

# SUPPORTING INFORMATION

## How Does Competition between Anionic Pollutants Affect Adsorption onto Mg-Al Layered Double Hydroxide? Three Competition Schemes

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## I. Materials and Methods

The preparation and structural properties of the non-calcined Mg-Al-LDH-NO<sub>3</sub> used in the present study was detailed previously (ref 16 in the main article). The solid substrate, represented by an empirical formula of Mg<sub>0.67</sub>Al<sub>0.33</sub>(OH)<sub>2</sub>[(CO<sub>3</sub>)<sub>0.027</sub>•(NO<sub>3</sub>)<sub>0.276</sub>•1.32H<sub>2</sub>O], had an anionic exchange capacity (AEC) of 3.2 meq g<sup>-1</sup>. The three Orange-type dyes of high purity (dye content > 99%) were purchased from Sigma-Aldrich and used without further purification. They are further designated as follows: MO = Methyl Orange, OII = Orange II or Acid Orange 7, OG = Orange G or Acid Orange 10. The maximum absorbance in the ultraviolet (UV) spectra was observed at a wavelength of 466 nm, MO; 483 nm, OII; and 480 nm, OG. The co-existing inorganic anions were provided with aqueous solutions of potassium chromate (K<sub>2</sub>CrO<sub>4</sub>, Sigma-Aldrich), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, Merck), and sodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>, Sigma-Aldrich). These salts were employed as received. The 18.2 MΩ cm water used in all experiments was obtained with the aid of a combined Purite Select Analyst (France Eau) and PURELAB<sup>®</sup> Classic (ELGA LabWater, France) water purification system.

### Measurements of the cumulative enthalpy of displacement in single-solute systems by isothermal titration calorimetry (ITC)

The overall enthalpy change upon the displacement process accompanying the retention of dye or inorganic anions from single-solute solutions onto Mg-Al-LDH-NO<sub>3</sub> at 298 K was measured using a differential TAM III microcalorimeter operating in a heat flow mode. A high precision liquid thermostat (oil heat exchanger with Peltier coolers) maintained the temperature constant within ± 0.0001 deg. The experimental setup was equipped with a computer-controlled micro-syringe injection device allowing small aliquots of a stock solution at a given molality to be injected into a 1 mL glass ampoule. More details about the operating procedures and data processing can be found elsewhere (ref 16 in the main article). Prior to measurements, about 1-2 mg of the LDH powder was suspended in 0.8 mL of ultrapure water in the measuring ampoule. The same amount of water was introduced into another 1 mL glass ampoule placed on the reference side. The two ampoules were subsequently

returned to the microcalorimeter and equilibrated thermally during 2 h. The homogeneity of the solid suspension was maintained by means of an agitation system equipped with a Teflon paddle stirrer. The concentration of the stock solution injected into the measuring ampoule was optimized to make the resulting plot of the heat flow,  $W$ , against time,  $\tau$ , easier to be recorded and further processed:  $8.5 \text{ mmol L}^{-1}$ , MO and  $\text{SO}_4^{2-}$ ;  $14 \text{ mmol L}^{-1}$ , OII and  $\text{HPO}_4^{2-}$ ;  $12 \text{ mmol L}^{-1}$ , OG;  $9 \text{ mmol L}^{-1}$ ,  $\text{CrO}_4^{2-}$ ;  $8.5 \text{ mmol L}^{-1}$ . Other experimental parameters (i.e., number of injections, injection volume and speed, agitation speed and equilibration time applied between two successive injections) have been collected in Table S1 in Supporting Information. Integration of the thermal peaks appearing in the thermogram recorded for each series of successive injections resulted in discrete  $\Delta_{\text{inj}}H_i$  enthalpy values related to the mass of solid in the measuring ampoule and expressed in  $\text{J g}^{-1}$ . The thermal effects of injections were corrected for dilution effects. For this purpose, analogous dilution experiments were carried out under exactly the same experimental conditions but without introducing a solid sample into the measuring ampoule. The resulting enthalpy values were summed up to obtain the cumulative enthalpy of displacement,  $\Delta_{\text{dpl}}H_{\text{cum}}$ , per unit mass of the LDH sample. The  $\Delta_{\text{dpl}}H_{\text{cum}}$  values were plotted as a function of the amount of a given species retained by LDH over an adsorption range matching with the quasi-vertical portion on the adsorption isotherm. The repeatability of the calorimetry measurements was assessed by carrying out two simultaneous experiments with the use of two microcalorimeters working under the same conditions; it was within 6%, MO; 17%, OII; 4%, OG; 23%,  $\text{CrO}_4^{2-}$ ; 20%,  $\text{HPO}_4^{2-}$ ; 7%,  $\text{SO}_4^{2-}$ . Nevertheless, the same trends in  $\Delta_{\text{dpl}}H_{\text{cum}}$  with the quantity of adsorption were recorded in the two calorimetric runs.

### **Measurements of the adsorption isotherms in single-solute and bi-solute systems**

The solution depletion method was used to determine the individual adsorption isotherms of the adsorbing organic and inorganic anions. The individual points on the adsorption isotherms were obtained by equilibrating about 2.5 mg of the solid sample with 10 ml of solution at a given concentration in 30 ml Nalgene® reactors. In the single-solute systems, the solute concentrations were varied within the following range:  $0.02 - 5 \text{ mmol L}^{-1}$ ,

MO and OII;  $0.02 - 3 \text{ mmol L}^{-1}$ , OG,  $0.03 - 1.2 \text{ mmol L}^{-1}$ ,  $\text{HPO}_4^{2-}$ ;  $0.03 - 0.7 \text{ mmol L}^{-1}$ ,  $\text{SO}_4^{2-}$  and  $\text{CrO}_4^{2-}$ . Note that the three adsorption isotherms for dyes had been reported previously (ref 16 in the main article). To determine the individual adsorption isotherms of the two anionic species from bi-solute solutions, mixed stock solutions were prepared at three molar ratios between the dye and inorganic anion of (2:1), (1:1), (1:2) and each stock solution was used to obtain appropriate diluted solutions to be poured into Nalgene® tubes. In the equimolar dye-inorganic anion solutions, the dye concentration was as follows:  $4 \text{ mmol L}^{-1}$ , MO;  $1.2 \text{ mmol L}^{-1}$ , OII and OG. For comparison purposes, the dilution schemes were designed to generate the individual adsorption isotherms for the dye species covering ranges of the equilibrium dye concentration similar to those obtained in the single-solute systems. The pH of the solid suspension in single-solute and bi-solute solutions was carefully checked before and after the attainment of the adsorption equilibrium. From the point of view of methodology, no effort was made to re-adjust this parameter to its initial value or minimize contact with atmospheric air during solution preparation. The initial pH of the solid suspension was around 7.5-8, owing to the intrinsic basic character of the Mg-Al-LDH- $\text{NO}_3$  sample. Then, some increase in the pH was observed with the progress of adsorption depending on the system components and the composition of the aqueous phase. The equilibrium pH value also increased along the adsorption isotherm and was greatest in the case of Methyl Orange but always within 1.5 pH unit.

Taking into account the fast kinetics of dye sorption demonstrated previously (ref 16 in the main article), the Nalgene® reactors were shaken overnight in a thermostated cage ( $\pm 0.1 \text{ deg}$ ) at 298 K. Then the solid phase was separated from the supernatant solution by centrifugation at 10 000 rpm for 10 min and the equilibrium concentration of a selected species in the bulk phase was determined either by UV-Vis spectroscopy (Jasco V-670 UV-Vis Spectrophotometer operating in the wavelength range from 350 to 550 nm) or by ion chromatography (Shimadzu HPLC apparatus equipped with a Shim-pack IC-A1 column and a conductivity detector; a flow rate of  $1.5 \text{ mL min}^{-1}$ , an injection volume of  $45 \text{ }\mu\text{L}$ , a column temperature of  $40 \text{ }^\circ\text{C}$ ; with the mobile phase depending on the nature of inorganic anion:  $2 \text{ mmol L}^{-1}$  potassium hydrogen phthalate (pH 4.2),  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ;  $4 \text{ mmol L}^{-1}$  sodium carbonate,  $\text{CrO}_4^{2-}$ ; a mixture of  $1.5 \text{ mmol L}^{-1}$  phthalic acid and  $0.7 \text{ mmol L}^{-1}$

<sup>1</sup> diethylenetriamine,  $\text{HPO}_4^{2-}$ . The amount adsorbed of a selected species was calculated from the following formula:

$$\Delta n = \frac{V_o(C_i - C_{eq})}{m_s}$$

where  $C_i$  and  $C_{eq}$  represent, respectively, the initial and final (after attaining the equilibrium) concentrations of the adsorbed species,  $V_o$  is the initial volume of the aqueous solution, and  $m_s$  is the mass of the adsorbent. The methodology applied to evaluate the repeatability and experimental uncertainties of the adsorption experiments was described previously (ref 16 in the main article).

### **X-ray diffraction (XRD) study of the LDH samples loaded with the adsorbate**

Some solid samples collected after their separation from the supernatant solution in the adsorption experiments were subsequently analyzed by X-ray diffraction so as to monitor changes in the layered structure induced by the incorporation of the adsorbed species. The choice of the samples for such studies was made in a way to represent 2-3 points on the adsorption isotherms localized within characteristic adsorption regions. Prior to XRD experiment, the powdered solid sample was dried at 373 K during 1-2 h. The XRD patterns were collected on a PHILIPS X'Pert MPD  $\theta$ - $\theta$  diffractometer (X'Celerator detector, Cu  $K\alpha$  radiation  $\lambda = 1.5418 \text{ \AA}$ , nickel filter) over the  $2\theta$  range from  $2^\circ$  to  $30^\circ$  at 30 mA, 45 kV, with a scan speed of  $0.003^\circ \text{ min}^{-1}$  and using an incident beam mask of 10 mm.

