

## Supplementary Material

# As(III, V) Uptake from Nanostructured Iron Oxides and Oxyhydroxides: The Complex Interplay between Sorbent Surface Chemistry and Arsenic Equilibria

Marco Sanna Angotzi <sup>1,2</sup>, Valentina Mameli <sup>1,2,\*</sup>, Alessandra Fantasia <sup>1</sup>, Claudio Cara <sup>1,2</sup>, Fausto Secci <sup>1,2</sup>, Stefano Enzo <sup>3</sup>, Marianna Gerina <sup>4</sup> and Carla Cannas <sup>1,2</sup>

<sup>1</sup> Department of Chemical and Geological Sciences, University of Cagliari, S.S. 554 bivio per Sestu, 09042 Monserrato, Italy; marcosanna@unica.it (M.S.A.); fantasia.91@hotmail.it (A.F.); cara.claudio16@gmail.com (C.C.); fausto.s1993@gmail.com (F.S.); ccannas@unica.it (C.C.)

<sup>2</sup> Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giuseppe Giusti 9, 50121 Firenze, Italy

<sup>3</sup> Department of Chemistry and Pharmacy, University of Sassari, Via Vienna 2, 07100 Sassari, Italy; enzo@uniss.it

<sup>4</sup> Department of Inorganic Chemistry, Charles University, Hlavova 8, 12800 Prague 2, Czech Republic; marygerina@hotmail.it

\* Correspondence: valentina.mameli@unica.it

**Citation:** Sanna Angotzi, M.; Mameli, V.; Fantasia, A.; Cara, C.; Secci, F.; Enzo, S.; Gerina, M.; Cannas, C. As(III, V) Uptake from Nanostructured Iron Oxides and Oxyhydroxides: The Complex Interplay between Sorbent Surface Chemistry and Arsenic Equilibria. *Nanomaterials* **2022**, *12*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor(s): Zheng Ling

Received: 17 December 2021

Accepted: 18 January 2022

Published: date

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## Table of Contents

1. Experimental Details	2
2. Characterization of the sorbents	2
3. Theoretical behaviour of the sorbents and the arsenic species	6
4. Adsorption tests: effect of pH As <sup>V</sup>	8
5. Adsorption tests: effect of pH As <sup>III</sup>	13
6. FTIR Spectra	17
7. Adsorption tests: effect of initial concentration	18
8. Adsorption tests: effect of contact time	19
9. Adsorption tests: effect of ionic strength	21
10. Adsorption tests: effect of competitors	22

## 1. Experimental Details

**Table S1.** Experimental parameters for adsorption tests. The sorbent amount was 50 mg and solution volume 20 mL for all the tests.

Sorb.	Effect	C <sub>0</sub> As <sup>V</sup> (mg L <sup>-1</sup> )	C <sub>0</sub> As <sup>III</sup> (mg L <sup>-1</sup> )	t (min)	pH <sub>0</sub>	NaCl (M)	As/Comp (mol/mol)
Aka, Fer, Mag, Comp	pH	100	0	960	2, 3, 4, 6, 8	0	0
Aka, Fer, Mag, Comp	pH	0	100	960	2, 3, 4, 6, 8	0	0
Aka, Fer	pH	500	0	960	2, 3, 4, 6, 8	0	0
Aka, Fer	pH	0	500	960	2	0	0
Aka	C <sub>0</sub>	10, 50, 100, 150, 200, 250, 350, 500	0	960	3, 8	0	0
Aka	Time	250	0	10, 30, 60, 120, 240, 960	3, 8	0	0
Aka	Ionic Strength	250	0	960	3, 8	0, 0.01, 0.1, 1	0
Aka	Competitor	250	0	960	3, 8	0	1:1, 1:10, 1:100

Sorbent name, studied effect, initial concentration (C<sub>0</sub>), contact time, initial pH (pH<sub>0</sub>), ionic strength concentration (NaCl), arsenic/competitor ratio (SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>).

## 2. Characterization of the sorbents

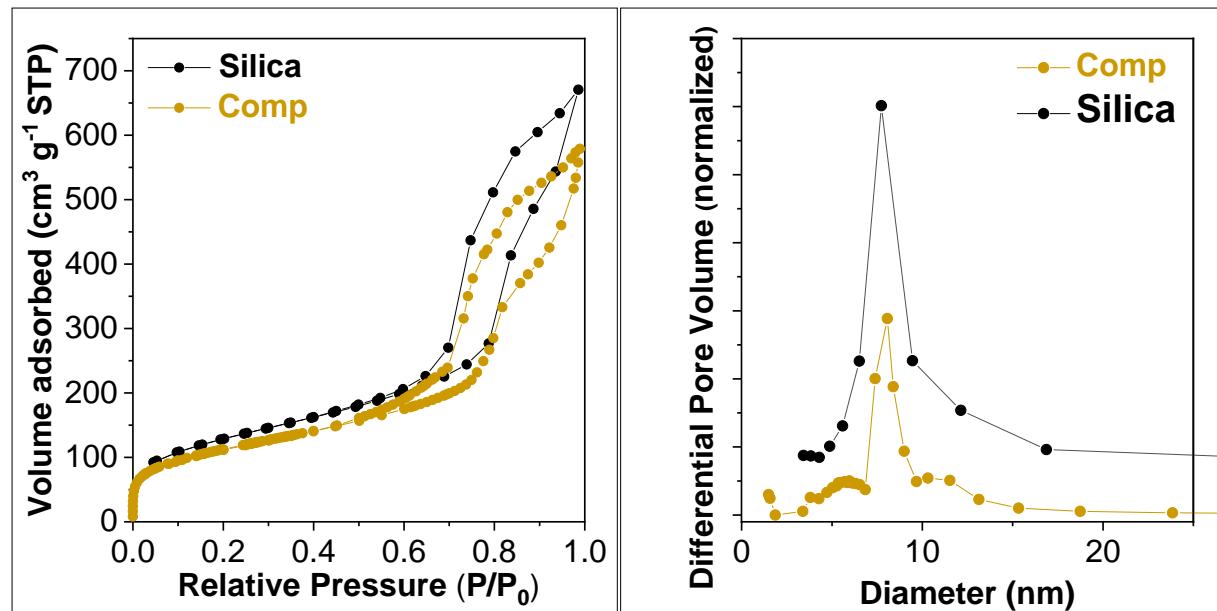
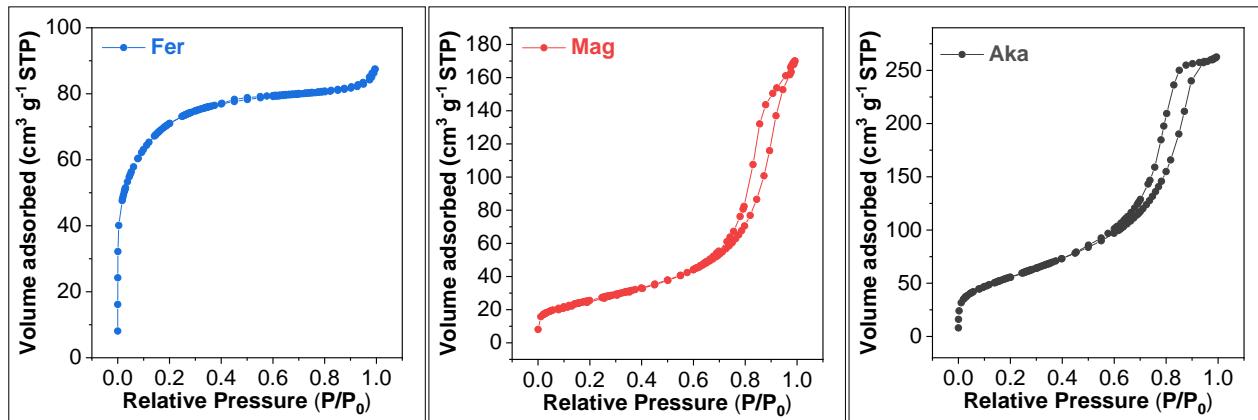
**Table S2.** Hyperfine parameters obtained by fitting procedure of the <sup>57</sup>Fe Mössbauer spectra of the sorbents.

Sample	Subspectrum	IS (mm s <sup>-1</sup> )	QS (mm s <sup>-1</sup> )	B <sub>Hf</sub> (T)	W (mm s <sup>-1</sup> )	D	A (%)
Aka	Doublet	0.373(1)	0.536(7)	-	0.330(7)	0.095(4)	57
	Doublet	0.379(2)	0.940(9)	-	0.346(8)	0.071(4)	43
Fer (1st attempt)	Doublet	0.338(2)	0.697(4)	-	0.615(6)	0.1977(9)	-
	Doublet	0.321(8)	0.38(3)	-	0.27(7)	0.02(1)	10
Fer (2nd attempt)	Doublet	0.340(3)	0.74(4)	-	0.59(1)	0.17(1)	88
	Doublet	0.34(1)	1.3(5)	-	0.2(1)	0.005(4)	2
Mag	Sextet	0.326(2)	0.007(6)	47.09(3)	0.44(1)	0.13(1)	50
	Sextet	0.328(3)	-0.043(8)	41.9(4)	0.58(2)	0.13(1)	50
Comp	Doublet	0.34(1)	0.74(2)	-	0.61(2)	0.008(1)	-

IS is isomer shift. QS is the quadrupole splitting, B<sub>Hf</sub> is the hyperfine field; W is the width; D is the depth; A is the area.

**Table S3.** FTIR bands of the sorbents.

Aka		Mag		Fer		Comp	
Wavenumber (cm <sup>-1</sup> )	Vibration mode	Wavenumber (cm <sup>-1</sup> )	Vibration mode	Wavenumber (cm <sup>-1</sup> )	Vibration mode	Wavenumber (cm <sup>-1</sup> )	Vibration mode
3300	v H <sub>2</sub> O	3300	v H <sub>2</sub> O	3400	v H <sub>2</sub> O	3400	v H <sub>2</sub> O
1615	δ H <sub>2</sub> O	1620	δ H <sub>2</sub> O	1630	δ H <sub>2</sub> O	1630	δ H <sub>2</sub> O
1360	v Fe-OH	820	v Fe-O	1500	v Fe-OH	1220	v Si-O-Si
1100	v Fe-OH	630	v Fe-O	1330	v Fe-OH	1090	v Si-O-Si
850	λ OH-Cl	570	v Fe-O	1065	v Fe-OH	970	v Si-O-H
680	v <sub>as</sub> Fe-O			850	v Fe-OH	810	v Si-O-Si
470	v <sub>s</sub> Fe-O			600	v Fe-O	470	v Fe-O
				440	v Fe-O		

**Figure S1.** N<sub>2</sub>-physisorption isotherms (left) and BJH-calculated pore size distributions (right) of the silica-based samples.**Figure S2.** N<sub>2</sub>-physisorption isotherms of the iron oxide sorbents.

