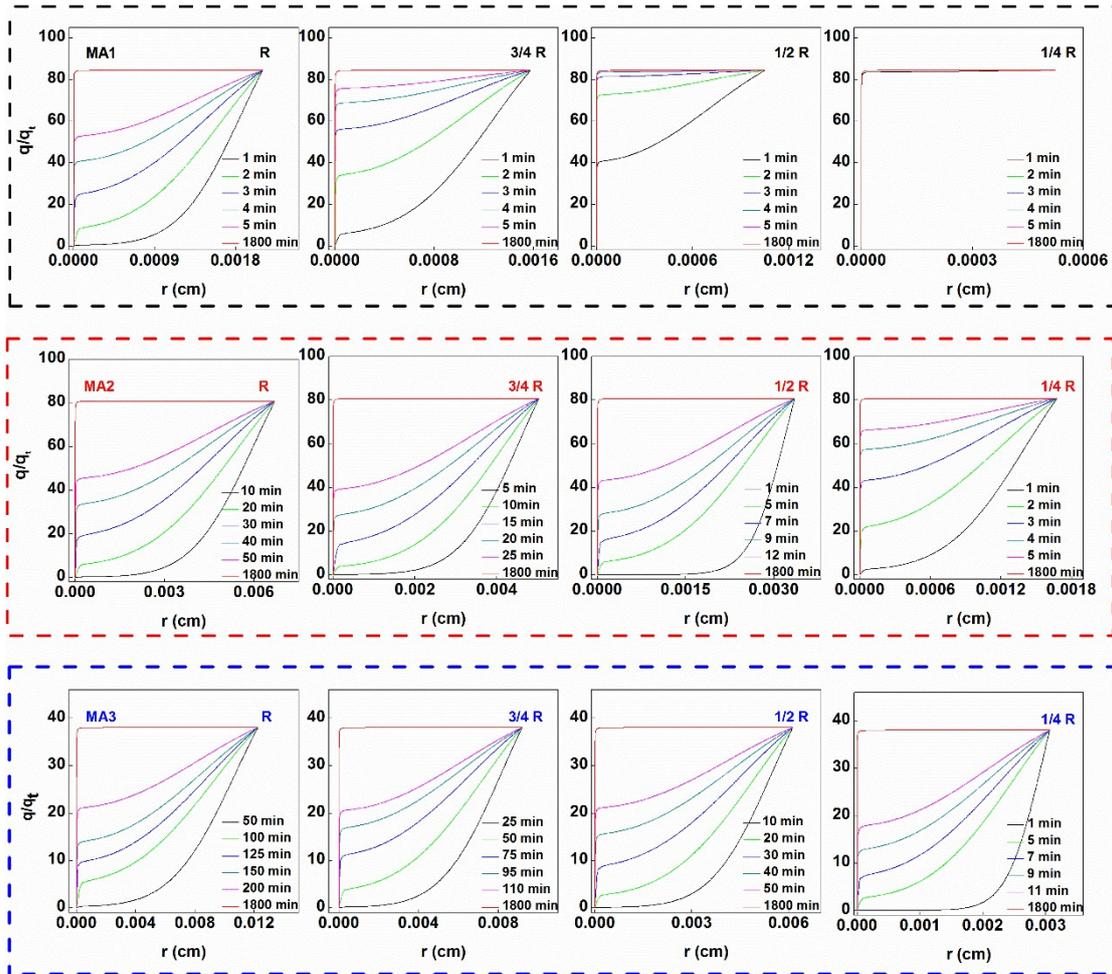
**S4 XPS observations of the As(V)-adsorbed alumina samples.** The XPS full scan, Al2p, As3d and As3p spectra of the three MA samples, before and after 30.0 mg/L As(V) adsorption at pH 5, are displayed in Fig. S5 (a, b, c and d). After As(V) adsorption, strong As3d and As3p peaks appeared for all the three MAs, confirming that As(V) was adsorbed on the adsorbents. In addition, a -0.29 eV, -0.67 eV and -0.10 eV shifts of Al2p peak were observed for MA1, MA2 and MA3, respectively. This indicates a change in the chemical bonding of O to Al, and electron transfer in the valence band resulting from chemical reaction between As-O and Al hydroxyl surface site. In short, chemical adsorptions of As(V) on MAs were confirmed.