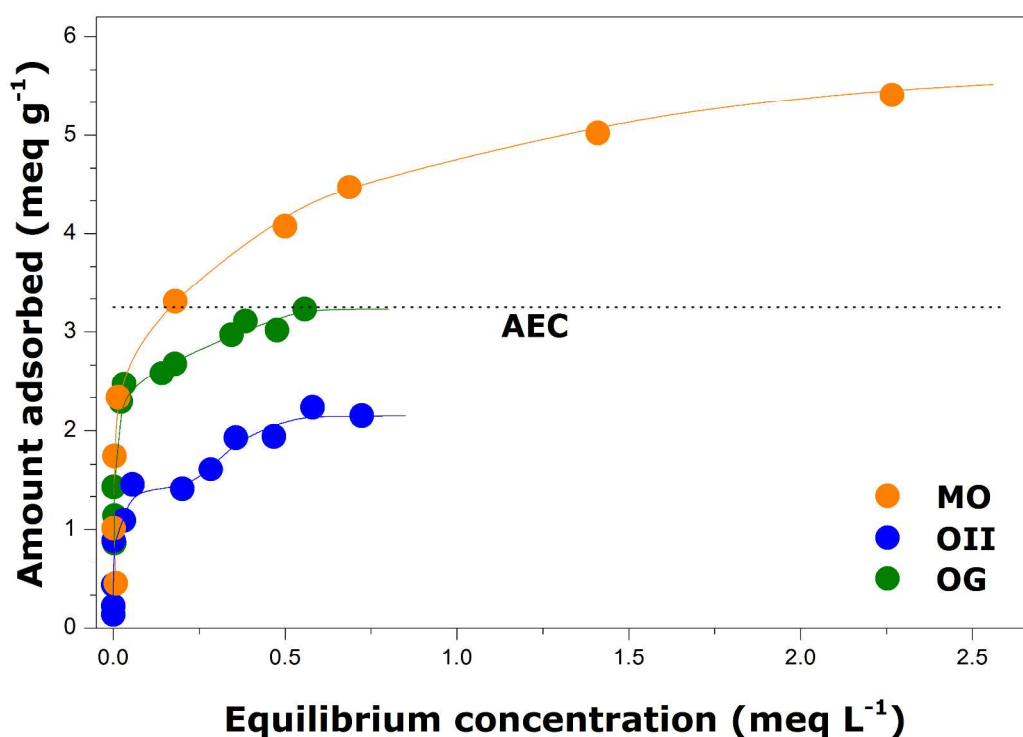
## II. Adsorption isotherms for dye or inorganic anions from single-solute solutions onto Mg-Al-LDH-NO<sub>3</sub>

### Dye anions:

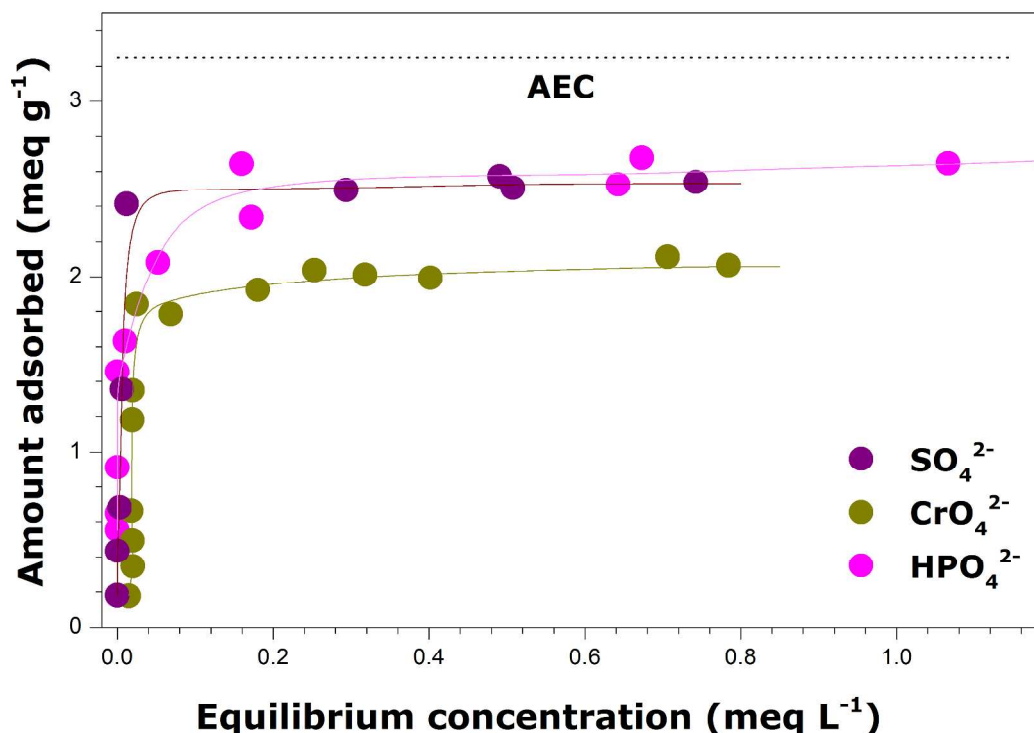
MO = Methyl Orange [C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>

OII = Orange II (Acid orange 7) [C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>SO<sub>4</sub>]<sup>-</sup>

OG = Orange G [C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub>O<sub>7</sub>]<sup>2-</sup>



**Figure S1.** Isotherms of dye adsorption from single-solute solutions onto Mg-Al-LDH-NO<sub>3</sub> at 298 K. The solid lines represent the smoothed isotherms constructed on the basis of the results of repeated adsorption experiments. The vertical dotted line is used to indicate the theoretical anion exchange capacity (AEC) of LDH. Adapted from G. Darmograi *et al.*, *Study of Adsorption and Intercalation of Orange-Type Dyes into Mg-Al Layered Double Hydroxide*, *J. Phys. Chem. C*, 2015, 119 (41), pp 23388–23397

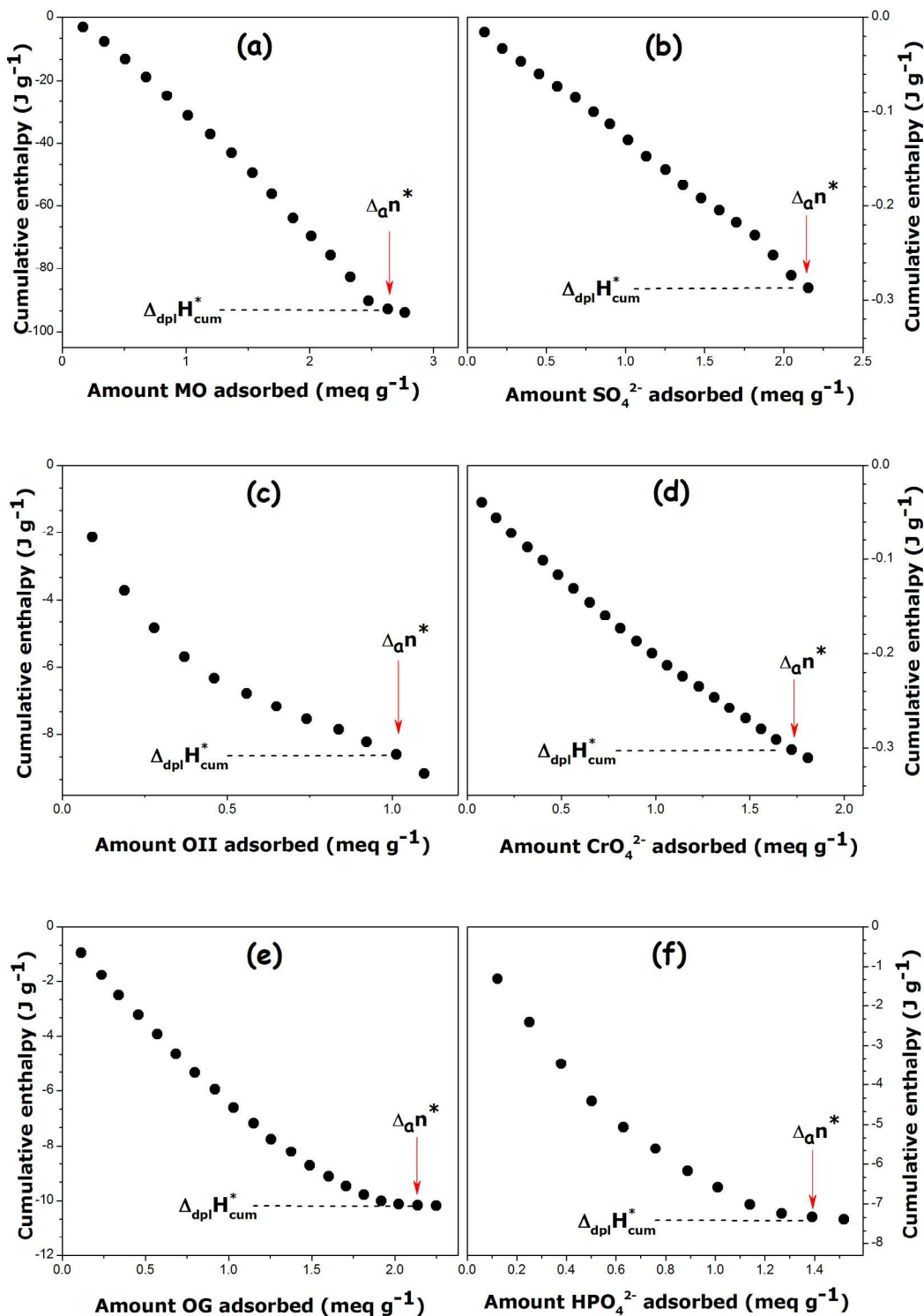


**Figure S2.** Adsorption isotherms for inorganic anions from single-solute solutions onto Mg-Al-LDH-NO<sub>3</sub> at 298 K. The solid lines represent the smoothed isotherms constructed on the basis of the results of repeated adsorption experiments. The vertical dotted line is used to indicate the theoretical anion exchange capacity (AEC) of LDH.

### III. Calorimetry measurements of the enthalpy of displacement accompanying the adsorption of dye or inorganic anions from single-solute solutions onto Mg-Al-LDH-NO<sub>3</sub> at 298 K

**Table S1.** Operating parameters used in the adsorption experiments carried out with the aid of isothermal titration calorimeter TAM III

Adsorbed species	Number of injections	Injection volume (μL)	Injection speed (sec)	Agitation speed (tpm)	Equilibration time between two successive injections (min)
Methyl Orange	33	30	30	120	90
Orange II	25	10	10	90	90
Orange G	25	10	10	120	180
Sulfates	25	10	10	90	90
Chromates	25	10	10	90	90
Hydrogen Phosphates	25	10	10	90	90