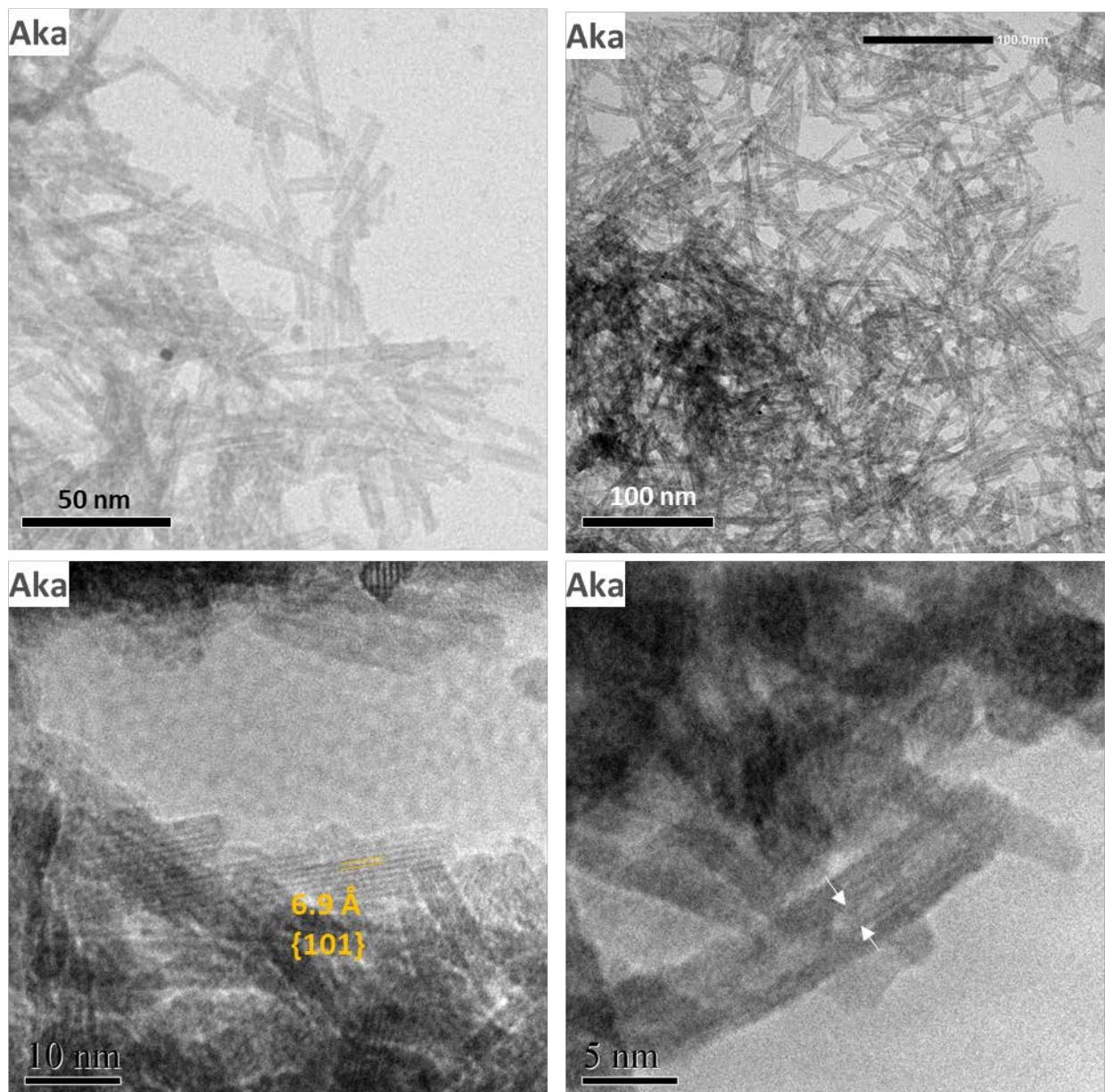


Figure S3. TEM and HRTEM micrographs of Aka nanorods.

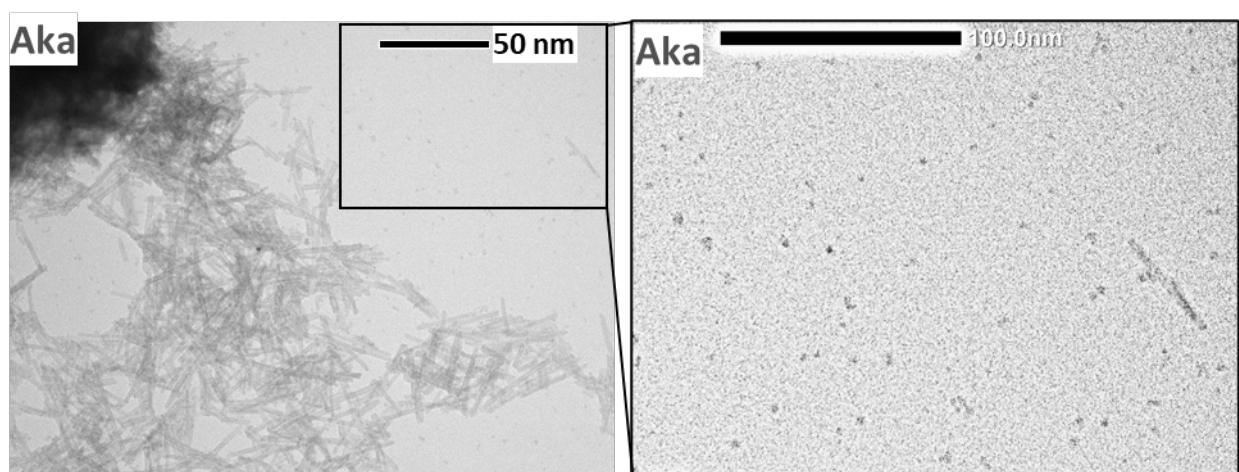
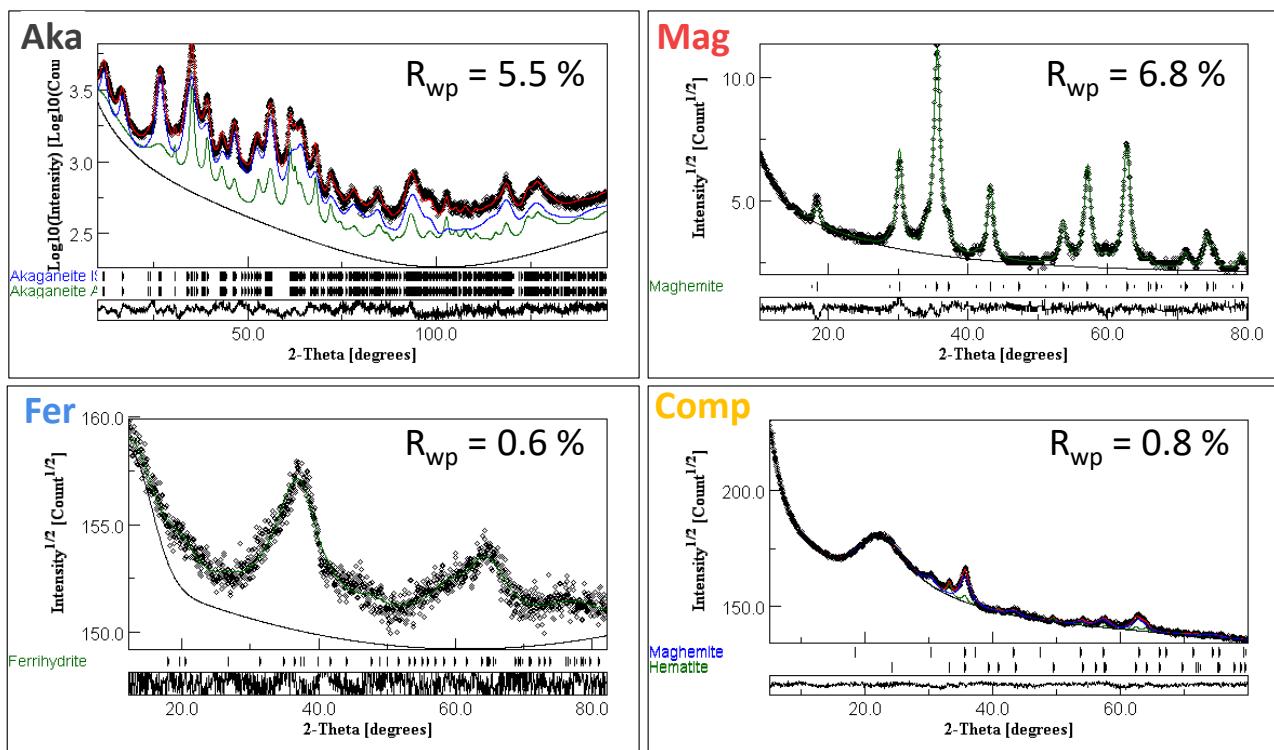
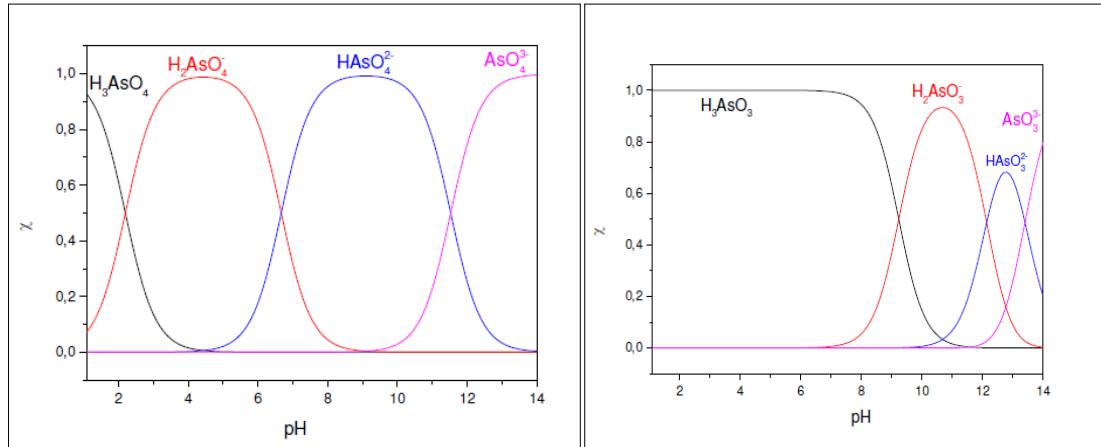


Figure S4. TEM micrograph of Aka and magnification to highlight the small nanoparticles.



