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Green synthesis of zirconium MOF-808 for simultaneous phosphate recovery and organophosphorus pesticide detoxification in wastewater†

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Agricultural wastewater possesses serious threats to the environment and human health. In this work, we report a green microwave assisted synthesis of MOF-808 with tuned particle size. These materials have been proved to simultaneously degrade a toxic pesticide and capture phosphate from water over several cycles. The adsorbed phosphate can be further recovered, favoring a P-circular economy.

Due to the continuous growth of the world population and the negative effects derived from global climate change, agrochemicals are essential to maintain the current crop yields and ensure food security.¹ However, their low efficiency together

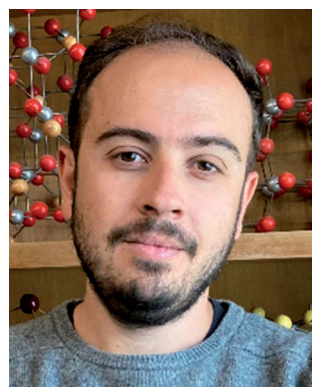
with their indiscriminate use implies severe threats to the environment and human health.^{2,3} In this context, phosphorus-based compounds are extensively employed in modern agriculture and manufactured from phosphoric rock, which is a non-renewable resource. In addition, less than 30% of the phosphorus applied to soils reaches the food chain, with the main P-losses occurring in croplands. Consequently, the P-compounds, which contaminate fresh waters, contribute to eutrophication and decimate biodiversity, which also entails a significant societal cost.⁴ On the other hand, organophosphorus pesticides (OPs), widely used in agriculture, are highly toxic compounds due to their ability to inhibit the activity of acetylcholinesterase, an enzyme present in several animals, including humans. Indeed, OP poisoning causes 110 000 deaths per year globally.^{5,6} For these reasons, the design of new strategies to decontaminate polluted wastewater and recover phosphate from it is of paramount importance and may contribute to the much-needed P circular economy.

In this regard, Zr-based metal-organic frameworks (Zr-MOFs) are robust and non-toxic crystalline porous materials composed of $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters connected by organic spacers. Their elevated porosity, together with the Pearson hard-acid nature of Zr(IV) sites and concomitant strong affinity for phosphate compounds, has led to Zr-MOFs being considered as promising materials towards the decontamination and recovery of P-polluted wastewater. Indeed, some Zr-MOFs have recently been proved to efficiently capture phosphate or pesticides. However, most of these examples are limited to the removal of a single pollutant,^{7–10} far from the real conditions of application. Only one very recent study, of our research group, reported the simultaneous capture and selective recovery of both P-pollutants by Zr-MOF NU-1000.¹¹ On the other hand, certain Zr-MOFs can hydrolytically degrade OPs in buffered media containing organic amines (e.g. *N*-ethylmorpholine).^{12,13} Nevertheless, the catalytic activity of these materials decreases dramatically in unbuffered media such as wastewater, suggesting the role of these molecules as co-catalysts (*i.e.* $t_{1/2} < 1$ min in *N*-ethylmorpholine solution and $t_{1/2} = 94$ min in Milli-

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† Electronic supplementary information (ESI) available: Details of experimental procedures, synthesis of compounds, PXRD diffractograms, adsorption isotherms and kinetics, ¹H and ³¹P NMR spectra, and recyclability and interference studies, including Fig. S1–S10 and Tables S1–S3. See <https://doi.org/10.1039/d2ta02074b>

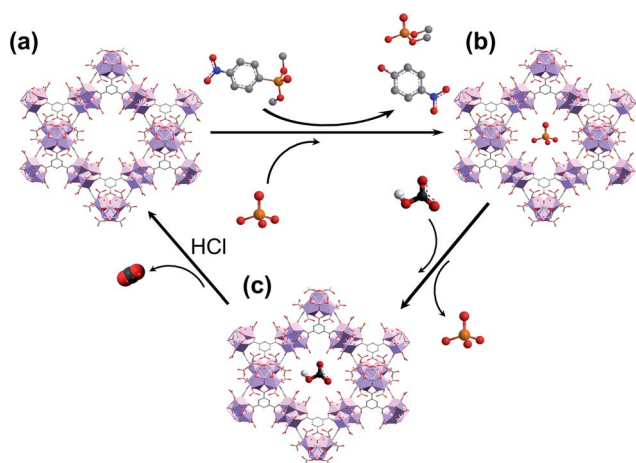


Dr Francisco J. Carmona obtained his PhD in Chemistry in 2017 at the University of Granada (Spain). Later, he worked as a postdoctoral researcher at Insubria University (Italy, 2017–2019) and Kyoto University (Japan, 2019–2020). In 2020, he received a Marie Skłodowska-Curie postdoctoral fellowship to join the Department of Inorganic Chemistry at the University of Granada (Spain). His current

research is focused on the green preparation of metal-organic frameworks (MOFs) and polyhedra (MOPs) with potential application in biomedicine and environmental remediation.