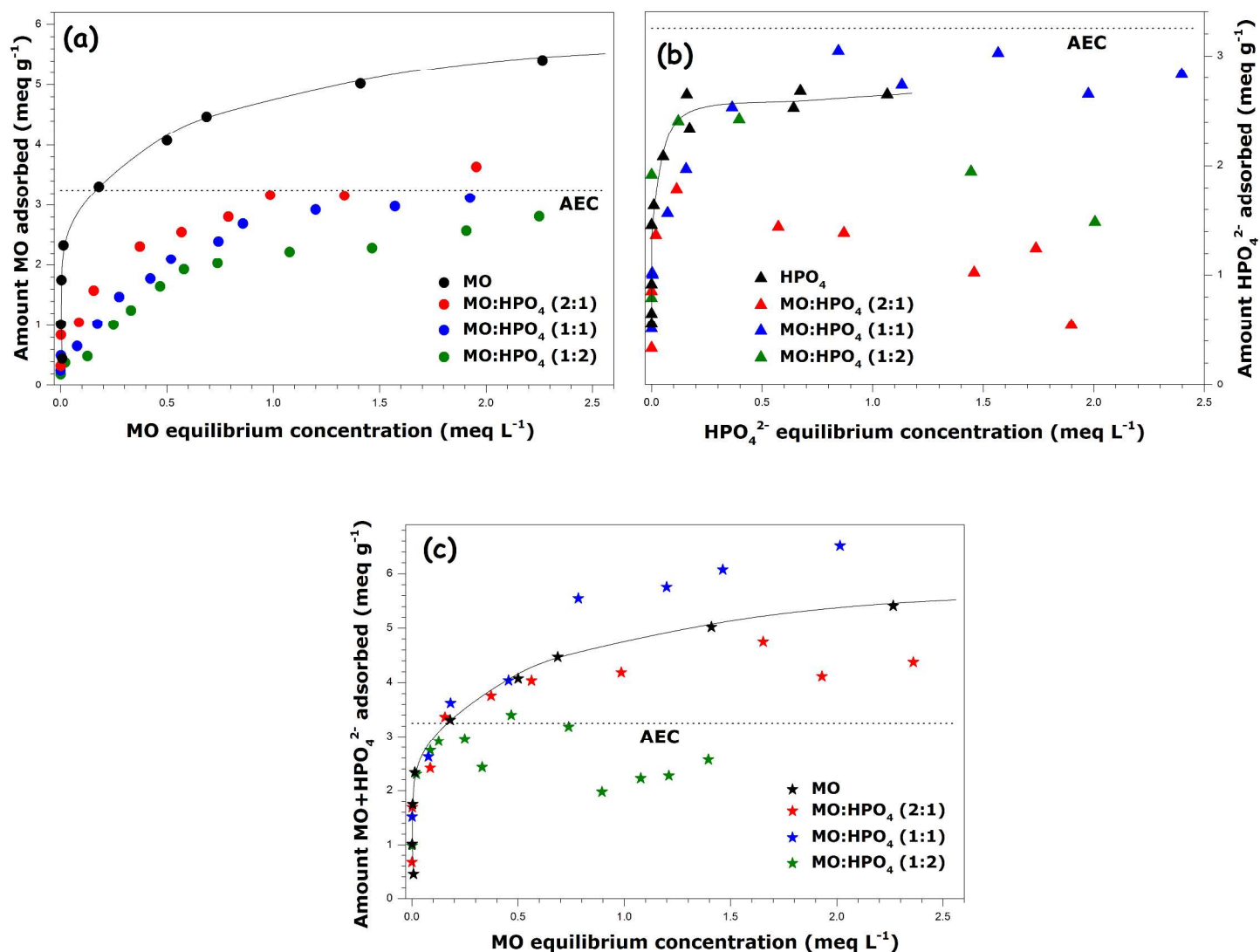


**Figure S3.** Variations of the cumulative enthalpy of displacement accompanying adsorption of dye and inorganic anions from single-solute solutions onto Mg-Al-LDH-NO<sub>3</sub> at 298 K as a function of the amount of a given species retained by the solid sample, as plotted in an adsorption range corresponding to the initial quasi-vertical portion on the adsorption isotherm, i.e., up to  $\Delta_a n^*$ ;  $\Delta_{dpl} H_{cum}^*$  represents the enthalpy value at the end of this interval: (a) Methyl Orange, (b)  $SO_4^{2-}$ , (c) Orange II, (d)  $CrO_4^{2-}$ , (e) Orange G, (f)  $HPO_4^{2-}$ .

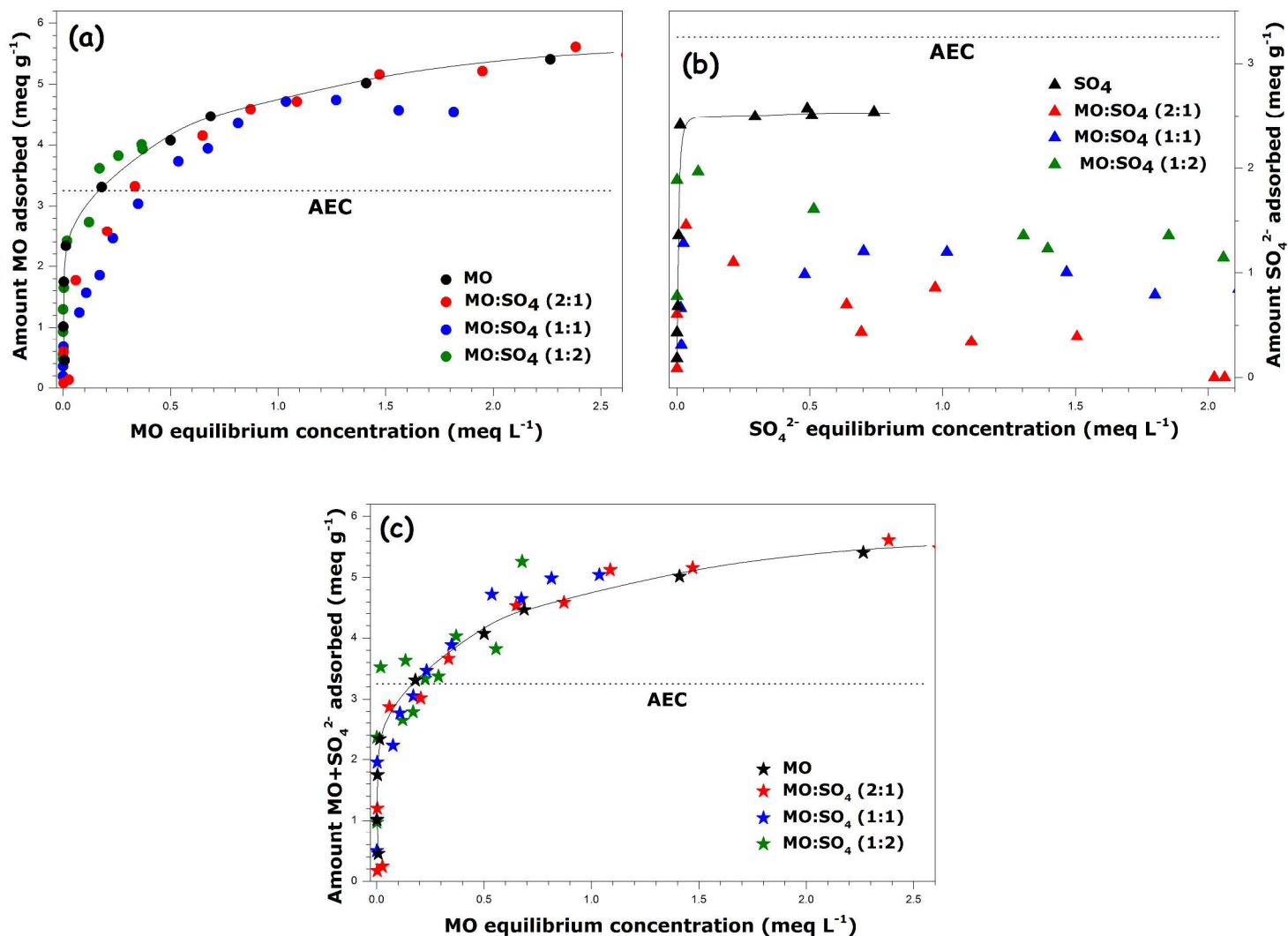


#### IV. Results of adsorption studies on systems containing bi-solute solutions of dye and inorganic anions

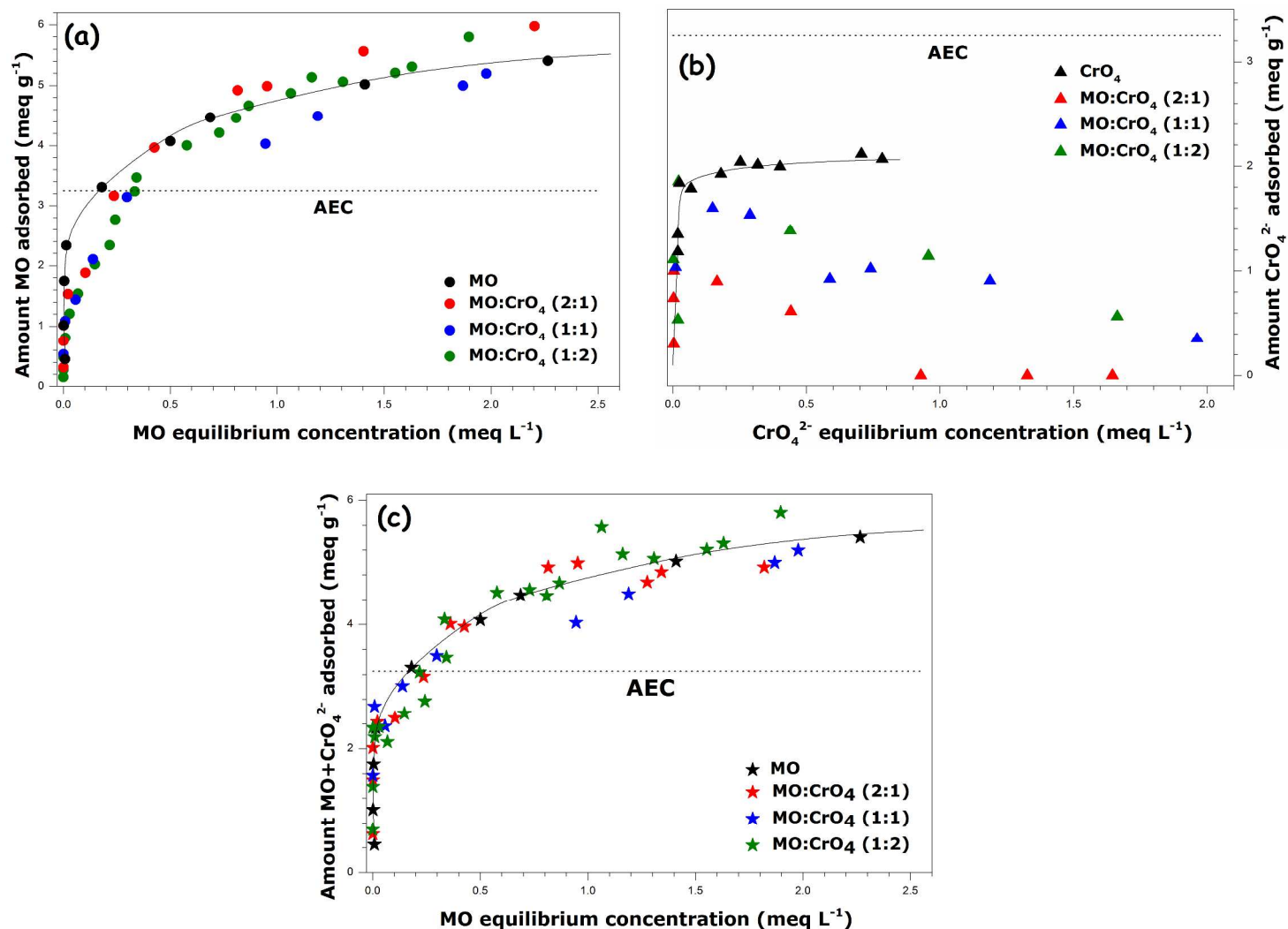
The results of adsorption studies made on systems containing bi-solute solutions have been collected below. Each figure shows a set of adsorption isotherms obtained for a given solute mixture and three molar ratios between dye and inorganic anion: (2:1), (1:1), (1:2). To construct the composite adsorption isotherm, the sum of the two amounts adsorbed has been plotted as a function of the dye concentration in the equilibrium bulk solution.