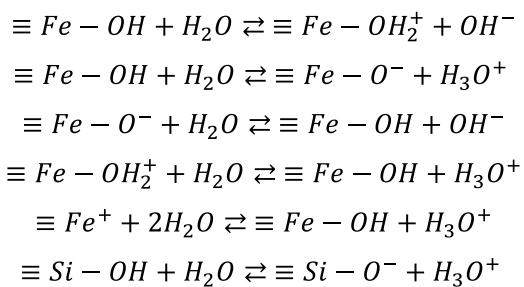
**Figure S5.** Rietveld refinement of XRD patterns of the samples. Inset of crystal shape modelled from Popa rule for the Aka sample.

### 3. Theoretical behaviour of the sorbents and the arsenic species



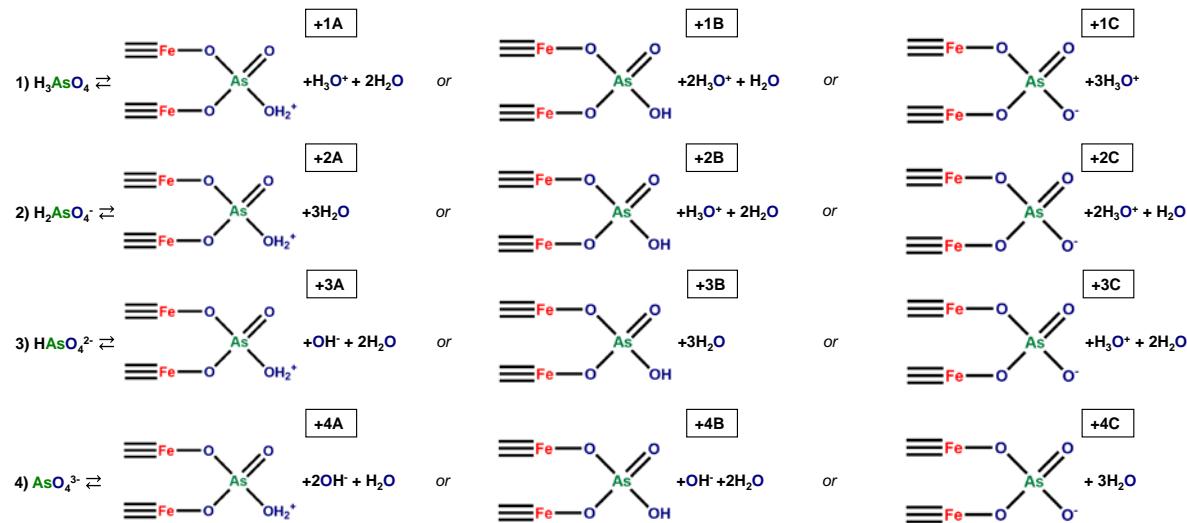
**Figure S6.** Bjerrum plot of arsenate (left) and arsenite (right) species reconstructed employing the dissociation constants of arsenic acid ( $\text{pK}_{\text{a}1} = 2.20$ ;  $\text{pK}_{\text{a}2} = 6.67$ ;  $\text{pK}_{\text{a}3} = 11.53$ ) and arsenious acid ( $\text{pK}_{\text{a}1} = 9.23$ ;  $\text{pK}_{\text{a}2} = 12.13$ ;  $\text{pK}_{\text{a}3} = 13.40$ ).

#### Sorbent surface in water

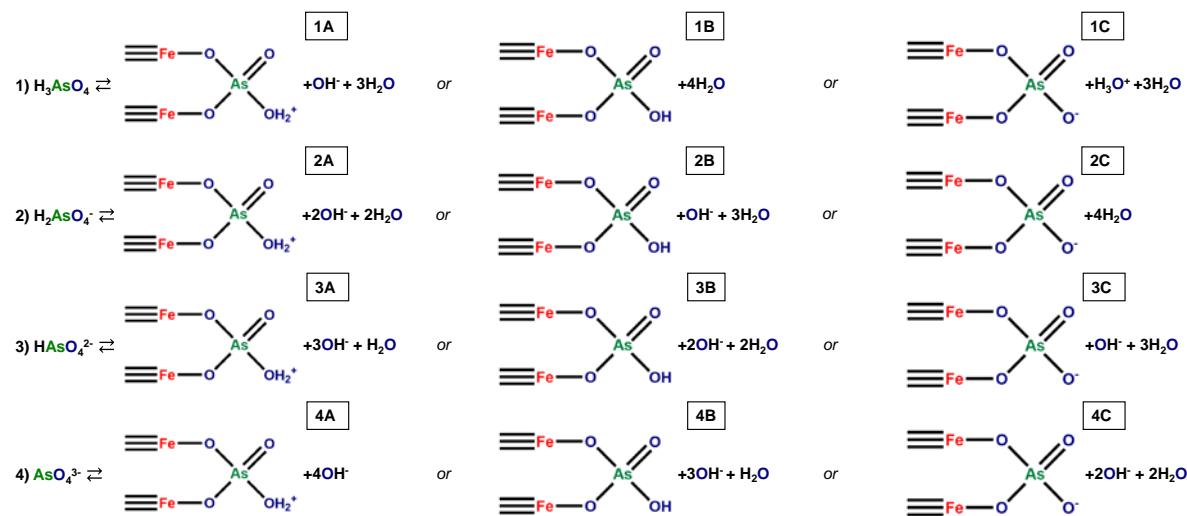


**Figure S7.** Reactions of the sorbent surface in water.

Positive surface of sorbent with  $\text{As}^V$  species (Bidentate Binuclear):  $2\equiv\text{Fe}-\text{OH}_2^+ + \text{H}_2\text{O} \rightleftharpoons$



Neutral surface of sorbent with  $\text{As}^V$  species (Bidentate Binuclear):  $2\equiv\text{Fe}-\text{OH} + 2\text{H}_2\text{O} \rightleftharpoons$



Negative surface of sorbent with  $\text{As}^V$  species (Bidentate Binuclear):  $2\equiv\text{Fe}-\text{O} + 4\text{H}_2\text{O} \rightleftharpoons$

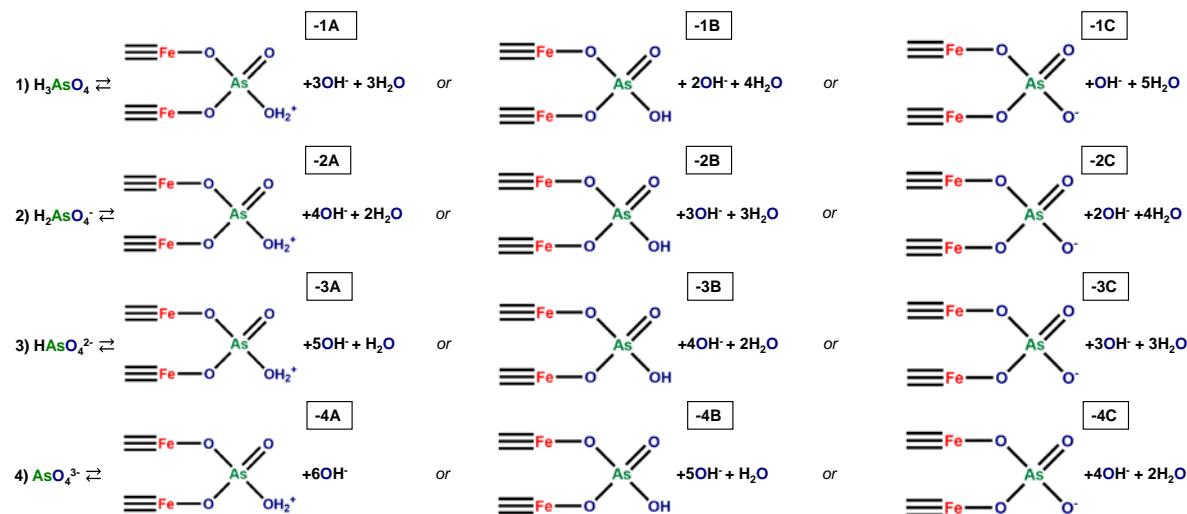


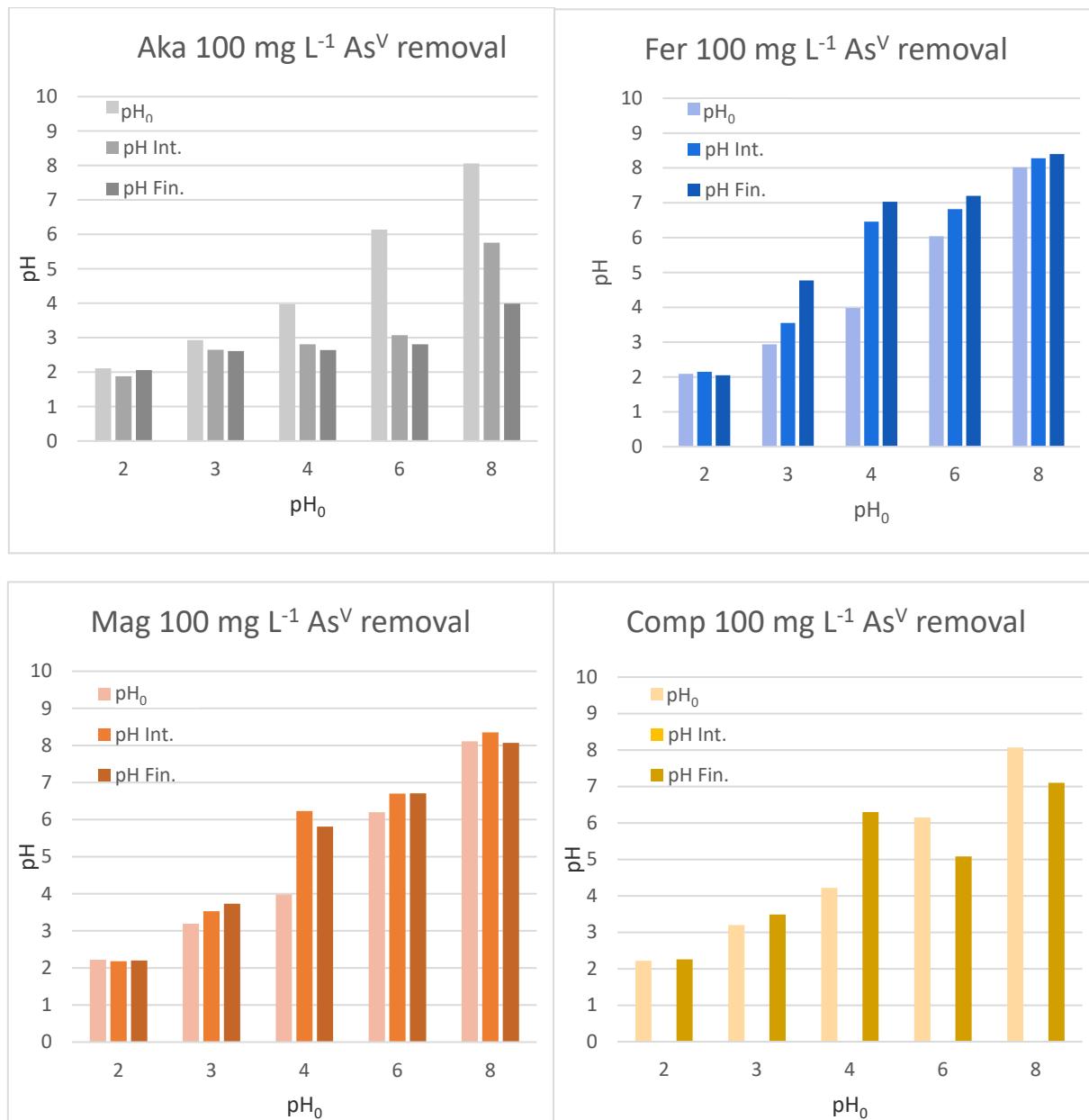
Figure S8. Possible reactions between the sorbent surface and arsenate species in water.

