

Arsenate Removal from the Groundwater Employing Maghemite Nanoparticles

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Text Section

Text S1. Operational details of XRD, Scanning Electron Microscopy, and High-Resolution Transmission Electron Microscopy

Before the characterization, a fine-powdered XRD sample was prepared using an agate pestle and mortar. The sample was compacted in the aluminium rack (hollowed) and measured at 40 kV and 40 mA, for an angular range of 10° to 90° (2θ) and with a scanning speed of 0.01 deg min⁻¹. Furthermore, the XRD data were smoothed with the subtraction of Kα₂ stripping followed by the background corrections. Then, the diffraction patterns were analysed for peak(s) identifications using several JCP-DS files available in the literature.

FE-SEM measurements for 3D imaging were taken with a gold sputtering of the powdered sample under vacuum conditions, primarily to increase the conductivity of the sample. Using a voltage of 15 kV, the images were recorded by an In-Lens detector with magnification and resolution values of 100 K and 7.9 mm, respectively.

HR-TEM imaging was performed by depositing the sample on a standard carbon-coated copper TEM grid (Mesh size: 200). Firstly, the sample's available amount (mg) was allowed to sonicate in water for 5 minutes at room temperature. Then, the grid preparation was performed by dipping the grid into a prepared colloidal solution of nanoparticles and drying at room temperature using forceps for further analysis. The high-resolution 3D images were recorded by applying an accelerating voltage of 200 keV and a beam current of 1 nA.

Text S2. Zeta-potential measurements and analyses of elements using ICP-MS and MP-AES

The electrophoretic measurements were performed by dispersing the nanoparticles in the water through sonication at room temperature. Several colloidal solutions were prepared in the pH range of 2 to 10. The pH was adjusted using different molar per-chloric acid and liquid ammonia solutions. Then, the interaction potential of these solutions was measured using a folded type capillary cell (disposable) at a measurement position of 2 mm along with an average run of 20 for each sample.

The acid-digested samples were allowed to be filtered through a Whatman™ 42 cellulose filter before analysing heavy metals using ICP-MS equipped with quadrupole mass spectrometry Q-MS technique, which allows the instrument to analyse the samples with high accuracy. The detection limit for all heavy metals is in the µg L⁻¹ range.

To prepare the samples for arsenic determination using (ICP-MS), the samples were treated with potassium iodide (KI, 1.5 g/100 ml) and hydrochloric acid (HCl, 1 ml/100 ml) at least one hour prior to the analysis. For calibration, the arsenate stock standard solution was diluted with a solution containing KI and HCl with a percentage ratio of 15:10 to prepare the desired standards. The reaction between potassium iodide and hydrochloric acid generates iodine gas, reducing any As^v to Asⁱⁱⁱ. The reaction is mentioned below:

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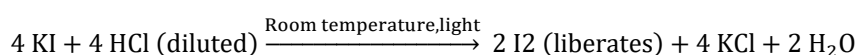
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The vapor generation apparatus aspirated the sample through a standard nebulizer to microwave magnetically excited nitrogen plasma at a flow uptake of 1.4 ml min⁻¹. The emission lines were recorded at two identical wavelengths of 193.695 nm and 234.984 nm.

Text S3. Spectrophotometric measurements for phosphates and silicates

The samples were filtered through a 0.45 µm-pore-diameter membrane filter to determine dissolved reactive phosphorous, which primarily measured the orthophosphates. The stannous chloride method was performed, and the developed colour was measured in a path length of 1 cm at a wavelength of 690 nm. The minimum detection limit is 0.01 PO₄³⁻-P mg L⁻¹.

The typical aqueous phases of silica are H₄SiO₄ and H₃SiO₄⁻. The spectrophotometric measurements were performed at a wavelength of 410 nm for a light path length of 1 cm using the molybdo-silicate method. The minimum detection limit is 0.04 SiO₂ mg L⁻¹.

Tables

Table S1. Elements contributed to the formulation of artificial water.

Element	Location I				Location II			
	Actual groundwater conc. (mg L ⁻¹)	Calculated values from the matrix	Measured synthetic water conc. (mg L ⁻¹)	Diff. (%)	Actual groundwater conc. (mg L ⁻¹)	Calculated values from the matrix	Artificial water conc. (mg L ⁻¹)	Diff. (%)
TDS (gravimetric)	435.9	-	411.5	5.6	1590.6	-	1405.7	11.6
TDS (calculated by ions)	337.4	261.4	310.6	7.9	1446	1171.1	1321.5	8.6
Chloride	132	67.1	112.0	15.2	435	222.7	346	20.5
Sodium	33	23.1	28.0	15.2	169	111.2	141	16.6
Bicarbonate	27	27.0	28.0	-3.7	115	114.8	113	1.7
Potassium	15	13.8	13.3	11.3	95	91.6	93	2.1
Fluoride	1.5	1.5	1.5	1.3	3	2.94	3.16	-5.3
Nitrate	20	20.0	21.2	-6.0	140	139.8	139	0.7
Calcium	29	28.9	26.4	9.0	185	185.3	181.5	1.9
Zinc	2	1.9	1.9	5.0	4	4.43	4.1	-2.5
Magnesium	27	27.0	24.5	9.3	33	33.2	32.4	1.8
Sulfate	30	30.1	32.4	-8.0	220	219.4	221.1	-0.5
Silica	18	18.1	18.6	-3.3	42	41.4	42.3	-0.7
Manganese	2	1.9	1.9	7.5	3	3.4	3.2	-6.7
Phosphates	0.91	1.1	1.0	-6.6	2	1.06	1.75	12.5
Arsenate*	0.055	-	0.057	-3.6	0.2	-	0.201	-0.5

Table S2. Calculation of crystallite size using Scherrer's formula for MNPs.