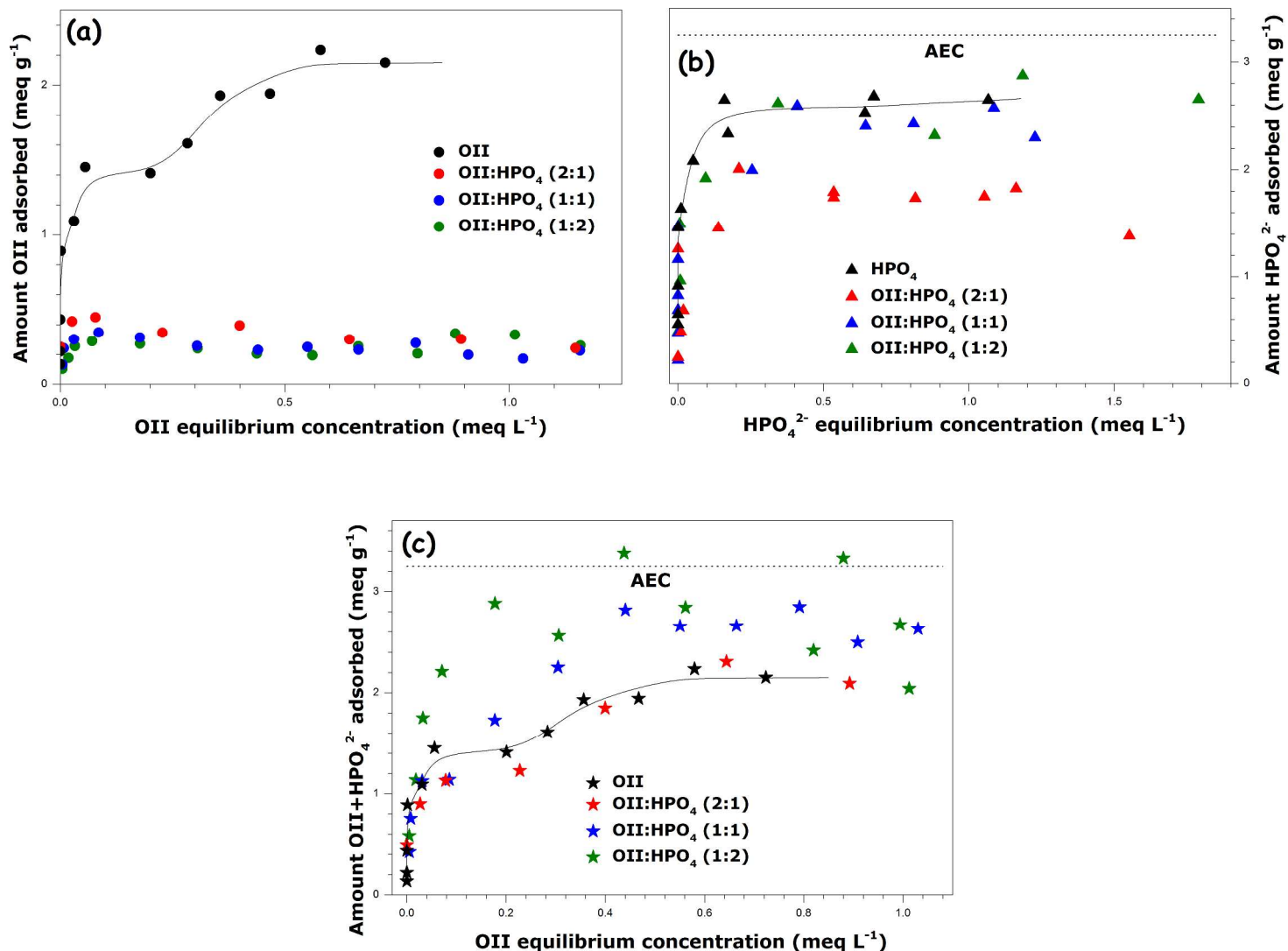
**Figure S4.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Methyl Orange and hydrogen phosphate anions adsorbed at 298 K onto Mg-Al-LDH-NO<sub>3</sub> from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample



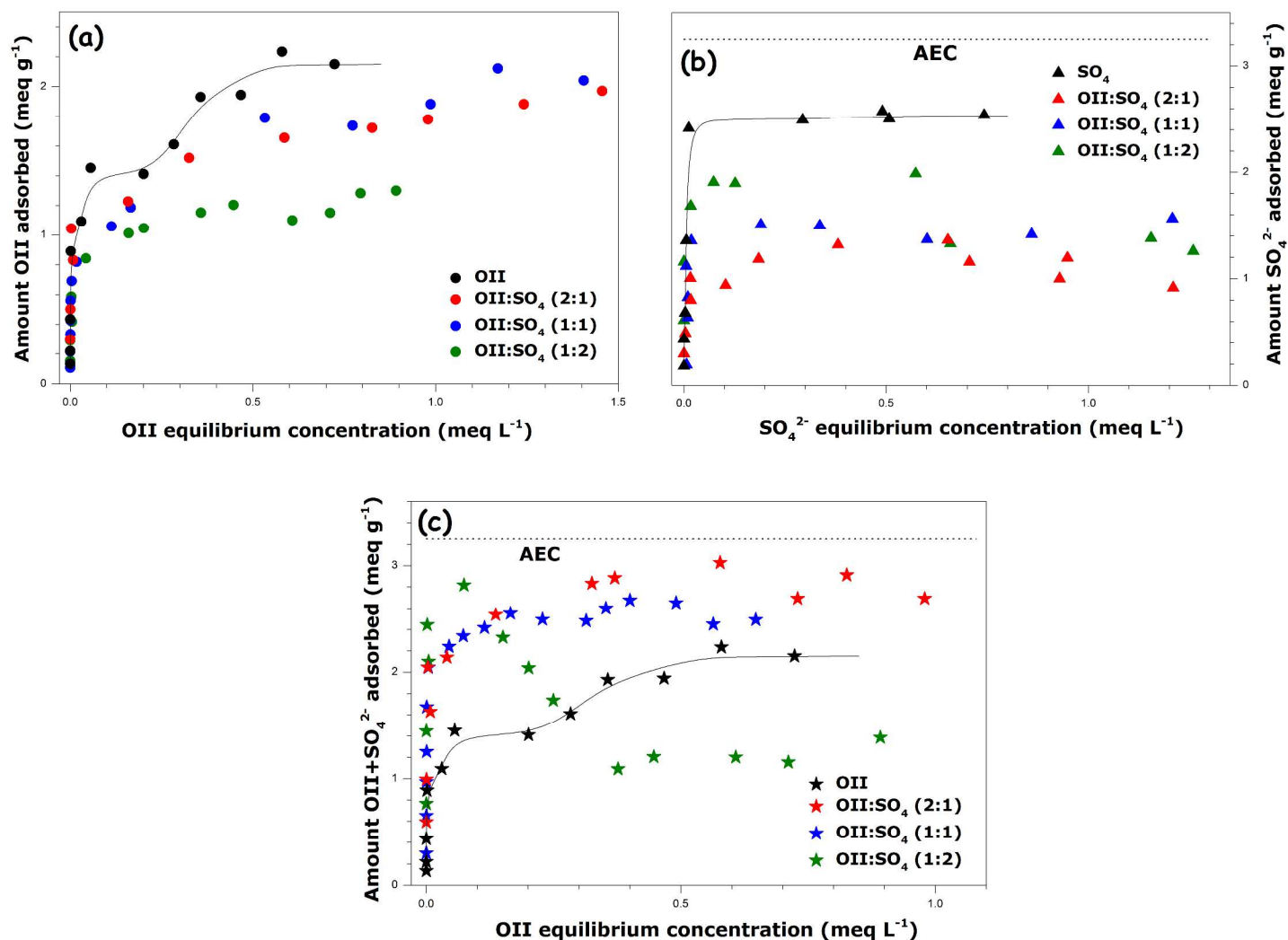
**Figure S5.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Methyl Orange and sulfate anions adsorbed at 298 K onto Mg-Al-LDH- $\text{NO}_3$  from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample.