#### 4. Adsorption tests: effect of pH As<sup>V</sup>

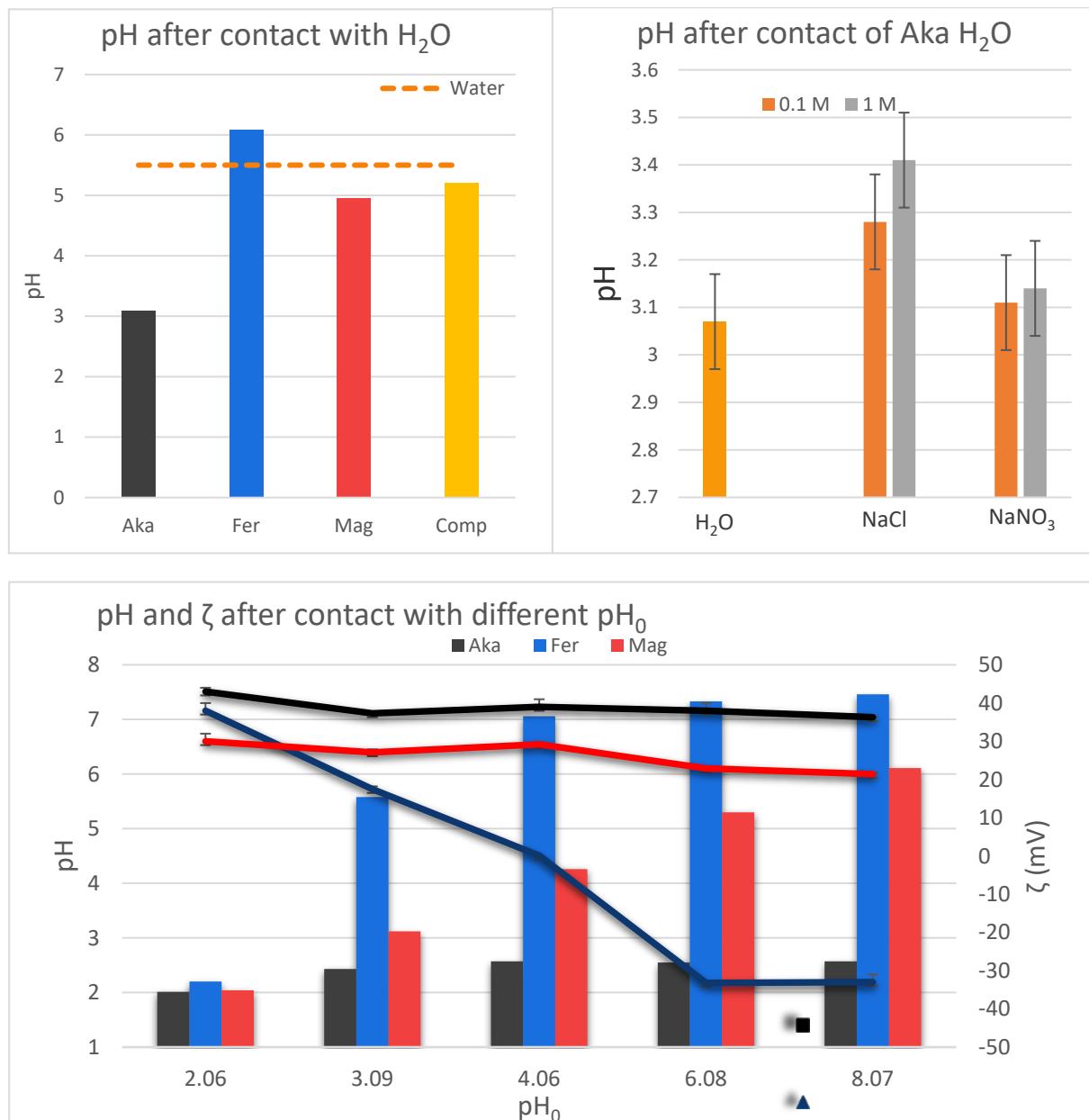
**Table S4.** Batch experiments results of the sorbents at initial concentration of 100 or 500 mg L<sup>-1</sup> of As<sup>V</sup> at various pH. Volume of the contaminant was 20 mL and adsorption time was 16 hours.

Sorbent	Moisture (%)	m (mg)	V (mL)	pH <sub>0</sub>	pH <sub>Int</sub>	pH <sub>Fin</sub>	C <sub>0</sub> (mg L <sup>-1</sup> )	C <sub>e</sub> As <sup>V</sup> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg/g)	As Ads (%)	q <sub>e</sub> (mg/m <sup>2</sup> )	C <sub>e</sub> Si (mg L <sup>-1</sup> )
Aka	7.24%	51.6	20	2.11	1.88	2.06	97.9	0.2	40.8	99.8%	0.202	n.a.
		49.2	20	2.93	2.65	2.61	95.5	0.2	41.8	99.8%	0.207	n.a.
		51.5	20	3.97	2.81	2.64	96.5	0.1	40.3	99.9%	0.200	n.a.
		51.2	20	6.14	3.07	2.81	96.7	0.1	40.7	99.9%	0.201	n.a.
		49.8	20	8.06	5.76	3.99	98.4	0.8	42.3	99.2%	0.209	n.a.
		49.8	20	2.15	1.90	1.81	459.0	258.3	86.9	43.7%	0.430	n.a.
		50.9	20	3.17	2.91	3.27	469.9	281.5	79.8	40.1%	0.395	n.a.
		49.8	20	3.05	2.89	2.82	484.2	279.7	88.5	42.2%	0.438	n.a.
		50.9	20	3.94	3.25	3.39	481.9	290.2	81.2	39.8%	0.402	n.a.
		50.9	20	6.16	6.28	6.41	481.2	339.3	60.1	29.5%	0.298	n.a.
Fer	10.67%	50.3	20	8.21	7.68	7.35	455.3	335.1	51.5	26.4%	0.255	n.a.
		45.5	20	2.09	2.15	2.05	104.7	0.4	45.9	99.7%	0.176	n.a.
		44.6	20	2.94	3.55	4.77	105.1	6.5	44.2	93.8%	0.170	n.a.
		45.3	20	3.98	6.46	7.03	105.8	46.2	26.3	56.3%	0.101	n.a.
		45.3	20	6.04	6.82	7.20	106.1	52.9	23.5	50.1%	0.090	n.a.
		45.3	20	8.02	8.28	8.40	105.0	80.9	10.6	22.9%	0.041	n.a.
		44.8	20	2.09	2.24	1.96	512.6	353.4	71.0	31.1%	0.273	n.a.
		45.0	20	3.05	3.32	4.33	518.5	379.4	61.9	26.8%	0.238	n.a.
		44.7	20	4.00	5.61	6.08	517.6	409.9	48.1	20.8%	0.185	n.a.
		45.3	20	5.96	6.15	6.28	520.7	414.7	46.8	20.4%	0.180	n.a.
Mag	1.31%	45.2	20	8.07	8.23	8.26	516.6	464.0	23.3	10.2%	0.089	n.a.
		49.9	20	2.22	2.18	2.20	92.3	29.1	25.7	68.5%	0.279	n.a.
		51.3	20	3.19	3.53	3.73	93.2	44.0	19.4	52.8%	0.211	n.a.
		51.5	20	3.98	6.23	5.81	93.7	60.9	12.9	35.0%	0.140	n.a.
		50.1	20	6.20	6.70	6.71	93.3	66.8	10.7	28.4%	0.117	n.a.
Comp	2.28%	50.1	20	8.11	8.35	8.07	94.6	79.3	6.2	16.2%	0.068	n.a.
		49.6	20	2.22	n.a.	2.26	98.4	79.8	7.7	18.9%	0.019	5.19
		50.5	20	3.20	n.a.	3.49	101.7	86.9	6.0	14.6%	0.015	7.36
		50.0	20	4.22	n.a.	6.30	103.9	92.0	4.9	11.4%	0.012	20.35
		50.6	20	6.15	n.a.	5.08	101.0	93.2	3.1	7.7%	0.008	32.19
		51.1	20	8.07	n.a.	7.10	101.3	95.2	2.5	6.1%	0.006	46.60