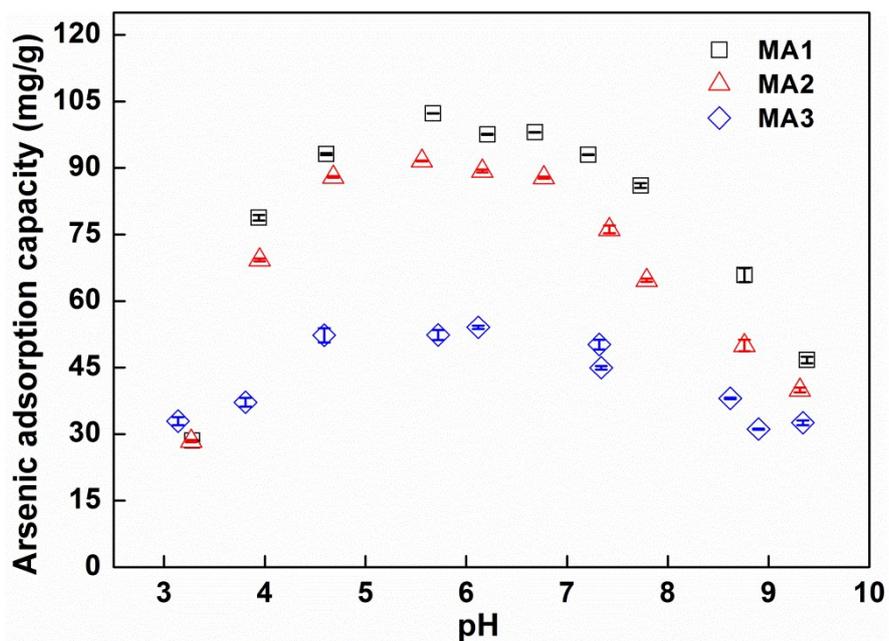
**Fig. S1.** Mo  $K\alpha$  XRD of patterns of the three mesoporous aluminas.



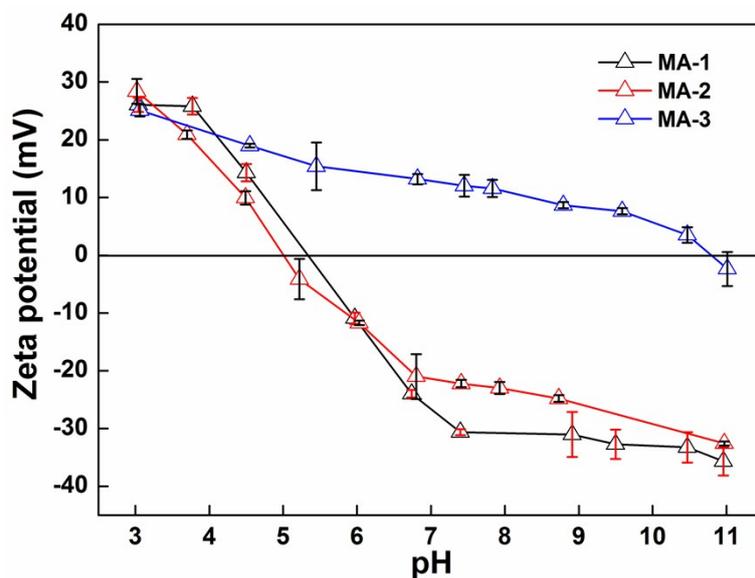
**Fig. S2.** Evolution of the dimensionless radial As(V) concentration profiles,  $C_{ar}$  versus  $r$  inside the particle calculated from the HSDM model for batch adsorption at initial As(V) 30 mg/L; adsorbent dose, 0.3 g/L; pH,  $5.0 \pm 0.1$ ; shaking time, 30 h; temperature,  $25 \pm 1$  °C