Peak no.	2θ/degree	Peak maxima (2θ)	Peak max. (y ₂)/count	$y_1 + \frac{(y_2 - y_1)}{2}$	2θ high/degree	2θ Low/degree	FWHM/radian	Peak max. (y ₂)/count	Crystallite size (nm)
1.	220	30.27	425.31	392.40	29.15	29.73	0.010123	425.31	14.20
2.	311	35.41	557.01	459.43	34.62	35.11	0.008552	557.01	17.03
3.	400	43.02	396.80	375.46	42.40	42.95	0.009599	396.80	15.54
4.	511	57.24	414.01	384.06	56.72	57.43	0.012392	414.01	12.75
5.	440	62.75	428.87	389.41	62.14	62.83	0.012043	428.87	13.49

Table S3. Identification of peaks observed during FTIR spectroscopic analysis.

Functional group/Surface moieties	Peak(s) (cm ⁻¹)
Fe-O	532 cm ⁻¹
	635 cm ⁻¹
Symm. SO ₄ ²⁻	1023 cm ⁻¹

C=S, CC alicyclic, aliphatic chain vibrations, and SO ₄ ²⁻ (asym.)	1105 cm ⁻¹
NH stretch	1628 cm ⁻¹
OH stretch	3212 and 3424 cm ⁻¹

Table S4. The final amount of constituents taken for synthetic water formulation.

Compounds	Molecular weight (g mol ⁻¹)	% contribution of each salt		Amount required (mg) (for per litre of solution)	
		Location I	Location II	Location I	Location II
ZnSO ₄ . 7H ₂ O	287.54	1.64	1.06	8.4094	19.4786
NaCl (anhy.)	58.45	0.70	0.94	3.5765	17.2316
CaCl ₂ . 2H ₂ O	147	20.74	37.13	106.1647	679.4825
MgCl ₂ . 6H ₂ O	203.3	44.05	15.15	225.5227	277.3068
NaHCO ₃ . (anhy.)	84.01	7.27	8.64	37.2290	158.0520
Na ₂ SO ₄ (anhy.)	142.04	6.09	16.03	31.1764	293.4096
NaF (anhy.)	41.99	0.65	0.35	3.3450	6.4957
MnSO ₄ . 6H ₂ O	169.06	1.16	0.57	5.9271	10.3408
K ₂ SO ₄ (anhy.)	174.26	1.02	0.85	5.2023	15.5235
Na ₃ PO ₄ . 12H ₂ O	380.12	0.86	0.23	4.4103	4.2673
KNO ₃ (anhy.)	101.1	6.38	12.46	32.6809	227.9586
Na ₂ SiO ₃ . 9H ₂ O	284.2	10.48	6.69	53.6529	122.4339

Table S5. Optimal values of architecture weights and biases contribute to the adsorption process for the ANN model.

The input I to hidden layer I		IW ^(1,1)							
Weight to layer	LW ^(2,1)	[0.9991	6.3943	-0.0779	0.37176	-1.4427	-0.1123	3.3727;	
		-0.2944	0.58393	3.6067	3.0947	-2.7787	-2.0128	2.1517;	
		-2.3273	0.2887	4.075	3.2756	-1.2876	0.61371	0.25236;	
		-0.0161	4.111	1.1027	1.2377	-0.2901	1.6878	1.2626;	
		2.185	3.9435	1.0082	0.43236	-0.8532	-2.811	1.9592;	
		-2.2928	-0.9783	-3.2384	-0.2984	-0.8305	-2.0942	0.30994;	
		-1.0901	0.12743	1.9988	0.19748	3.1668	-1.0989	-1.0024;	
		0.66173	-1.1256	2.2898	-1.0681	-1.5092	1.5585	-1.2733]	
Bias to layer I	b ⁽¹⁾	[-2.2556	-0.9860	-0.6726	0.19133	2.5928	-0.2696	-0.3228	0.4914]
Bias to layer II		[-0.036;							
		-4.5493;							
		1.2352;							
		0.15689;							
		0.95491;							
		-0.5649;							
		-2.8714;							
		4.3622]							
		[-0.965]							

Figures

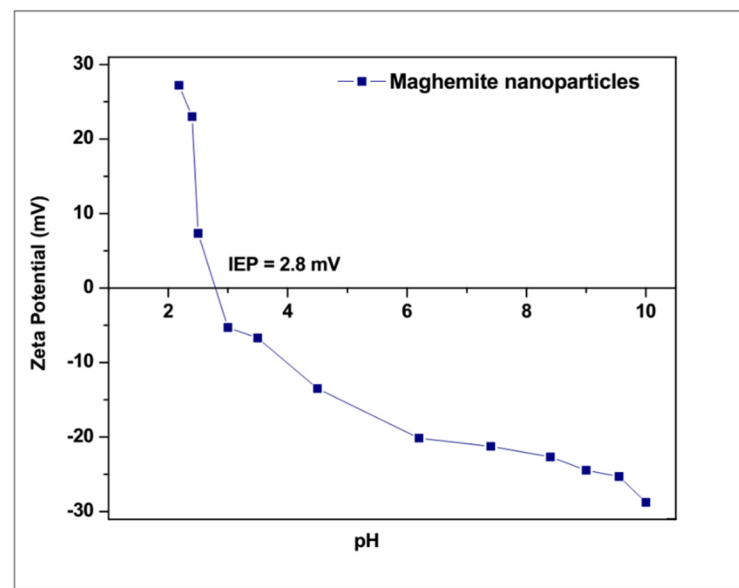


Figure S1. The zeta potential measurement of maghemite nanoparticles.