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Supporting Information

Mg(OH)₂-MgO@Reduced Graphene Oxide Nanocomposites: The Roles of Composition and Nanostructure on Arsenite Sorption

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Figure S1. Nitrogen adsorption-desorption isotherms of nanocomposites (a) before and (b) after hydration for 60 min in aqueous solution.



Figure S2. HR-TEM images of nanocomposites (a)S-200, close view of lattice fringe corresponding to the (200) plane from MgO in (b) S-400 and (c) S-700.

A high-resolution TEM image (Figure S2c) shows well-resolved lattice fringe with an interplanar distance of 0.21 nm, corresponding to the (200) plane of MgO and a cube size of 21 nm, consistent with the crystallite domain size determined by the Scherrer equation using the intensive (200) diffraction peak.



Figure S3. (a, b) TEM images of S-as-prepared.



Figure S4. (a)TEM images for $Mg(OH)_2$ bare particle as prepared; (b) N_2 sorption isotherm for S-as prepared and bare $Mg(OH)_2$.



Figure S5. (a) Close view of lattice fringe corresponding to the (101) plane from Mg(OH)₂; and (b) the (200) plane from MgO in S-250.



Figure S6. FTIR spectra of composite samples (a) before and (b) after hydration in aqueous medium for 1 h.

The FTIR spectra of GO and composite materials annealed at 200, 250, 400 and 700 °C are presented in figure S6a. A broadband in the range of 3500-3300cm⁻¹ for all samples is due to the presence of -OH and H-O-H stretching and bending vibration of the adsorbed water molecules in GO and samples. It is observed that the peaks ranging from 750 to 1750 cm⁻¹ are from GO itself that contains many oxygen functional moieties.¹ The absorption band at 1443 and 1581 cm⁻¹ are attributed to the stretching vibration of C=C in rGO and other peaks at 1217 cm⁻¹ and 1054 cm⁻¹ correspond to C-O and epoxy group stretching vibration, respectively.² However, in the composite samples (Figure S6a S-200, S-250, S-400, S-700) these peaks of oxygen containing moieties decreased and even disappeared confirming the reduction of GO to rGO due to the heat treatment at elevated temperatures. After hydration, as seen in Figure S6b, the band at 3700 cm⁻¹ associated with v(OH) stretching vibration in Mg(OH)₂ was observed at different intensity, indicating the conversion into Mg(OH)₂ at certain degree.



Figure S7. (a) Wide scan spectra and (b) High-resolution spectra of Mg 2p of S-250 (i) before and (ii) after hydration in water for 60 min (iii) after As(III) sorption.

In Figure S7a, wide scan spectra and high-resolution spectra of Mg 2p before and after hydration as well as after As(III) sorption of S-250 are presented. In figure S7b, the Mg 2p spectra before hydration exhibited two peaks at binding energies of 49.7 eV and 50.4 eV which correspond to the presence of Mg(OH)₂ and MgO, respectively in S-250.^{3,4} As shown in Figure S7b, the Mg 2p spectra of S-250 after hydration can only be decomposable into one single spectral component of Mg-OH at 49.7 eV indicating the fully transformation into Mg(OH)₂.



Figure S8. Linearized Freundlich isotherm onto S-250 sample.



Figure S9. Weight change of GO, pure Mg(OH)₂ and S-250 composites between 25 °C to 700 °C under an air environment.

Figure S9 shows the weight change of GO, pure Mg(OH)₂ and S-250 composites in the air when the temperature increases from 25 to 700 °C. GO shows the weight change from 60.01 mg at 25 °C to 0.76 mg at 700 °C. This significant weight loss indicates ~ 99% of the GO has been oxidized into CO₂. At the same temperature, the weight change of pure Mg(OH)₂ is from 6.92 mg to 4.83 mg. Thus, the weight retention of pure Mg(OH)₂ is 69.88%, in accordance with the weight retention in the chemical reaction of Mg(OH)₂ \rightarrow MgO + H₂O at high temperature (Mw_{MgO}/Mw_{Mg(OH)2} = 40.30/58.32 = 69.10%). It indicates that Mg(OH)₂ can be completely converted to MgO at 700 °C. S-250 composite shows a weight change of 70.55 to 55.50 mg, giving a MgO weight retention of 78.67%. Therefore, the maximum sorption capacity based on the content of active material MgO is determined to be $\frac{681.3 mg g^{-1}}{78.67\%} = 866.0 mg g^{-1}$



Figure S10. Low magnification SEM image of S-250.



Figure S11. Point of Zero Charge of S-250.



Figure S12. High resolution XPS scan of Mg 2p and As 3d of Mg(OH)₂-MgO bare nanoparticles annealed at 250 °C after As(III) sorption.



Figure S13. Effect of competing anions present in the water.