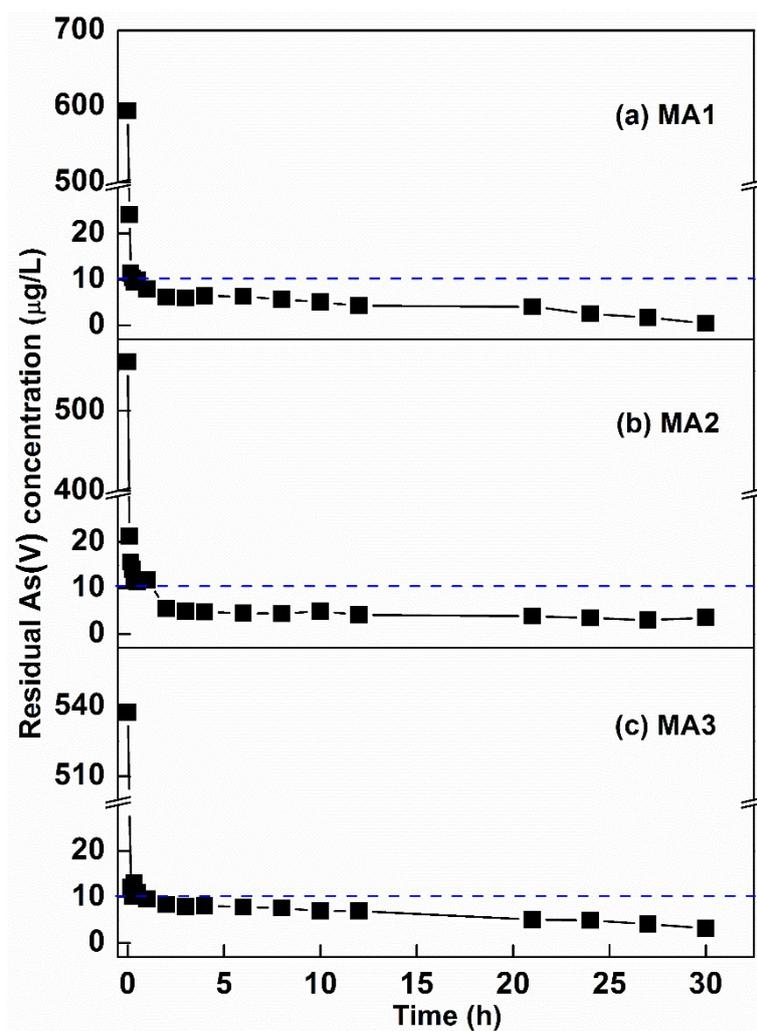
**Fig. S3.** Calculation the effect of particle size on As(V) diffusion kinetics inside adsorbent particles.



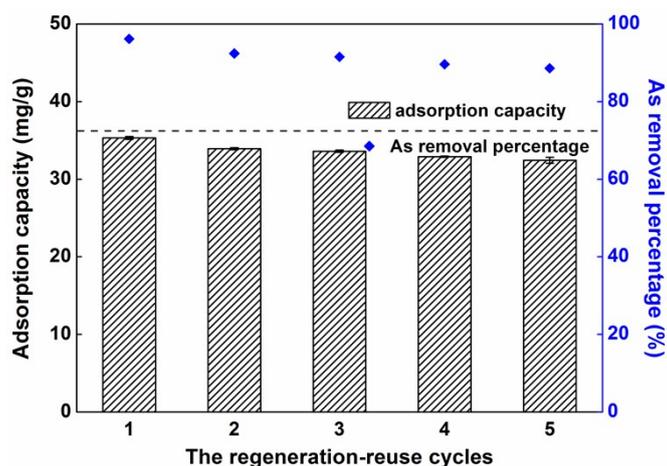
**Fig. S4.** Effect of pH on As(V) adsorption onto the three mesoporous aluminas. Initial As(V) concentrations, 30 mg/L; adsorbent dose, 0.3 g/L; total solution volumes, 100 ml; pH range, 3 - 10; temperature,  $25 \pm 1$  °C, and shaking time, 24 h.