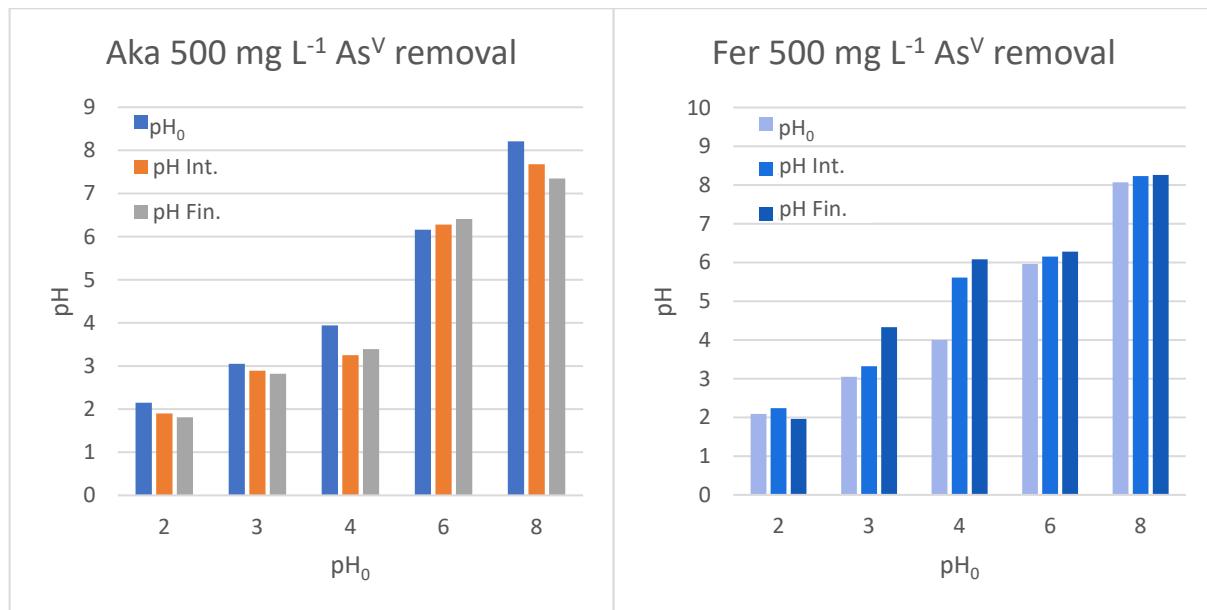
pH<sub>0</sub> is the pH of the solution before contact with the sorbent. pH<sub>int</sub> is the pH of the solution immediately after contact with the sorbent. pH<sub>fin</sub> is the pH of the solution after adsorption test and separation of the sorbent from the liquid. C<sub>0</sub> is the initial arsenic concentration. C<sub>e</sub> is the final arsenic concentration. q<sub>e</sub> is the adsorbed amount of arsenic, calculated with Eq.1. Relative errors (E<sub>r</sub>): E<sub>r</sub>(Moisture) = 2%; E<sub>r</sub>(m) = 1%; E<sub>r</sub>(V) = 1%; E<sub>r</sub>(pH) = 2%; E<sub>r</sub>(C) = 2%; E<sub>r</sub>(q<sub>e</sub>) = 7%.



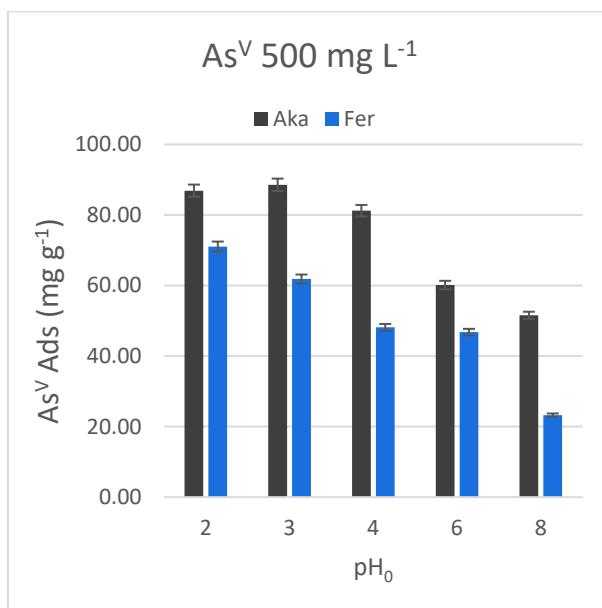
**Figure S9.** Evolution of initial pH (pH<sub>0</sub>), intermediate pH (pH<sub>Int.</sub>) and final pH (pH<sub>Fin.</sub>) for various starting pH (pH<sub>0</sub>) for the sorbents with initial concentration of As<sup>V</sup> equal to 100 mg L<sup>-1</sup>.



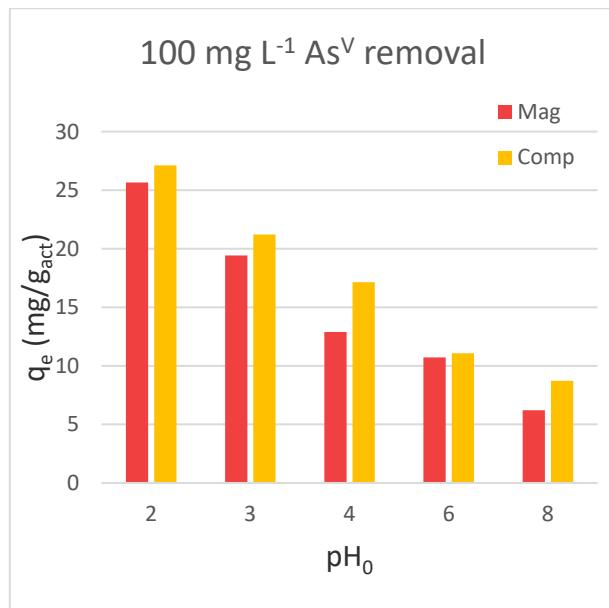
**Figure S10.** pH of solution after contact with sorbents.



**Figure S11.** Evolution of initial pH ( $\text{pH}_0$ ), intermediate pH ( $\text{pH}_{\text{Int.}}$ ) and final pH ( $\text{pH}_{\text{Fin.}}$ ) for various starting pH ( $\text{pH}_0$ ) for the sorbents with initial concentration of  $\text{As}^{3+}$  equal to  $500 \text{ mg L}^{-1}$ .



**Figure S12.** Adsorption capacity from batch adsorption experiments with  $500 \text{ mg L}^{-1}$   $\text{As}^{3+}$  solution on Aka (black) and Fer (blue) at different initial pH ( $\text{pH}_0$ ).



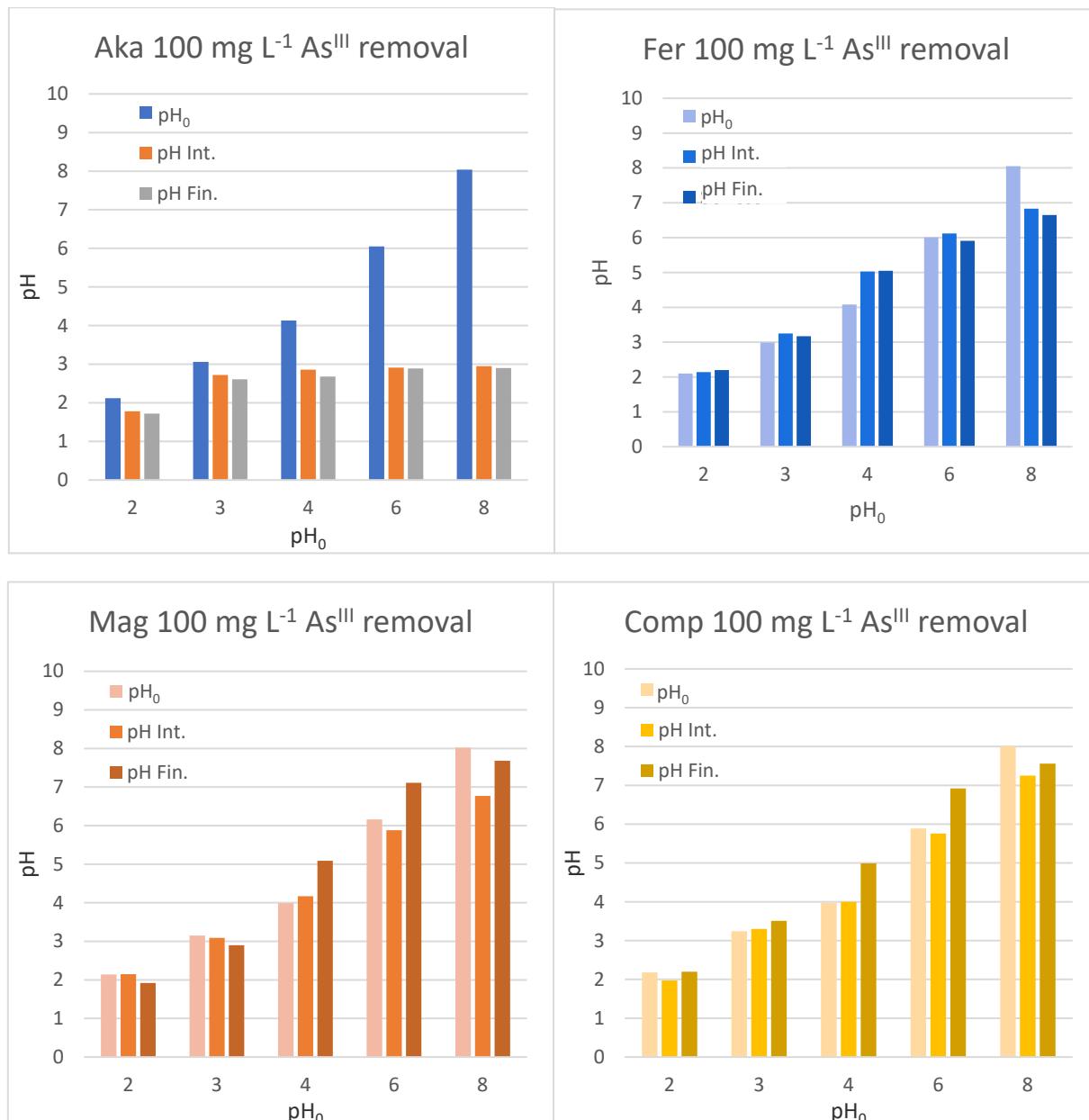
**Figure S13.** Adsorption capacity from batch adsorption experiments with 100 mg L<sup>-1</sup> As<sup>V</sup> solution on maghemite and composite normalized for its active phase (28.3%) at different initial pH (pH<sub>0</sub>).