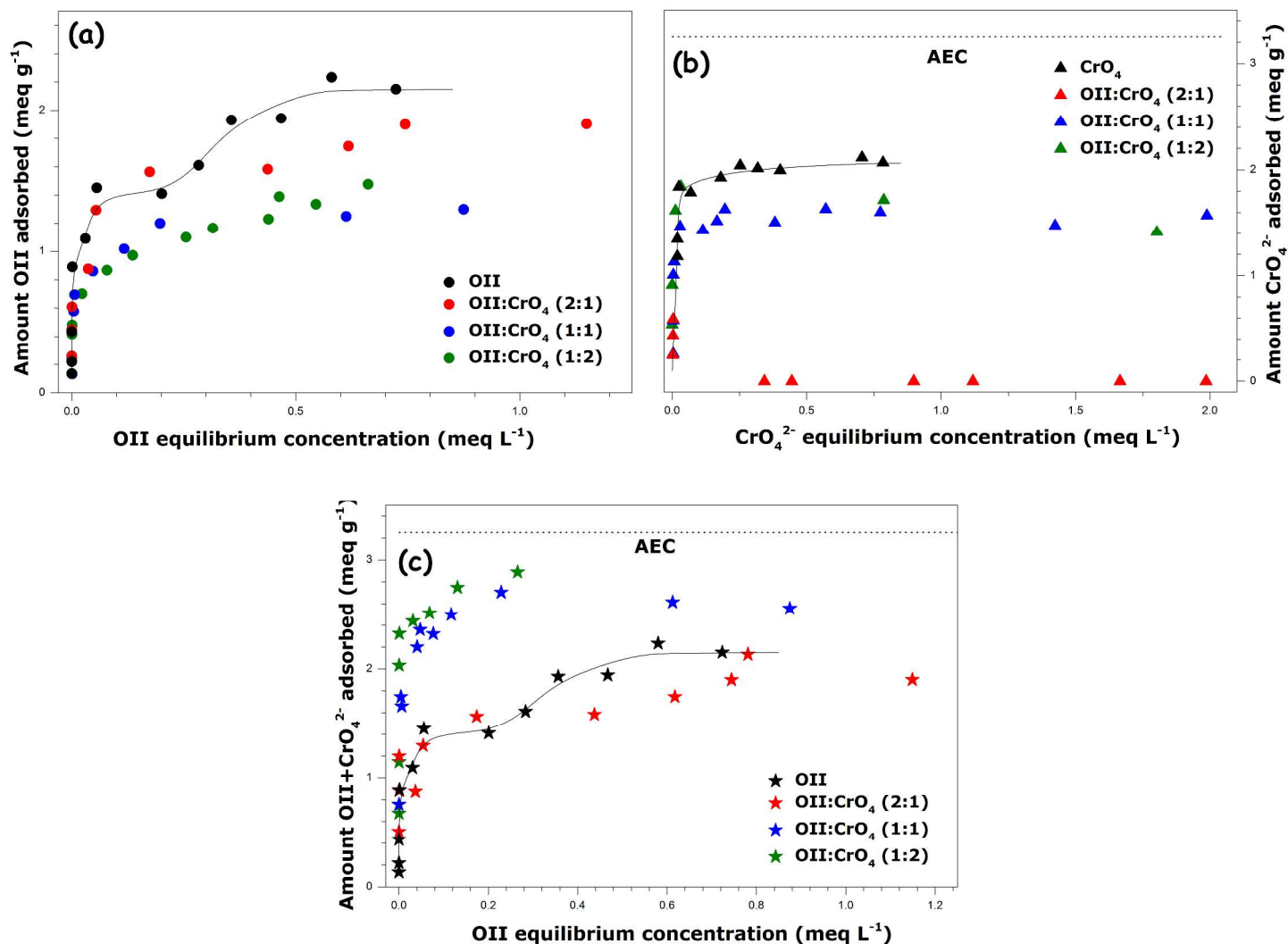
**Figure S6.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Methyl Orange and chromate anions adsorbed at 298 K onto Mg-Al-LDH- $\text{NO}_3$  from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample.



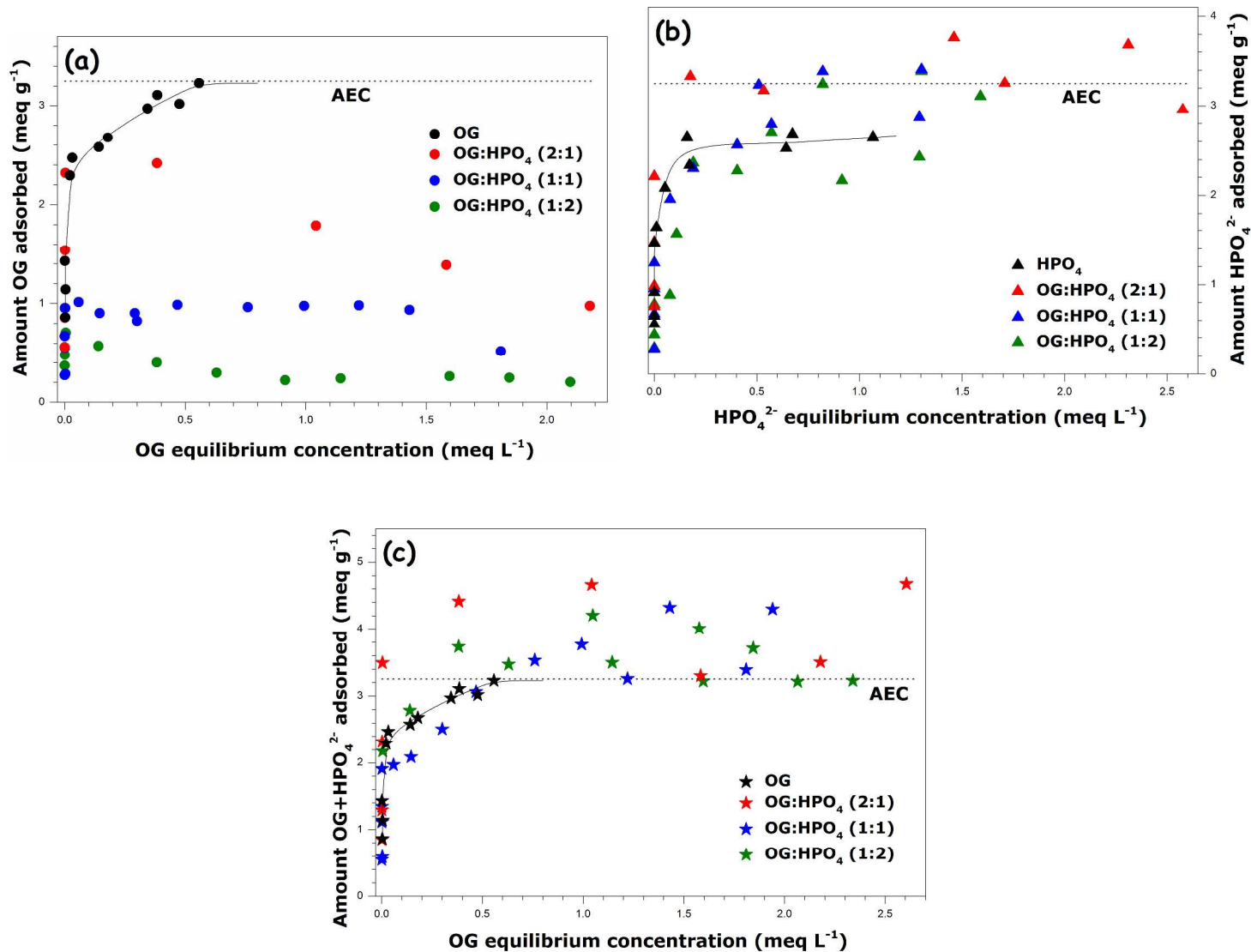
**Figure S7.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Orange II and hydrogen phosphate anions adsorbed at 298 K onto Mg-Al-LDH- $\text{NO}_3$  from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample.



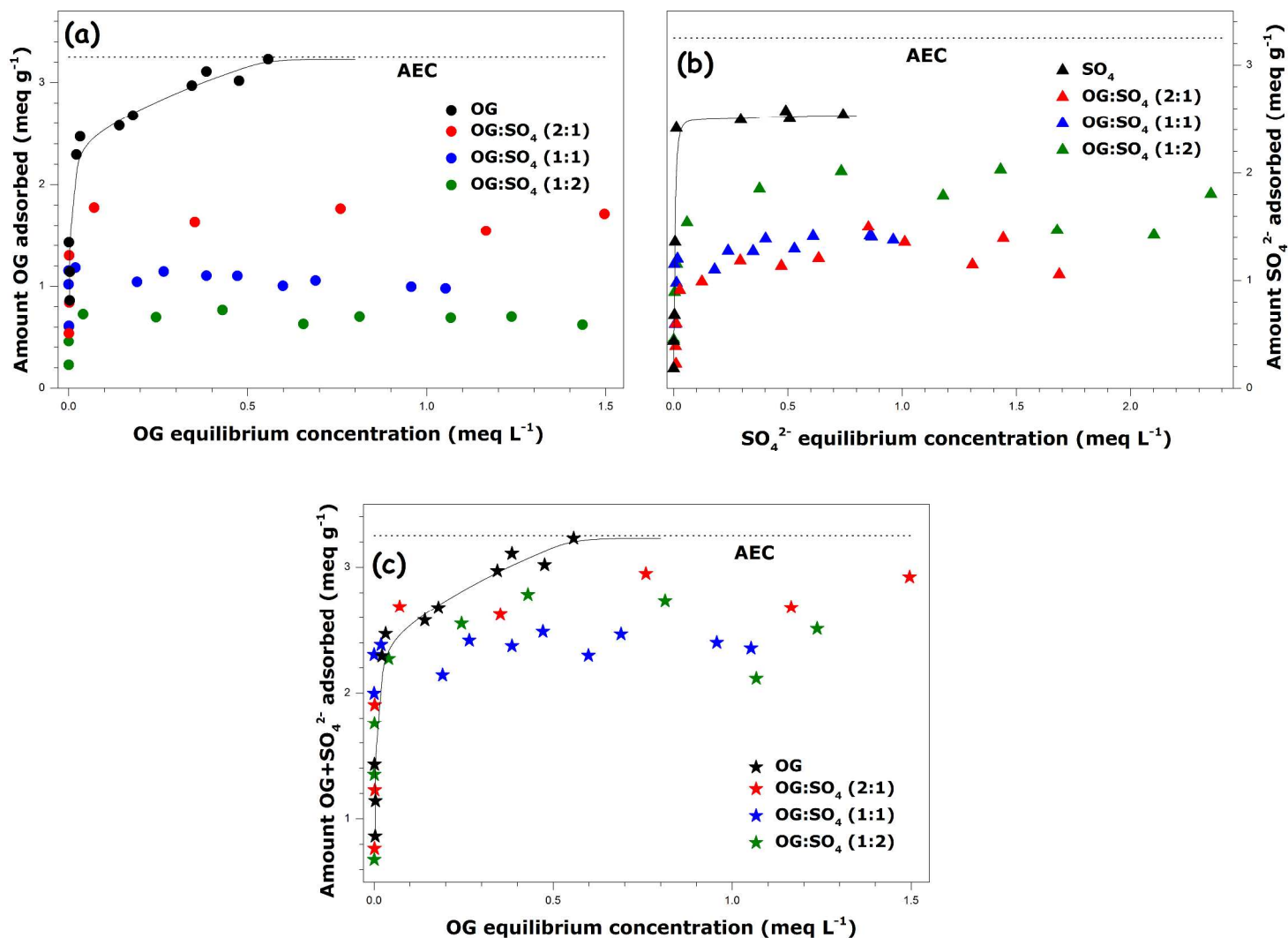
**Figure S8.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Orange II and sulfate anions adsorbed at 298 K onto Mg-Al-LDH- $\text{NO}_3$  from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample.



**Figure S9.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Orange II and chromate anions adsorbed at 298 K onto Mg-Al-LDH- $\text{NO}_3$  from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample.