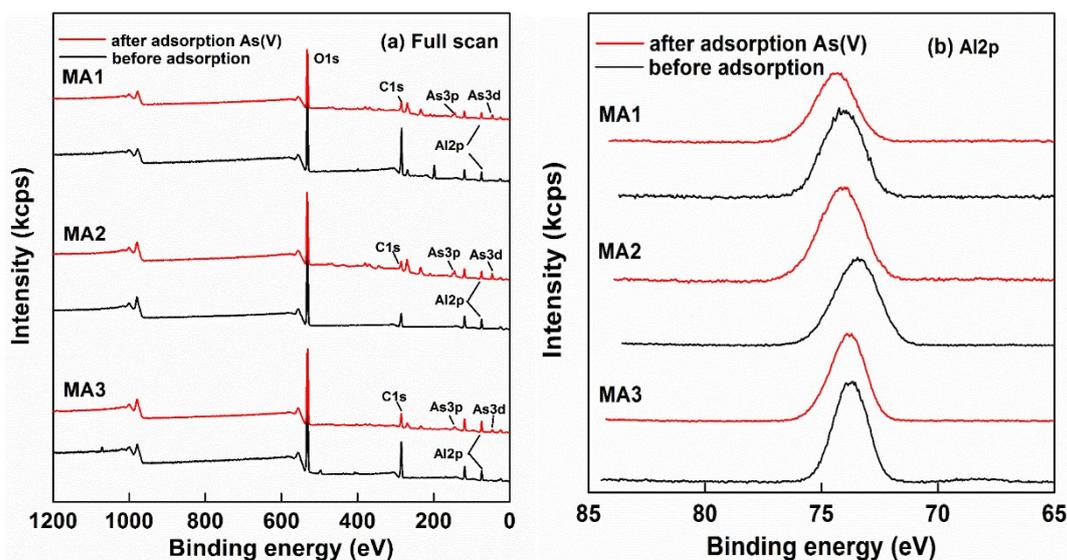
**Fig. S5.** Zeta potentials of MA in different pH solutions with an adsorbent dosage of 0.05 g/L. temperature,  $25 \pm 1$  °C, and shaking time, 24 h.

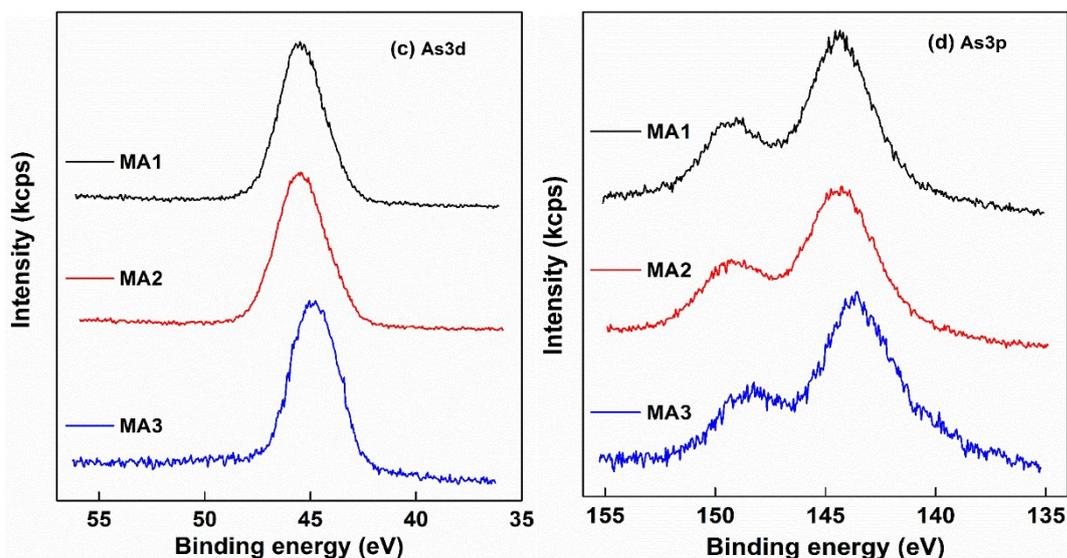


**Fig. S6.** Removal of As(V) from spiked well water by the MA adsorbents. Initial As(V) concentrations, 1.10 mg/L; adsorbent dose, MA1, MA2 and MA3, 0.1 g/L, 0.1 g/L and 0.5 g/L, respectively; total solution volumes, 1000 ml; pH, 7.57; temperature,  $25 \pm 1$  °C, and shaking time, 0-30 h (see Table S3 for  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$  concentrations).