### 5. Adsorption tests: effect of pH As<sup>III</sup>

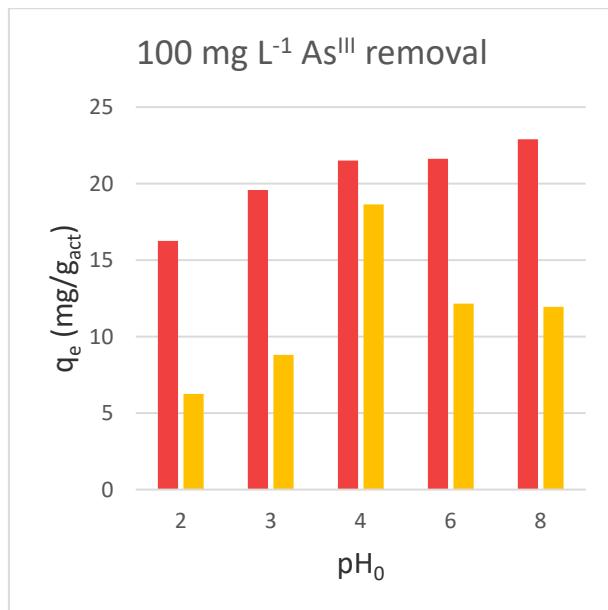
**Table S5.** Batch experiments results of the sorbents at initial concentration of 100 or 500 mg L<sup>-1</sup> of As<sup>III</sup> at various pH. Volume of the contaminant was 20 mL and adsorption time was 16 hours.

Sorbent	Moisture (%)	m (mg)	V (mL)	pH <sub>0</sub>	pH <sub>Int</sub>	pH <sub>Fin</sub>	C <sub>0</sub> (mg L <sup>-1</sup> )	C <sub>e</sub> As <sup>III</sup> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg/g)	As Ads (%)	q <sub>e</sub> (mg/m <sup>2</sup> )	C <sub>e</sub> Si (mg L <sup>-1</sup> )
Aka	7.24%	49.8	20	2.12	1.78	1.72	102.6	37.2	28.3	63.8%	0.140	n.a.
		50.8	20	3.06	2.72	2.61	103.9	19.5	35.8	81.2%	0.177	n.a.
		49.3	20	4.13	2.86	2.68	103.9	18.4	37.4	82.3%	0.185	n.a.
		49.4	20	6.05	2.91	2.89	103.1	20.8	35.9	79.8%	0.178	n.a.
		50.8	20	8.04	2.95	2.90	102.9	17.0	36.4	83.4%	0.180	n.a.
		46.6	20	2.04	2.06	2.07	518.3	364.9	65.9	29.6%	0.326	n.a.
		46.6	20	2.97	2.99	2.49	567.1	355.8	90.7	37.3%	0.449	n.a.
		46.8	20	4.09	3.14	2.63	549.5	351.1	84.8	36.1%	0.420	n.a.
		46.8	20	6.05	3.06	2.43	564.6	352.9	90.5	37.5%	0.448	n.a.
		46.7	20	7.98	3.33	2.56	570.6	356.9	91.4	37.5%	0.453	n.a.
Fer	10.67%	45.0	20	2.10	2.14	2.20	115.8	14.5	45.1	87.5%	0.173	n.a.
		45.2	20	2.99	3.25	3.17	119.8	7.1	49.9	94.1%	0.192	n.a.
		44.7	20	4.08	5.03	5.05	119.7	5.1	51.2	95.7%	0.197	n.a.
		44.8	20	6.01	6.12	5.91	119.3	4.5	51.3	96.2%	0.197	n.a.
		45.5	20	8.05	6.83	6.65	119.2	4.3	50.6	96.4%	0.194	n.a.
		50.37	20	2.07	2.16	1.89	544.2	293.0	111.7	46.2%	0.429	n.a.
		50.19	20	2.97	3.47	3.08	567.1	260.6	136.7	54.0%	0.526	n.a.
		50.33	20	4.09	5.20	4.78	549.5	248.6	133.9	54.8%	0.515	n.a.
		50.30	20	6.05	6.16	5.78	564.6	248.4	140.7	56.0%	0.541	n.a.
		50.37	20	7.98	7.45	6.77	570.6	245.8	144.4	56.9%	0.555	n.a.
Mag	1.31%	52.0	20	2.14	2.15	1.92	99.5	57.8	16.3	41.9%	0.177	n.a.
		51.5	20	3.15	3.09	2.90	98.7	48.9	19.6	50.4%	0.213	n.a.
		50.0	20	3.99	4.17	5.09	98.1	45.1	21.5	54.1%	0.234	n.a.
		50.3	20	6.16	5.88	7.11	97.8	44.2	21.6	54.9%	0.235	n.a.
		50.8	20	8.02	6.77	7.68	98.6	41.2	22.9	58.2%	0.249	n.a.
Comp	2.28%	50.8	20	2.18	1.97	2.20	97.7	93.3	1.8	4.5%	0.004	4.39
		51.0	20	3.24	3.30	3.51	101.3	95.0	2.5	6.1%	0.006	5.56
		49.7	20	3.97	4.00	4.99	106.1	93.3	5.3	12.1%	0.013	7.42
		50.6	20	5.89	5.76	6.92	99.7	91.2	3.4	8.5%	0.008	12.78
		49.7	20	8.01	7.25	7.56	98.3	90.1	3.4	8.3%	0.008	28.59

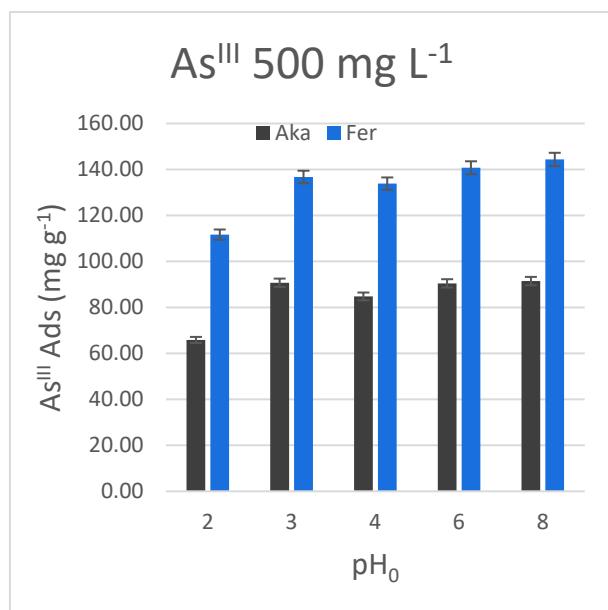
pH<sub>0</sub> is the pH of the solution before contact with the sorbent. pH<sub>Int</sub> is the pH of the solution immediately after contact with the sorbent. pH<sub>Fin</sub> is the pH of the solution after adsorption test and separation of the sorbent from the liquid. C<sub>0</sub> is the initial arsenic concentration. C<sub>e</sub> is the final arsenic concentration. q<sub>e</sub> is the adsorbed amount of arsenic, calculated with Eq.1. Relative errors (E<sub>r</sub>): E<sub>r</sub>(Moisture) = 2%; E<sub>r</sub>(m) = 1%; E<sub>r</sub>(V) = 1%; E<sub>r</sub>(pH) = 2%; E<sub>r</sub>(C) = 2%; E<sub>r</sub>(q<sub>e</sub>) = 7%.



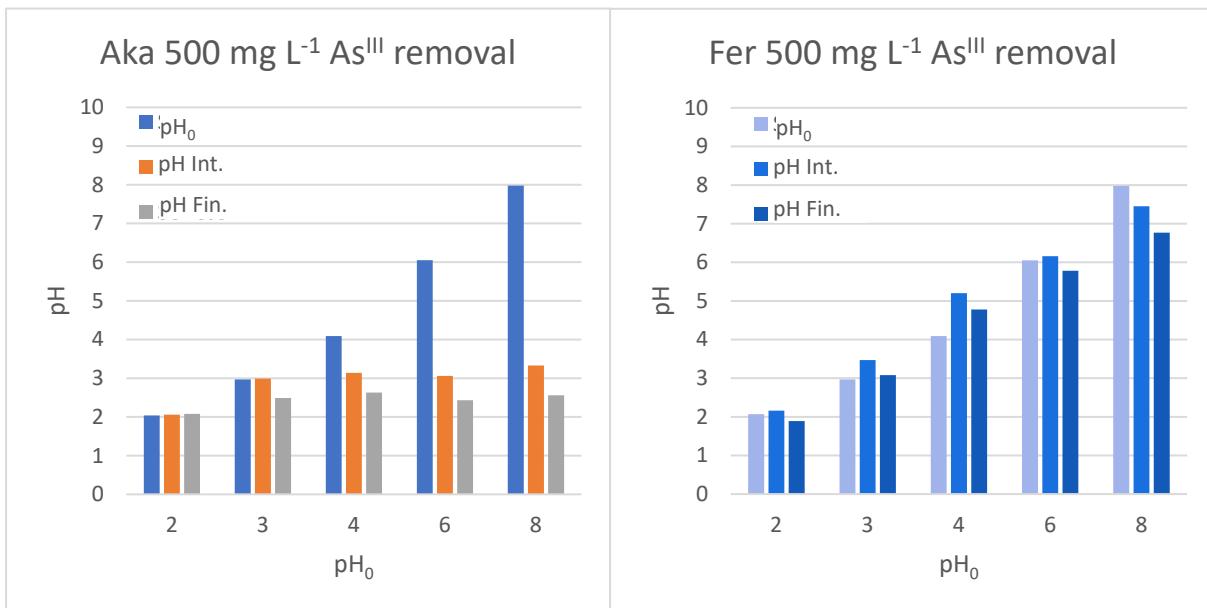
**Figure S14.** Evolution of initial pH (pH<sub>0</sub>), intermediate pH (pH<sub>Int.</sub>) and final pH (pH<sub>Fin.</sub>) for various starting pH (pH<sub>0</sub>) for the sorbents with initial concentration of As<sup>III</sup> equal to 100 mg L<sup>-1</sup>.



**Figure S15.** Adsorption capacity from batch adsorption experiments with 100 mg L<sup>-1</sup> As<sup>III</sup> solution on maghemite and composite normalized for its active phase (28.3%) at different initial pH (pH<sub>0</sub>).

