Supporting Information

Lead(II) Uptake by Aluminium Based Magnetic Framework Composites (MFCs) in Water

Raffaele Ricco,^{a*} Kristina Konstas,^a Mark J. Styles,^a Joseph J. Richardson,^a Ravinchandar Babarao,^a Kiyonori Suzuki,^b Paolo Scopece,^c and Paolo Falcaro^{a*}

- a. CSIRO Manufacturing Flagship, Private Bag 10, Clayton South VIC 3169, Australi
- b. Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia
 - c. Veneto Nanotech, via delle Industrie 5, 30175 Marghera VE, Italy

*Corresponding Author. Email: raffaele.ricco@csiro.au; paolo.falcaro@csiro.au

Solvent	Dielectric constant	Pb(NO ₃) ₂ solubility (g/L)
Methanol	32.7	13
Dimethylsulfoxide	46.7	200
Water	80.1	542

Table S1. Physical and chemical parameters for methanol, dimethylsulfoxide, and water



Figure S1 – Powder X-ray diffraction patterns of MIL-53(Al) with (a) 0%, (b) 50%, and (c) 100% amino groups synthesized using conventional reflux (black lines) and under solvothermal conditions in autoclave (red lines). Giving the breathing behaviour found in the MIL-53 class and according with the peak positions, the materials were all in open form (i.e. the materials were not contracted) as suggested in: T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Férey, *Chem. – Eur. J.*, **2004**, *10*, 1373–1382.



Figure S2 – SEM images and TGA evaluations of the as synthesized NH₂-MIL-53(Al) with reflux conditions (upper pictures) and with standard autoclave conditions (lower pictures).



Figure S3 – N_2 sorption isotherms of MIL-53(Al) MOFs with different amount of amino groups (0%, 50%, and 100%), acquired at 77K. Activation: 150°C/18h in vacuum.



Figure S4 – TEM images of composite made using NH₂-MIL-53(Al) (100% amino groups) with IOMNs, revealing the intimate MFC structure composed by domains of IOMN nanoparticles and aggregates of MOF nanocrystals. The higher picture shows the different domains of aggregates within the same composite cluster. The lower picture reveals the different morphology and the boundary region between the magnetic particles (dark gray particles, left side) and the MOF crystals (light gray particles, right side)

For the sample preparation, 4 µL of MFCs in solution were allowed to adsorb onto a carboncoated Formvar film mounted on 300-mesh copper grids (ProSciTech, Australia). After drying, the samples were analyzed using a Philips CM120 BioTWIN TEM, operated at 120 kV.



Figure S5 – Magnetization curves of NH₂-MIL-53(Al) MOF, IOMNs, and the IOMNs@NH₂-MIL-53(Al) MFC (from upper to lower image). The inset shows the MFC attracted by a commercial Nd-Fe-B permanent magnet (magnetic polarization: 0.57 T).



Figure S6 – SEM images of the NH₂-MIL-53(Al) MOF subjected to different conditions for 21 days. Clockwise from upper left: HCl 10 mM, deionized water, NaOH 10 mM, phosphate buffer pH 7.4 with EDTA 2 mM.



Figure S7 – Evolution of the residual concentration of Pb(II) in solution with the contact time, after 1, 2, 4, 7, 24, and 30 hours. The difference from the initial 8000 ppm concentration accounted for a MFC loading of ca. 330 mg/g Pb(II).



Figure S8 – Rietveld refinements of a) NH₂-MIL53(Al) MOF containing 100% amino groups after synthesis, and washed in water for 24h: b) without Pb(II); with Pb(II) c) 10 ppm, d) 100 ppm, e) 1000 ppm, and f) 10000 ppm; corresponding MFC containing IOMNs g) without and h) with 10000 ppm Pb(II) are also reported for comparison.

Location and binding energy of Pb(0) atoms with MOFs were calculated using dispersion– corrected semi-empirical DFT-D2 method.¹ The effect of solvent is not considered in the calculations. All calculations were performed using Vienna *ab* initio simulation package (VASP)^{2,3} with a plane-wave energy cut-off of 400 eV and k-point sampling at the gamma-point. The interaction between core and valence electrons were described by the projector-augmented-wave (PAW) method and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)⁴ was used to parameterize the exchange-correlation functional. The initial location of the lead atoms in the periodic cell is obtained from classical simulated annealing technique. In the simulated annealing method, the temperature is lowered in succession allowing the atoms to reach a desirable configuration based on different moves such as translate and re-position with preset probabilities of occurrence. This process of heating and cooling the system was repeated in several heating cycles to find the local minima. Forty heating cycles were performed; the maximum temperature and the final temperature were 10^5 K and 100 K, respectively. Static binding energies (Δ E) at 0 K were calculated using the following expression;

$$\Delta E = E_{MOF+Pb(0)} - E_{MOF} - E_{Pb(0)}$$

where E_x refers, respectively, to the total energies of the MOF + Pb(0) complex, the MOF alone, and Pb(0).

References

- (1) Grimme, S. J. Comput. Chem. 2006, 27, 1787-1799.
- (2) Kresse, G.; Furthmuller, J. Comput. Mater. Sci. 1996, 6, 15-50.
- (3) Kresse, G.; Hafner, J. Phys. Rev. B 1993, 48, 13115-13118.
- (4) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865-3868.



Figure S9 – Thermal images of the magnetic heating experiment conducted on IOMN@NH₂-MIL-53(Al) previously filled with aqueous 8000 ppm solution of Pb(II) for 3 days. The temperature indicated in the upper left corner of each image has been registered at the position marked by the crosshair (center of the images).