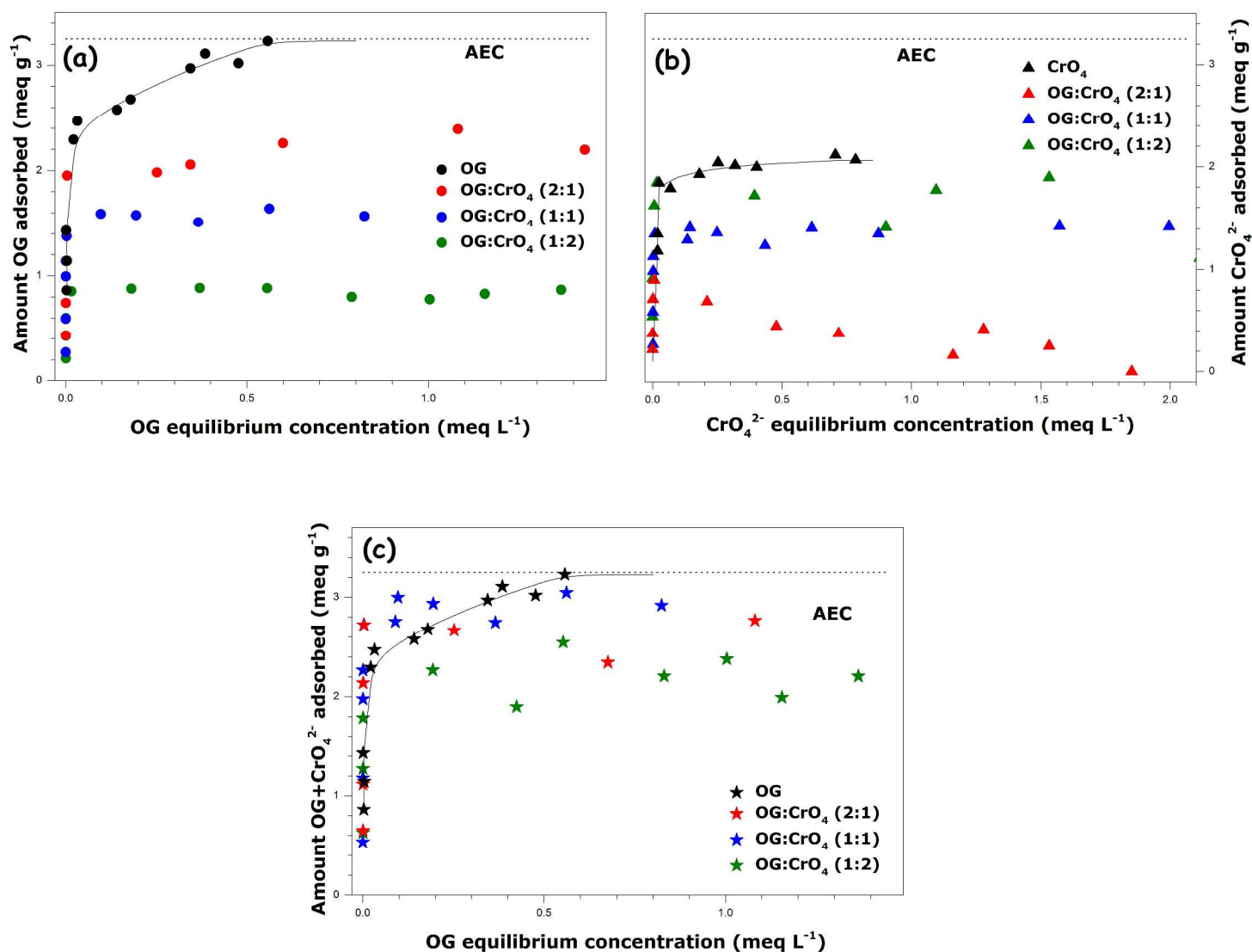


**Figure S10.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Orange G and hydrogen phosphate anions adsorbed at 298 K onto Mg-Al-LDH- $\text{NO}_3$  from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample.



**Figure S11.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Orange G and sulfate anions adsorbed at 298 K onto Mg-Al-LDH- $\text{NO}_3$  from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample.

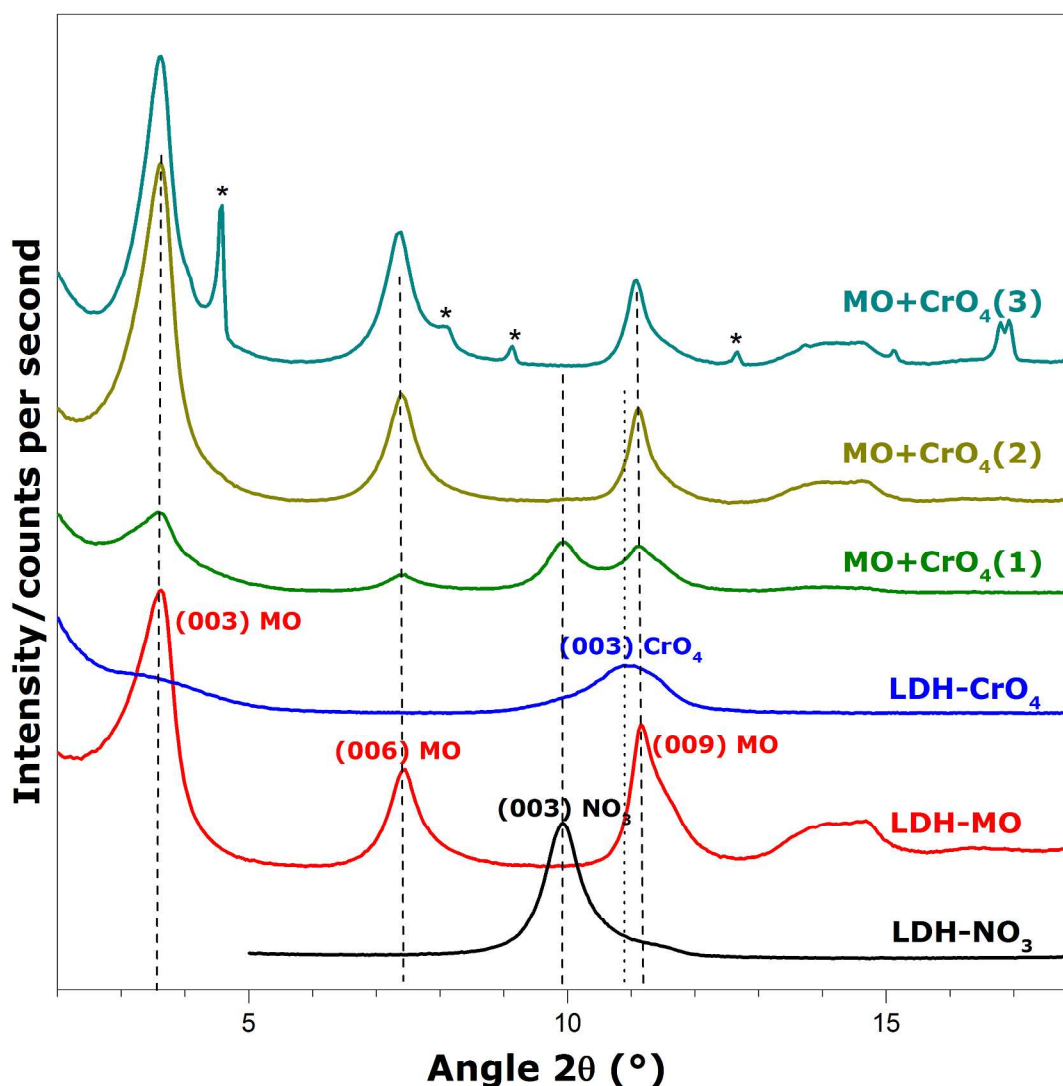




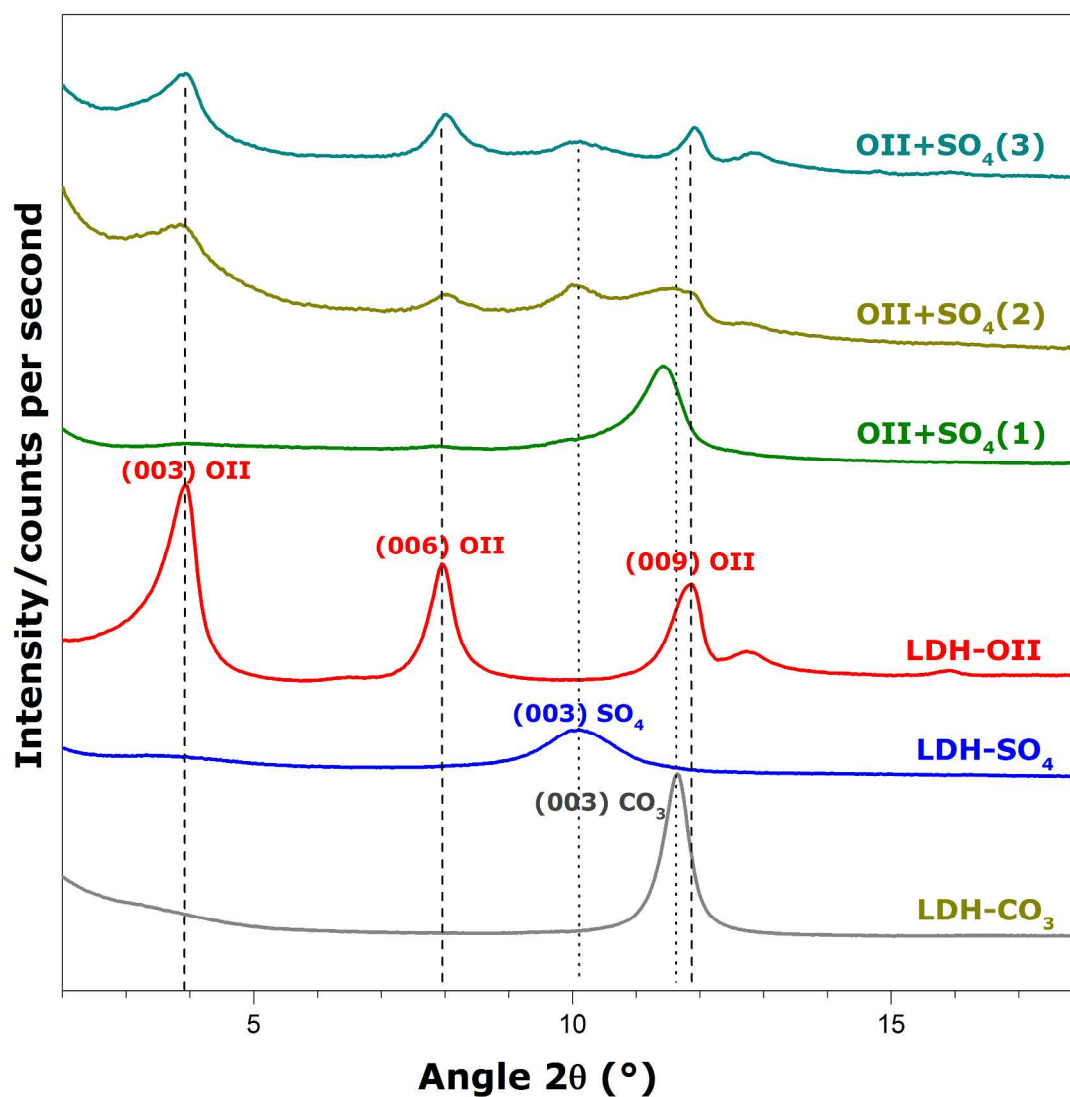
**Figure S12.** Individual (panels a and b) and composite (panel c) adsorption isotherms for Orange G and chromate anions adsorbed at 298 K onto Mg-Al-LDH- $\text{NO}_3$  from bi-solute solutions at different molar ratios between dye and inorganic anion under conditions of exposure to the ambient atmosphere employed in the present study. The dotted lines are used to indicate the anion exchange capacity (AEC) of the LDH sample.