**Fig. S7.** The re-adsorption ability of MA1 after separation followed by regeneration. Initial As(V) concentration = 12.3 mg/L; adsorbent dose = 0.3 g/L; shaking time = 10 h; pH =  $5.0 \pm 0.2$ , and temperature =  $25 \pm 1$  °C. The used adsorbent was regenerated in a 0.01 M NaOH for 6 h and then was neutralized in 0.01 M HCl for 2 h. (Dash line corresponding to the capacity of the fresh adsorbent).





**Fig. S8.** (a) Full scan, (b) Al2p, (c) As3d and (d) As3p XPS spectra of the three mesoporous aluminas before and after As(V) adsorption at pH  $5.0 \pm 0.1$ .

**Table S1** Adsorption isotherm parameters for As(V) adsorption on the MA adsorbents.

Equations	Parameters	MA1	MA2	MA3
		Values	Values	Values
Langmuir $q_e = \frac{q_{\max} b C_e}{1 + b C_e}$	$q_{\max}$ (mg/g)	180.08	174.69	41.58
	$b$ (L/mg)	3.805	1.94	2.864
	$R_L^2$	0.951	0.983	0.977
	$RMSE$	13.346	8.534	1.806
Freundlich $q_e = k C_e^{1/n}$	$k$	108.51	97.59	27.72
	$n$	4.568	4.143	8.178
	$R_F^2$	0.803	0.934	0.975
	$RMSE$	26.368	14.717	1.901

**Table S2** A performance comparison between the three mesoporous aluminas and various adsorbents for As removal from water.

Adsorbent	Initial concentration range (mg/L)	Dose (g/L)	pH	Adsorption capacity (mg/g)	Adsorbate	Reference
MA1	17	0.03	5	175.7	As (V)	Present study
MA2	17	0.03	5	140.2	As (V)	Present study
MA3	56	0.03	5	43.8	As (V)	Present study
AlOOH	30	0.03	5	41.7	As (V)	Present study <sup>a</sup>
AA1	30	0.03	5	38.2	As (V)	Present study <sup>b</sup>
AA2	30	0.03	5	38.5	As (V)	Present study <sup>c</sup>
AA3	30	0.03	5	7.7	As (V)	Present study <sup>d</sup>
AA4	30	0.03	5	8.0	As (V)	Present study <sup>e</sup>
Mesoporous alumina	10	0.4	4	24.8 (Kinetic)	As (V)	5
Mesoporous alumina	130	0.05	4	39.1	As (V)	6
Meso-Al-400	0.1	1	7	5	As (III)	7
MA-400	11.175-178.816	0.05	6.6	36.6 (Langmuir)	As (V)	8
Manganese oxide-coated-alumina	2-300	5	7	29.2 (Langmuir)	As (III)	9
Activated Alumina	2-300	5	7	19.6 (Langmuir)	As (III)	9

Lanthanum-impregnated activated alumina	20	5	6	0.2 ( Kinetic )	As (V)	10
Fe-montmorillonites	5	4	-	1.2	As (V)	11
Al <sub>2</sub> O <sub>3</sub>	0.2	4	6	0.1	As (V)	12
Zirconium polyacrylamide hybrid starch-stabilized	100	13	≤5	15.4 ( Kinetic)	As (III)	13
magnetite nanoparticles	0.03-8.24	0.1	6.8	62.1 (Langmuir)	As (III)	14

<sup>a</sup>Amorphous aluminium hydroxide (AlOOH) was prepared following a procedure reported by Gong et al.<sup>15</sup> <sup>b</sup>AA1 was from Mizusawa Industrial Chemicals, Ltd., Japan, <sup>c</sup>AA2 from Wenzhou Jingjing Aluminum Oxide Co. Ltd., China, <sup>d</sup>AA3 from Sinopharm Chemical Reagent Co. Ltd., China, and <sup>e</sup>AA4 was ordered from Alfa Aesar, USA.

**Table S3** The water quality conditions of spiked well water.

pH	Total As (mg/L)	Cl <sup>-</sup> (mg/L)	F <sup>-</sup> (mg/L)	Fe <sup>3+</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	Na <sup>+</sup> (mg/L)	K <sup>+</sup> (mg/L)	Al <sup>3+</sup> (mg/L)
7.57	1.1	178	1.59	4.2	332	118	3	1.11

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