Figure S14. pH dependent sorption capacity and Mg^{2+} leaching amount of S-250, with adsorbent dose of 0.4 g L⁻¹ and initial concentration As(III) of 400 mg L⁻¹

In an effort to investigate the sorption behavior of nanocomposites, S-250 as the most efficient in adsorbing As(III), was used to study the effect of pH solution on As(III) removal and stability of adsorbent. Figure S14 presents the effect of pH solution on the sorption of As(III) and shows that the sorption of As(III) on S-250 is pH dependent. It is observed that a linear increase of As(III) sorption with an increase pH from 5-9 with slight decrease from pH 9-10. The difference in adsorption capacities as a function of Solution pH can be explained by the change of the arsenic speciation and the surface charge of S-250. According to the E_h -pH diagram⁵, arsenic exists in the -3, 0, +3 and +5 oxidation states depending on the pH and redox potential. For As(III) at pH 2-9, the uncharged species H₃AsO₃ is dominantly exist, from pH 9-12, it exists as H₂AsO₃²⁻. In addition to that, the point of zero charge for this composite material was found to be approximately 11.8 (Figure S11). At pH< pH_{PZC}, the surface of S-250 is positively charged. Hence, the possible reason for the increase of sorption in pH range of 5-9 could be due to (1) the electrostatic interaction between positively charged of S-250 and the increasing number of anionic As(III) species (2) chemisorption may act as dominant sorption type under pH 5-9. The decrease at pH 10-12 is attributed to the surface charge of S-250.

becoming less positive, which may weaken the electrostatic sorption between As(III) and adsorbent. In addition, the increase of sorption capacity at higher pH may also be attributed to the good stability of this adsorbent itself. We found that the concentration of leached Mg^{2+} is also pH dependent (Figure S14). After 24 h sorption, at the pH value of 5, 6, 7, 8, 9, 10, 11 and 12 the leached Mg^{2+} was 8.9%, 8.8%, 8.6%, 6.6%, 1.5%, 0.01%, 0.2% and 0.1% respectively.



Figure S15. Digital image of 10 g of S-250 obtained from large-scale synthesis.

Composite Material	Surface Area (m ⁻² g ⁻¹)	As concentration range (mg g ⁻¹)	As(III) max. removal capacity (mg g ⁻¹)	Ref.
S-250	73	50-700	681.3	This work
Fe ₃ O ₄ /rGO	148	3-7	13	ACS Nano, 2010, 4 (7), 3979–3986
Fe ₂ O ₃ @C	877	0.2-30	29.4	Adv. Mater. 2012, 24, 485–491
Magnetic Graphene Nanoplatelet Composites	n/a	3-6	11.9	J. Solid State Sci. Technol, 2012, 1, M1
Graphene Aerogel/α-FeOOH	n/a	1-16	13.42	ACS Appl. Mater. Interfaces 2015, 7, 9758–9766
Fe ₃ O ₄ -RGO-MnO ₂	115	0.01-10	14.04	Chemical Engineering Journal 187 (2012) 45–52
3D-G-CNT-Fe	45-63	n/a	7	Environ. Sci. Technol. 2013, 47, 10510–10517
Fe ₃ O ₄ @2D-CF	35	10-100	57.47	ACS Appl. Mater. Interfaces 2016, 8, 23876–23885
Zirconia in Carbon Nanowires	n/a	20-300	25.61	ACS Appl. Mater. Interfaces 2016, 8, 18912–18921
Hollow Iron Cerium Alkoxide	217.5	1-100	266	ACS Appl. Mater. Interfaces, 2014, 6 (16), 4016–14025.
Mg-Doped Iron Oxide	438	n/a	127.4	Water Res. 2013, 47(11), 3624-3634

Table S1. Comparison of As(III) sorption capacity to other reported works.

Sample	Intensity of (110) Mg(OH) ₂ [<i>I</i> Mg(OH) ₂]	Intensity of (200) MgO [/ MgO]	γMgO	As(III) Sorption capacity (mg g ⁻¹)
GO	-	-	-	0
S-200	854	12	≈ 0	110
S-225	105	85	0.45	585
S-250	172	175	0.5	655
S-300	338	879	0.73	550
S-350	232	1098	0.83	500
S-400	298	1777	0.86	410
S-700	28	2904	≈ 1	264
S-250 bare	376	313	≈ 0.5	174

Table S2. Summary of the intensity of selected diffraction peaks, γ MgO and As(III) sorption capacity of nanocomposites

Calculation method: γ MgO is calculated based on comparing the intensity of prominent peak of (110) from Mg(OH)₂ and the intensity of prominent peak of (200) from MgO.⁶

$$\frac{[I Mg O]}{([I Mg (OH)2] + [I Mg O])}$$

For S-250, γ MgO of 0.5 is obtained from: $\frac{175}{(175 + 172)} \approx 0.5$

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