## V. XRD diffraction patterns recorded on Mg-Al-LDH-NO<sub>3</sub> loaded with different species adsorbed from equimolar bi-solute solutions of dye and inorganic anions

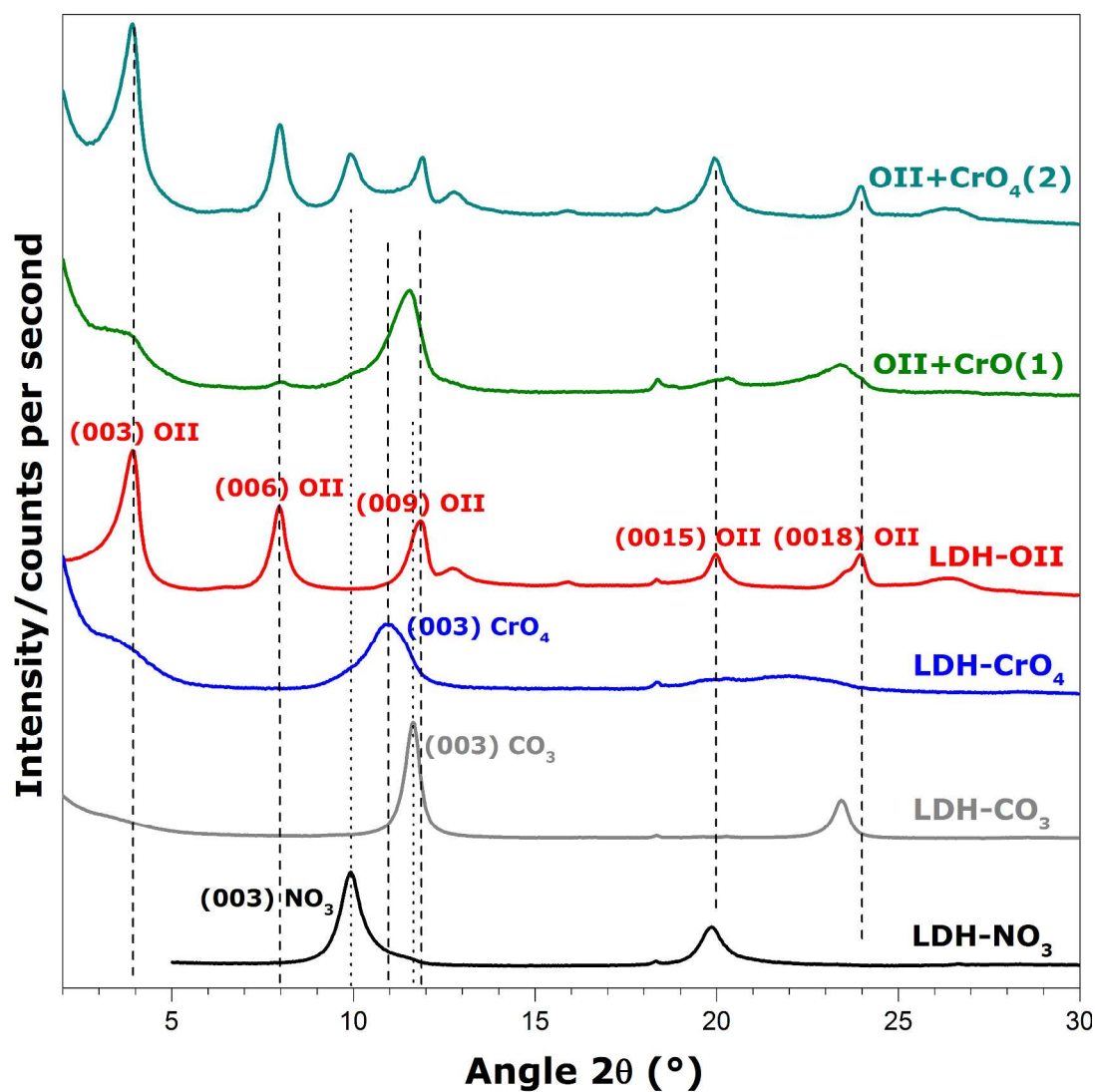
The LDH samples loaded with different anions for XRD studies have been chosen such that they represent some specific portions of the corresponding adsorption isotherms. For example, the first sample denoted by 'dye+inorganic anion(1)' corresponds to the quasi-vertical portions of the adsorption curves, whereas the last one usually refers to the plateau adsorption regions.



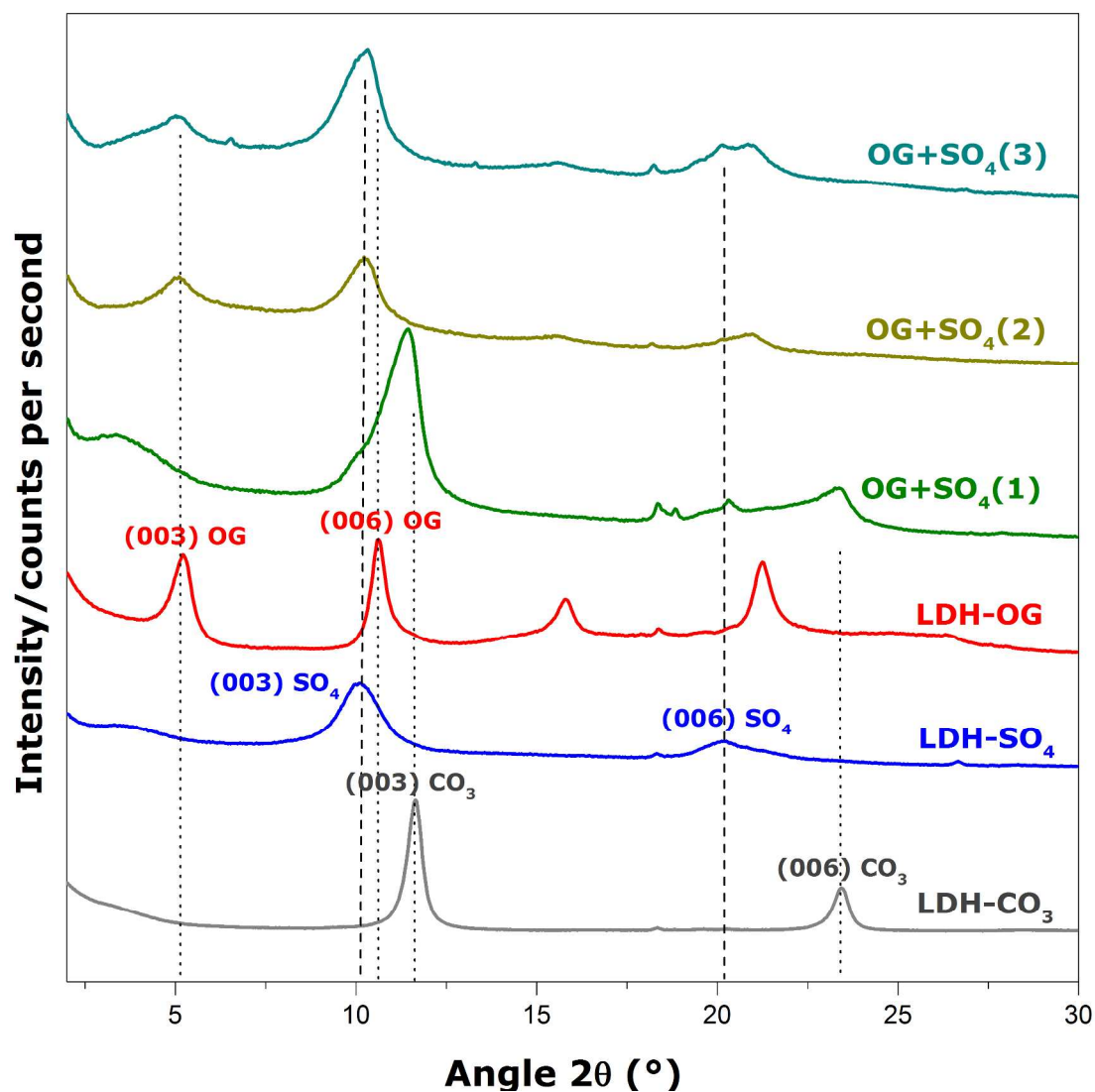
**Figure S13.** X-ray diffraction patterns in a  $2\theta$  range from  $2^\circ$  to  $18^\circ$  for Mg-Al-LDH-NO<sub>3</sub> loaded with various anionic species from single- and bi-solute equimolar solutions. For the three mixtures of MO and chromate anions, the amounts adsorbed are as follows: (1)  $0.99 \text{ meq g}^{-1}$ , MO;  $1.86 \text{ meq g}^{-1}$ ,  $\text{CrO}_4^{2-}$ ; (2)  $2.95 \text{ meq g}^{-1}$ , MO;  $1.53 \text{ meq g}^{-1}$ ,  $\text{CrO}_4^{2-}$ ; (3)  $5.72 \text{ meq g}^{-1}$ , MO;  $0 \text{ meq g}^{-1}$ ,  $\text{CrO}_4^{2-}$ .