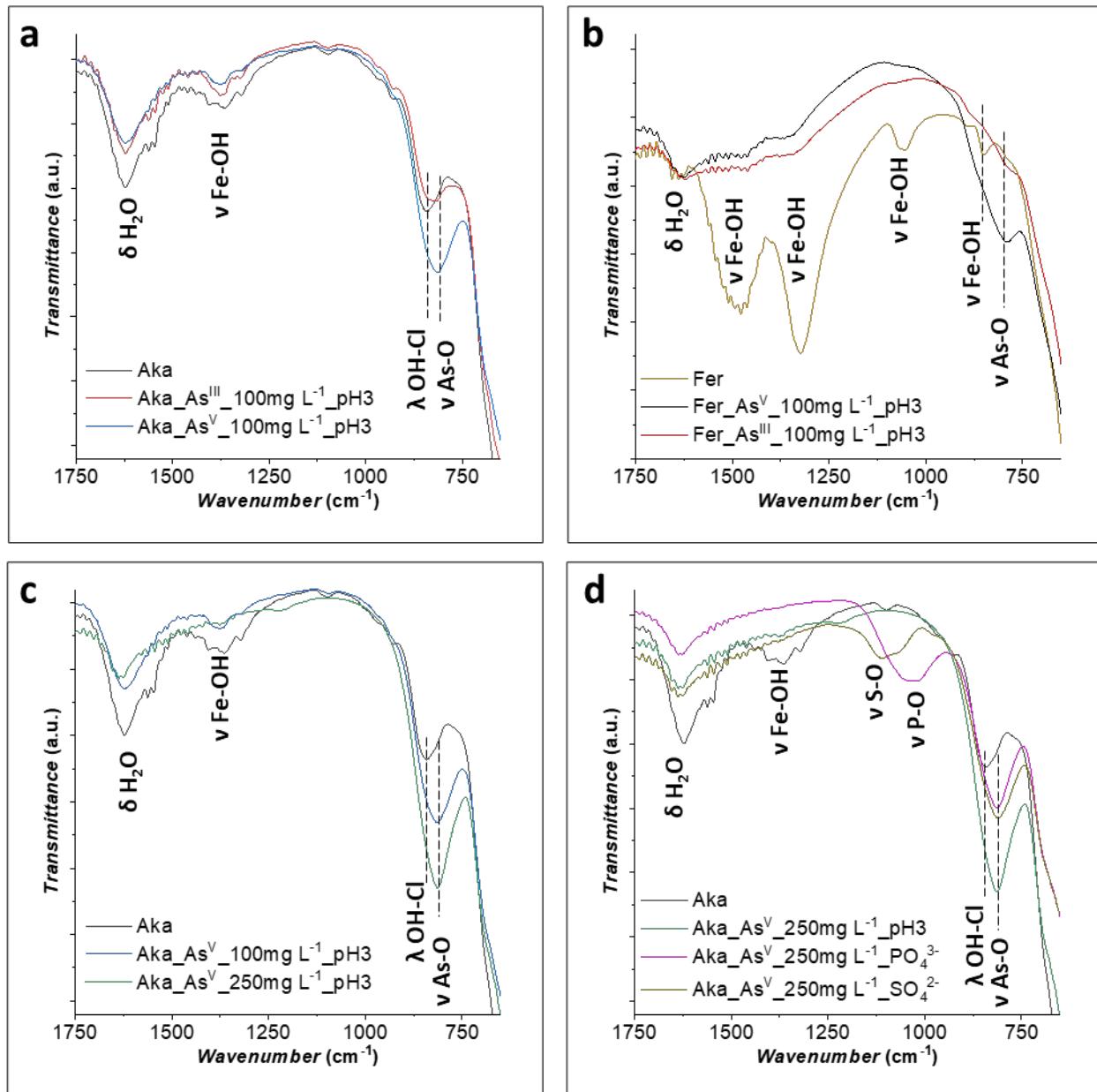


**Figure S16.** Adsorption capacity from batch adsorption experiments with 500 mg L<sup>-1</sup> As<sup>III</sup> solution on Aka (black) and Fer (blue) at different initial pH (pH<sub>0</sub>).



**Figure S17.** Evolution of initial pH ( $pH_0$ ), intermediate pH ( $pH_{Int.}$ ) and final pH ( $pH_{Fin.}$ ) for various starting pH ( $pH_0$ ) for the sorbents with initial concentration of As<sup>III</sup> equal to 500 mg L<sup>-1</sup>.

## 6. FTIR Spectra



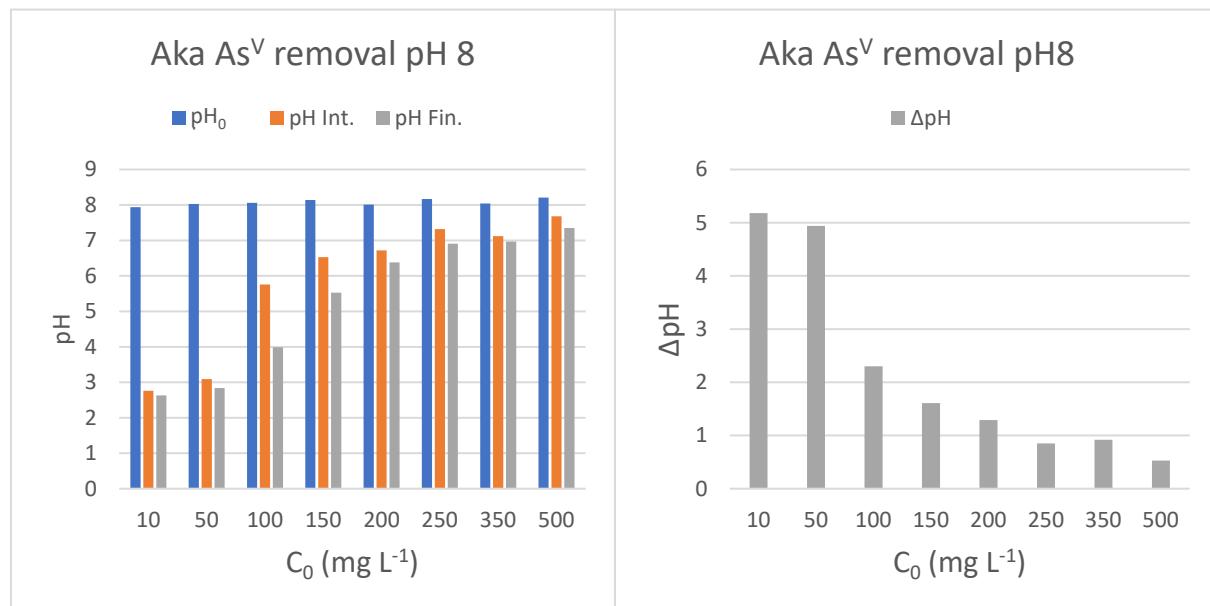
**Figure S18.** FTIR spectra of akaganeite and ferrihydrite after arsenic removal.

## 7. Adsorption tests: effect of initial concentration

**Table S6.** Batch experiments results of the sorbents at various initial concentration of As<sup>V</sup> at pH 3 and 8. Volume of the contaminant was 20 mL and adsorption time was 16 hours.

Sorbent	Moisture (%)	m (mg)	V (mL)	pH <sub>0</sub>	pH <sub>Int</sub>	pH <sub>Fin</sub>	C <sub>0</sub> (mg L <sup>-1</sup> )	C <sub>e</sub> As <sup>V</sup> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	As Ads (%)	q <sub>e</sub> (mg m <sup>-2</sup> )
Aka	7.24%	49.9	20	2.99	2.52	2.59	10.0	0.0	4.3	99.7%	0.021
		50	20	3.13	2.82	2.65	46.8	0.0	20.2	99.9%	0.100
		49.2	20	2.93	2.65	2.61	95.5	0.2	41.8	99.8%	0.207
		49.5	20	3.12	2.69	2.68	145.3	3.9	61.6	97.3%	0.305
		51.5	20	3.01	2.77	2.67	205.9	20.8	77.5	89.9%	0.384
		50.3	20	2.95	2.63	2.84	255.6	74.7	77.5	70.8%	0.384
		51.4	20	3.03	2.81	2.79	363.0	151.4	88.8	58.3%	0.439
		49.8	20	3.05	2.89	2.82	484.2	279.7	88.5	42.2%	0.438
		51.1	20	7.94	2.76	2.63	9.9	0.1	4.2	99.4%	0.021
		51.1	20	8.03	3.09	2.84	45.7	0.1	19.3	99.9%	0.095
		49.8	20	8.06	5.76	3.99	98.4	0.8	42.3	99.2%	0.209
		51.2	20	8.14	6.53	5.53	142.4	31.3	46.8	78.0%	0.232
		49.9	20	8.01	6.72	6.38	212.8	104.5	46.8	50.9%	0.232
		49.9	20	8.17	7.32	6.91	242.1	130.3	48.3	46.2%	0.239
		50.4	20	8.04	7.12	6.97	376.8	264.8	47.9	29.7%	0.237
		50.3	20	8.21	7.68	7.35	455.3	335.1	51.5	26.4%	0.255

pH<sub>0</sub> is the pH of the solution before contact with the sorbent. pH<sub>Int</sub> is the pH of the solution immediately after contact with the sorbent. pH<sub>Fin</sub> is the pH of the solution after adsorption test and separation of the sorbent from the liquid. C<sub>0</sub> is the initial arsenic concentration. C<sub>e</sub> is the final arsenic concentration. q<sub>e</sub> is the adsorbed amount of arsenic, calculated with Eq.1. Relative errors (E<sub>r</sub>): E<sub>r</sub>(Moisture) = 2%; E<sub>r</sub>(m) = 1%; E<sub>r</sub>(V) = 1%; E<sub>r</sub>(pH) = 2%; E<sub>r</sub>(C) = 2%; E<sub>r</sub>(q<sub>e</sub>) = 7%.



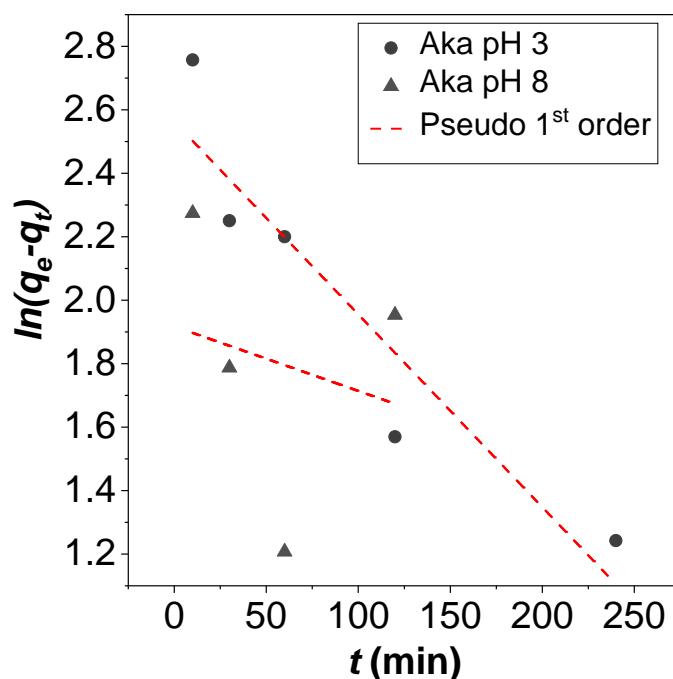
**Figure S19.** Evolution of initial pH (pH<sub>0</sub>), intermediate pH (pH<sub>Int</sub>) and final pH (pH<sub>Fin</sub>) (left) and ΔpH between intermediate and initial pH (right) at various As<sup>V</sup> initial concentration for Aka.

