Supporting Information:

Surface Defect of Mg(OH)₂ Enhances the Adsorption of Heavy Metal Ions As(V) and Cr(VI) at Low Concentration: A Combined Theoretical and Experimental Study

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Computational details.

The optimized primitive unit cell is characterized by the parameters a = b = 3.16 Å, c = 4.82 Å and $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$, agreeing well with the experimental values.¹ The Mg(OH)₂ (001) surface is cleaved from the optimized bulk structure, and a 3 × 3 × 2 supercell is built. A vacuum slab of 18 Å is placed above the Mg(OH)₂ substrate. The binding energy (E_b) of oxyanions onto Mg(OH)₂ (001) surface is calculated according to the following equation: $E_b = E_{sc} - E'_{sc}^2$ where Esc is the energy of the optimized surface complex, and E'_{sc} corresponds to the energy of the optimized system for which the oxyanion and the Mg(OH)₂ (001) surface are kept apart at least 9 Å. In addition, the Bader charge analysis is carried out to investigate the electrostatic interaction of the adsorption process.^{3,4}

The reasonability of the defective $Mg(OH)_2$ model is evaluated by the AIMD simulations are at 300 K. The fluctuation of c-axis lengths during the AIMD simulations are monitored and plotted in Figure S1. It is clear that the average of caxis length for the defective $Mg(OH)_2$ is around 4.63 Å, which is similar to the corresponding value (4.68 Å) of the defect-poor $Mg(OH)_2$. The AIMD simulations verify that $Mg(OH)_2$ nanostructure with surface OH defect can be well maintained in aqueous solution and should reasonably reflect the adsorption behavior.

The charge-charge and chemical binding interaction.

As illustrated by the deformation charge density in Figure S2, the oxygen atoms of As(V) are polarized with negative charge, while the surface defect is positively charged, indicating the charged nature plays an important role in the adsorption process. Both As(V) and Cr(VI) are found to have charge transfer to the defective Mg(OH)₂. The As(V) is negatively -1.73 charged after the adsorption, smaller than the value of -2 |e| for the isolated As(V), indicating a charge transfer of -0.27 |e| from the As(V) to the defective Mg(OH)₂. Similar phenomena of charge transfer can be found for the Cr(VI) inner-sphere complex, indicating the charge distribution of heavy metal oxyanion in the surface defect is somewhat delocalized, and the strong chemical bond is formed between them.

The inserted oxygen atom of heavy metal oxyanion As(V) adsorbed in the surface defect has stronger orbital overlap with the surface Mg atom. The partial local density of states analysis is also carried out for the As(V) tridentate complex at the defect-poor surface (Figure S3). There is hardly any overlap between the arsenic oxygen atom O(p) and the Mg(s, p) of surface Mg atom, showing no strong chemical interaction formed between them, and the adsorption should be dominated by the hydrogen bonding interaction.

Preparation of Defect-rich and Defect-poor Mg(OH)₂.

Defective Mg(OH)₂ is prepared by fast hydration of MgO.^{5, 6} For the fast hydration of

porous MgO, the MgO powder is first heated at 600 °C for 1.5 h, and Mg(OH)₂ is then obtained by quenching the heated MgO powder into deionized water. To acquire defect-poor Mg(OH)₂, the aforementioned defective Mg(OH)₂ adsorbents are further treated by annealing to 300 °C at a temperature scan rate of 3 °C/min.

Table S1. The adsorption capacity of heavy metal oxyanions and BET specific surface areas for the defect-rich and defect-poor $Mg(OH)_2$ adsorbents. 10 mg $Mg(OH)_2$ adsorbent is added to 50 mL arsenate solution, and 100 mg $Mg(OH)_2$ adsorbent is added to 50 mL chromate solution.^a

Samples	$C_0 (\mathrm{mg/L})$	$C_{\rm e}$ (mg/L)	Qe (mg/g)	SA (m ² /g)	AM (mg/m ²)
As: defect-rich Mg(OH) ₂	0.496	0.006	2.450	4.995	0.490
As: defect-poor Mg(OH) ₂	0.560	0.003	2.785	9.617	0.290
Cr: defect-rich Mg(OH) ₂	0.526	0.155	0.186	4.995	0.037
Cr: defect-poor Mg(OH) ₂	0.526	0.240	0.143	9.617	0.015

^a C_0 represents the initial concentration, C_e represents the equilibrium concentration, Q_e represents the adsorption amount at equilibrium, SA represents the BET specific surface area, and AM represents the adsorption amount per unit surface area.



Figure S1. The c-axis lengths of both defect-free (a) and defective (b) $Mg(OH)_2$ as a function of simulation time during AIMD simulations.



Figure S2. The deformation charge density for As(V) adsorption onto the surface OH defect of the Mg(OH)₂ (001) surface.



Figure S3. The partial density of states (PDOS) for As(V) adsorption on the defect-free $Mg(OH)_2$ surface.



Figure S4. The aggregation states of multiple particles for the defect-rich (a) and annealing-treated (b) nano-Mg(OH)2 characterized by TEM.



Figure S5. The influence of contact time on the adsorption of arsenate (0.5 mg/L As(V) solution) and the results are fitted by a pseudo second order equation.



Figure S6. Adsorption isotherm experiment and the fitting result by Langmuir model for As(V) adsorbed by defect-rich (a) and defect-poor (b) nano-Mg(OH)₂.

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