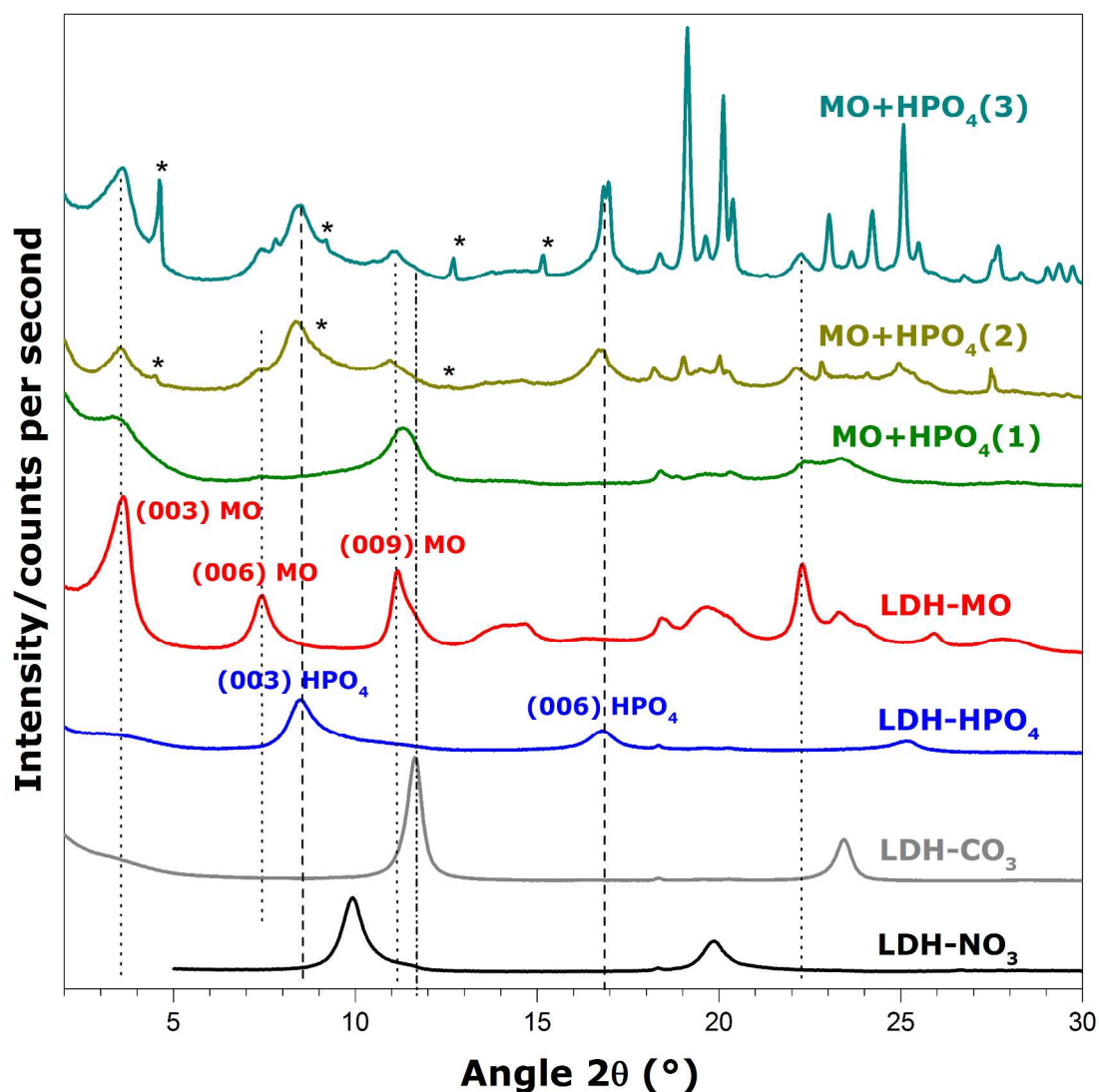
**Figure S14.** X-ray diffraction patterns in a  $2\theta$  range from  $2^\circ$  to  $18^\circ$  for Mg-Al-LDH-NO<sub>3</sub> loaded with various anionic species from single- and bi-solute equimolar solutions. For the three mixtures of OII and sulfate anions, the amounts adsorbed are as follows: (1)  $0.25 \text{ meq g}^{-1}$ , OII;  $0.52 \text{ meq g}^{-1}$ , SO<sub>4</sub><sup>2-</sup>; (2)  $0.70 \text{ meq g}^{-1}$ , OII;  $1.41 \text{ meq g}^{-1}$ , SO<sub>4</sub><sup>2-</sup>; (3)  $0.94 \text{ meq g}^{-1}$ , OII;  $1.61 \text{ meq g}^{-1}$ , SO<sub>4</sub><sup>2-</sup>.



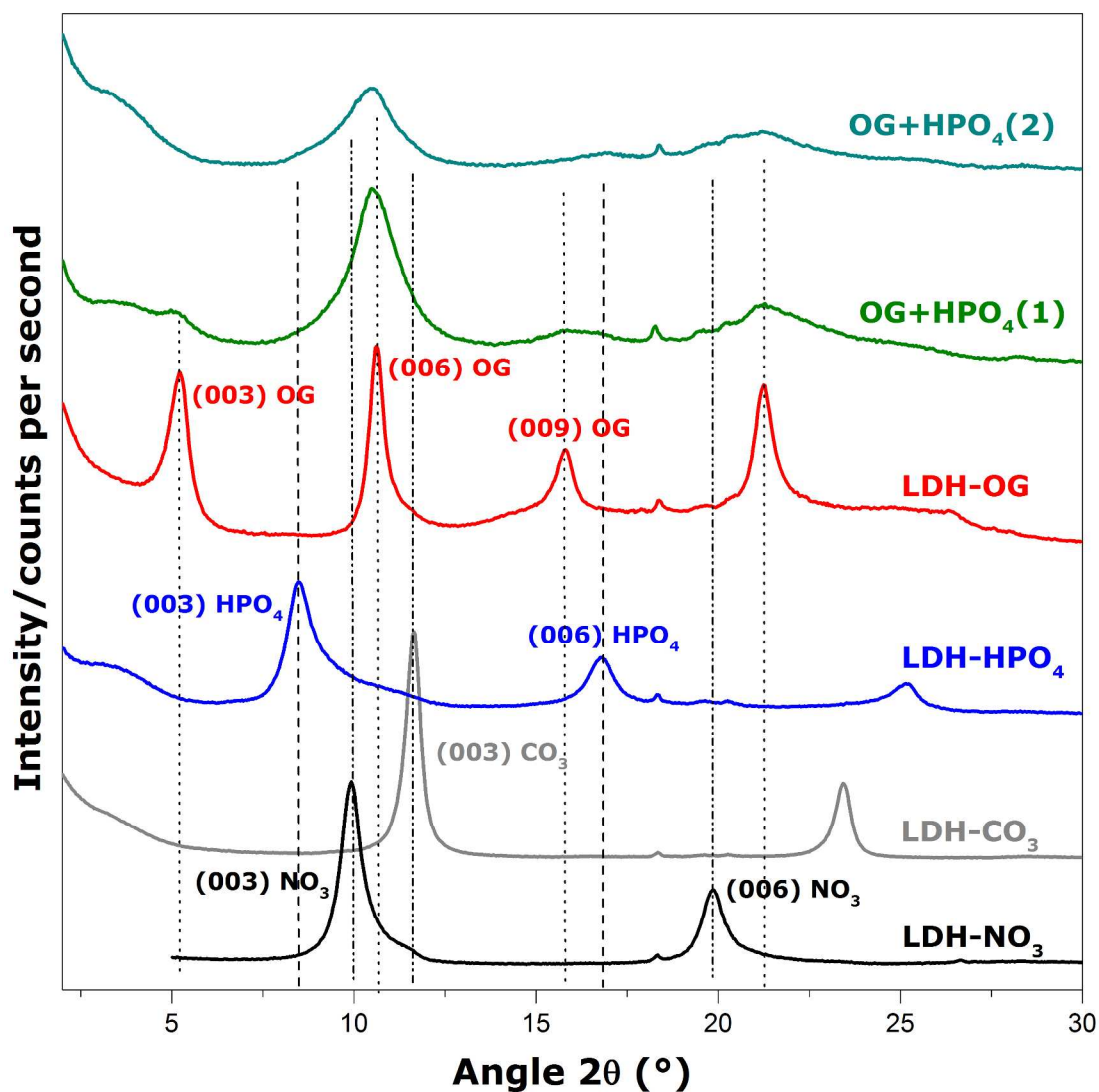
**Figure S15.** X-ray diffraction patterns in a  $2\theta$  range from  $2^\circ$  to  $30^\circ$  for Mg-Al-LDH-NO<sub>3</sub> loaded with various anionic species from single- and bi-solute equimolar solutions. For the two mixtures of OII and chromate anions, the amounts adsorbed are as follows: (1)  $0.58 \text{ meq g}^{-1}$ , OII;  $1.14 \text{ meq g}^{-1}$ , CrO<sub>4</sub><sup>2-</sup>; (2)  $1.15 \text{ meq g}^{-1}$ , OII;  $1.34 \text{ meq g}^{-1}$ , CrO<sub>4</sub><sup>2-</sup>.



**Figure S16.** X-ray diffraction patterns in a  $2\theta$  range from  $2^\circ$  to  $30^\circ$  for Mg-Al-LDH- $\text{NO}_3$  loaded with various anionic species from single- and bi-solute equimolar solutions. For the three mixtures of OG and sulfate anions, the amounts adsorbed are as follows: (1)  $0.93 \text{ meq g}^{-1}$ , OG;  $0.95 \text{ meq g}^{-1}$ ,  $\text{SO}_4^{2-}$ ; (2)  $1.05 \text{ meq g}^{-1}$ , OG;  $1.18 \text{ meq g}^{-1}$ ,  $\text{SO}_4^{2-}$ ; (3)  $0.92 \text{ meq g}^{-1}$ , OG;  $1.46 \text{ meq g}^{-1}$ ,  $\text{SO}_4^{2-}$ .



**Figure S17.** X-ray diffraction patterns in a  $2\theta$  range from  $2^\circ$  to  $30^\circ$  for Mg-Al-LDH- $\text{NO}_3$  loaded with various anionic species from single- and bi-solute equimolar solutions. For the three mixtures of MO and hydrogen phosphate anions, the amounts adsorbed are as follows: (1)  $0.40 \text{ meq g}^{-1}$ , MO;  $0.81 \text{ meq g}^{-1}$ ,  $\text{HPO}_4^{2-}$ ; (2)  $1.33 \text{ meq g}^{-1}$ , MO;  $2.54 \text{ meq g}^{-1}$ ,  $\text{HPO}_4^{2-}$ ; (3)  $2.6 \text{ meq g}^{-1}$ , MO;  $2.11 \text{ meq g}^{-1}$ ,  $\text{HPO}_4^{2-}$ .



**Figure S18.** X-ray diffraction patterns in a  $2\theta$  range from  $2^\circ$  to  $30^\circ$  for Mg-Al-LDH- $\text{NO}_3$  loaded with various anionic species from single- and bi-solute equimolar solutions. For the two mixtures of OG and hydrogen phosphate anions, the amounts adsorbed are as follows: (1)  $0.70 \text{ meq g}^{-1}$ , OG;  $2.01 \text{ meq g}^{-1}$ ,  $\text{HPO}_4^{2-}$ ; (2)  $0.28 \text{ meq g}^{-1}$ , OG;  $2.95 \text{ meq g}^{-1}$ ,  $\text{HPO}_4^{2-}$ .