## 8. Adsorption tests: effect of contact time

**Table S7.** Batch experiments results of the sorbents at various contact time with As<sup>V</sup> at pH 3 and 8. Volume of the contaminant was 20 mL initial concentration of about 250 mg L<sup>-1</sup>.

Sorbent	Moisture (%)	m (mg)	V (mL)	t (min)	pH <sub>0</sub>	pH <sub>fin.</sub>	C <sub>0</sub> (mg L <sup>-1</sup> )	C <sub>e</sub> As <sup>V</sup> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	As Ads (%)	q <sub>e</sub> (mg m <sup>-2</sup> )
Aka	7.24%	50.0	20	10	3.14	3.15	269.8	126.6	61.7	53.1%	0.306
		50.2	20	30	3.14	3.26	269.8	111.5	68.0	58.7%	0.337
		49.5	20	60	3.14	3.22	269.8	112.6	68.5	58.3%	0.339
		50.1	20	120	3.14	2.78	269.8	100.9	72.7	62.6%	0.360
		50.6	20	240	3.14	2.90	269.8	96.1	74.0	64.4%	0.367
		50.3	20	960	3.14	2.81	255.6	74.7	77.5	70.8%	0.384
		50.2	20	10	7.97	6.79	263.6	173.7	38.6	34.1%	0.191
		50.7	20	30	7.97	6.72	263.6	164.0	42.3	37.8%	0.210
		50.3	20	60	7.97	6.81	263.6	158.7	45.0	39.8%	0.223
		50.7	20	120	7.97	6.60	263.6	166.6	41.2	36.8%	0.204
		49.6	20	240	7.97	6.50	263.6	148.5	50.0	43.7%	0.248
		49.9	20	960	8.17	6.91	242.1	130.3	48.3	46.2%	0.239

pH<sub>0</sub> is the pH of the solution before contact with the sorbent. pH<sub>fin.</sub> is the pH of the solution after adsorption test and separation of the sorbent from the liquid. C<sub>0</sub> is the initial arsenic concentration. C<sub>e</sub> is the final arsenic concentration. q<sub>e</sub> is the adsorbed amount of arsenic at a certain time, calculated with Eq.8. Relative errors (E<sub>r</sub>): E<sub>r</sub>(Moisture) = 2%; E<sub>r</sub>(m) = 1%; E<sub>r</sub>(V) = 1%; E<sub>r</sub>(pH) = 2%; E<sub>r</sub>(C) = 2%; E<sub>r</sub>(q<sub>e</sub>) = 7%.



**Figure S20.** Sorption kinetics of As<sup>V</sup> on Aka at pH 3 and 8 fitted by linearized pseudo 1<sup>st</sup> order fitting.

**Table S8.** Linear pseudo 2<sup>nd</sup> order and intraparticle diffusion models fitting parameters for adsorption of As<sup>V</sup> onto Aka at pH<sub>0</sub> 3 and 8.

Sample	pH <sub>0</sub>	q <sub>e</sub> <sup>exp</sup> (mg g <sup>-1</sup> )	q <sub>e</sub> <sup>''calc</sup> (mg g <sup>-1</sup> )	K'' (g mg <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>	k <sub>i</sub> (g mg <sup>-1</sup> min <sup>-0.5</sup> )	x <sub>i</sub> (mg g <sup>-1</sup> )	R <sup>2</sup>
Aka	3	78(5)	78.0(4)	1.8(5)·10 <sup>-3</sup>	0.99	1.5(7); 0.24(1)	58(4); 70.2(3)	0.81; 0.99
	8	48(3)	48.7(6)	4(3)·10 <sup>-3</sup>	0.99	1.4(1); 0.2(4)	34.3(8); 42(8)	0.99; 0.28

## 9. Adsorption tests: effect of ionic strength

**Table S9.** Batch experiments results of the sorbents at different ionic strength with As<sup>V</sup> at pH 3 and 8. Volume of the contaminant was 20 mL initial concentration of about 250 mg L<sup>-1</sup>. pH<sub>0</sub> is the pH of the solution before contact with the sorbent.

Sorbent	Moisture (%)	m (mg)	V (mL)	NaCl (M)	pH <sub>0</sub>	pH <sub>Int</sub>	pH <sub>Fin</sub>	C <sub>0</sub> As <sup>V</sup> (mg L <sup>-1</sup> )	C <sub>e</sub> As <sup>V</sup> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	As Ads (%)	q <sub>e</sub> (mg m <sup>-2</sup> )
Aka	7.24%	50.3	20	0	3.14	2.83	2.81	255.6	74.7	77.5	70.8%	0.384
		50.7	20	0.01	3.01	2.8	3.06	262.9	89.0	74.0	66.2%	0.366
		50.3	20	0.1	3.12	2.89	2.95	256.7	86.0	73.2	66.5%	0.362
		50.5	20	1	3.16	2.98	2.86	284.6	120.1	70.3	57.8%	0.348
		49.9	20	0	8.17	7.32	6.91	242.1	130.3	48.3	46.2%	0.239
		50.7	20	0.01	8.12	6.88	6.57	260.4	138.6	51.8	46.8%	0.257
		49.7	20	0.1	7.98	6.98	7.02	252.7	126.3	54.8	50.0%	0.272
		50.7	20	1	8.08	7.09	6.64	299.7	153.3	62.3	48.9%	0.308

pH<sub>fin</sub> is the pH of the solution after adsorption test and separation of the sorbent from the liquid. C<sub>0</sub> is the initial arsenic concentration. C<sub>e</sub> is the final arsenic concentration. q<sub>e</sub> is the adsorbed amount of arsenic at a certain time, calculated with Eq.1. Relative errors (E<sub>r</sub>): E<sub>r</sub>(Moisture) = 2%; E<sub>r</sub>(m) = 1%; E<sub>r</sub>(V) = 1%; E<sub>r</sub>(pH) = 2%; E<sub>r</sub>(C) = 2%; E<sub>r</sub>(q<sub>e</sub>) = 7%.

## 10. Adsorption tests: effect of competitors

**Table S10.** Batch experiments results of the sorbents at different sulfate competitor concentration with As<sup>V</sup> at pH 3 and 8. Volume of the contaminant was 20 mL initial concentration of about 250 mg L<sup>-1</sup>.

Sorbent	Moisture (%)	M (mg)	V (mL)	SO <sub>4</sub> <sup>2-</sup> (M)	pH <sub>0</sub>	pH <sub>Int</sub>	pH <sub>Fin</sub>	C <sub>0</sub> (mg L <sup>-1</sup> )	C <sub>e</sub> As <sup>V</sup> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	As Ads (%)	q <sub>e</sub> (mg m <sup>-2</sup> )
Aka	7.24%	50.3	20	0.00	3.14	2.83	2.81	255.6	74.7	77.5	70.8%	0.384
		49.6	20	0.003	3.11	3.2	2.92	259.2	105.2	66.9	59.4%	0.331
		50.6	20	0.033	3.04	3.12	2.62	274.9	125.7	63.6	54.3%	0.315
		50.7	20	0.334	3.15	3.18	2.76	252.8	137.6	49.0	45.6%	0.243
		49.9	20	0.00	8.17	7.32	6.91	242.1	130.3	48.3	46.2%	0.239
		50.8	20	0.003	8.07	7.09	6.49	260.9	131.1	55.1	49.8%	0.273
		49.6	20	0.033	7.94	7.1	6.55	267.8	131.1	59.4	51.1%	0.294
		50.2	20	0.334	7.97	7.38	6.51	273.8	142.8	56.2	47.8%	0.278

pH<sub>0</sub> is the pH of the solution before contact with the sorbent. pH<sub>fin</sub> is the pH of the solution after adsorption test and separation of the sorbent from the liquid. C<sub>0</sub> is the initial arsenic concentration. C<sub>e</sub> is the final arsenic concentration. q<sub>e</sub> is the adsorbed amount of arsenic at a certain time, calculated with Eq.1. Relative errors (E<sub>r</sub>): E<sub>r</sub>(Moisture) = 2%; E<sub>r</sub>(m) = 1%; E<sub>r</sub>(V) = 1%; E<sub>r</sub>(pH) = 2%; E<sub>r</sub>(C) = 2%; E<sub>r</sub>(q<sub>e</sub>) = 7%.

**Table S11.** Batch experiments results of the sorbents at different phosphate concentration with As<sup>V</sup> at pH 3 and 8. Volume of the contaminant was 20 mL initial concentration of about 250 mg L<sup>-1</sup>.

Sorbent	Moisture (%)	m (mg)	V (mL)	PO <sub>4</sub> <sup>3-</sup> (M)	pH <sub>0</sub>	pH <sub>Int</sub>	pH <sub>Fin</sub>	C <sub>0</sub> (mg L <sup>-1</sup> )	C <sub>e</sub> As <sup>V</sup> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	As Ads (%)	q <sub>e</sub> (mg m <sup>-2</sup> )
Aka	7.24%	50.3	20	0.00	3.14	2.83	2.81	255.6	74.7	77.5	70.8%	0.384
		49.3	20	0.003	3.16	2.83	2.99	264.2	125.4	60.7	52.5%	0.301
		50.4	20	0.033	3.16	3.01	3.36	251.8	175.0	32.9	30.5%	0.163
		50.1	20	0.334	3.15	3.27	3.43	166.6	146.1	8.8	12.3%	0.044
		49.9	20	0.00	8.17	7.32	6.91	242.1	130.3	48.3	46.2%	0.239
		49.6	20	0.003	7.96	7.27	7.15	267.6	169.8	42.5	36.5%	0.210
		50.5	20	0.033	8.09	7.91	7.98	262.4	207.6	23.4	20.9%	0.116
		50.1	20	0.334	8.06	8.11	8.18	201.1	203.3	0.0	0.0%	0.000

pH<sub>0</sub> is the pH of the solution before contact with the sorbent. pH<sub>fin</sub> is the pH of the solution after adsorption test and separation of the sorbent from the liquid. C<sub>0</sub> is the initial arsenic concentration. C<sub>e</sub> is the final arsenic concentration. q<sub>e</sub> is the adsorbed amount of arsenic at a certain time, calculated with Eq.1. Relative errors (E<sub>r</sub>): E<sub>r</sub>(Moisture) = 2%; E<sub>r</sub>(m) = 1%; E<sub>r</sub>(V) = 1%; E<sub>r</sub>(pH) = 2%; E<sub>r</sub>(C) = 2%; E<sub>r</sub>(q<sub>e</sub>) = 7%.