Firstly, three MOF-808 materials, with particle size ranging from 345 to 570 nm, were prepared by water-based microwave (MW) assisted synthesis using different heating ramps. It should be highlighted that this environmentally friendly approach allowed the reaction time to be significantly shortened (from days to a few hours) in comparison with typical solvothermal methods, which employ a two-day synthesis and toxic DMF as solvent.^{21,22} The designed synthetic procedure encompasses four different steps: (i) a heating ramp of 15, 60 and 120 min up to 95 °C for MOF-808 15, MOF-808 60 and

Once MOF-808_15, MOF-808_60 and MOF-808_120 materials were fully characterized, we proceeded to assess their behaviour towards the adsorption of phosphate ions and the degradation of the organophosphorus pesticide methyl paraxon (MP). Firstly, experimental data confirmed the incorporation of phosphate from aqueous solutions in all MOF-808 structures. The corresponding solid-liquid adsorption isotherms at 25 °C could be successfully fitted to a Langmuir model with maximum adsorption capacities of 1.60 (MOF-808_15), 1.26 (MOF-808_60) and 0.77 (MOF-808_120) mol mol⁻¹ (Fig. S4†). Since the three samples showed similar porosity, the difference in maximum phosphate loading



Scheme 1 Schematic representation of (a) simultaneous phosphate removal and pesticide degradation, (b) recovery of phosphate by hydrogen carbonate treatment, and (c) regeneration of MOF-808 with hydrochloric acid.

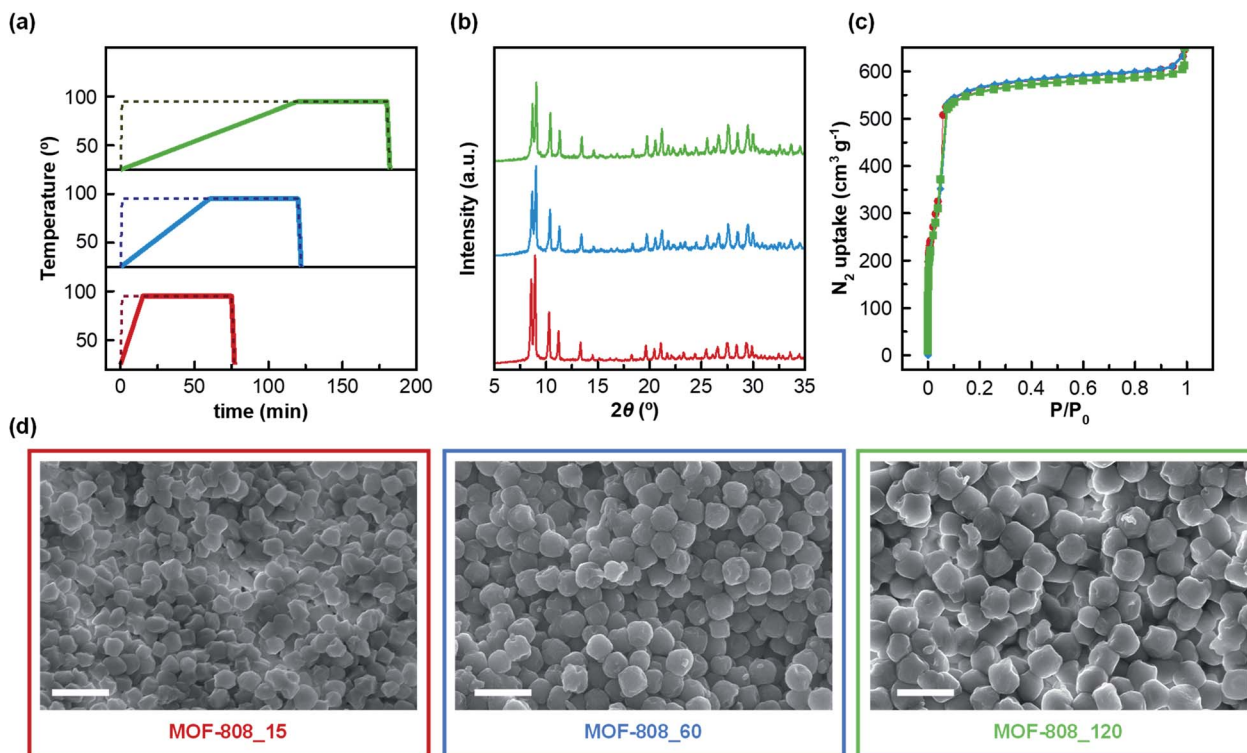


Fig. 1 (a) Controlled-heating ramp used in the preparation of MOF-808 (continuous lines) and control materials (dashed lines). (b) Powder X-ray diffractograms, (c) N₂ adsorption at 77 K and (d) SEM images of MOF-808_15 (red), MOF-808_60 (blue) and MOF-808_120 (green). Scale bar: 1 μm.

capacities could be attributed to a hindered diffusion of phosphate in the inner pore structure. Consequently, the adsorbate loading inversely correlates with MOF particle size. In addition, an aqueous solution of phosphate (0.08 mM, 1 mL, pH = 6.9) was exposed to an equimolar amount of MOF-808 materials (0.08 μmol) to evaluate their adsorption kinetics. A pseudo-second order kinetic model was the best to fit the experimental data (Fig. 2a and Table S2[†]), demonstrating in all cases a fast diffusion and high affinity of phosphate anions for the pore structure (MOF-808_15: $t_{1/2}$ = 20.9 min; MOF-808_60: $t_{1/2}$ = 24.8 min and MOF-808_120: $t_{1/2}$ = 26.2 min). A nearly complete uptake of this pollutant was reached after 24 hours for MOF-808_15 ($98.0 \pm 2.3\%$) and MOF-808_60 ($96.1 \pm 0.9\%$), while a lower payload was observed for MOF-808_120 ($79.9 \pm 5.1\%$). These results are in agreement with the solid-liquid adsorption isotherms (Fig. S4[†]). In addition, we evaluated the ability of MOF-808 materials to catalyse the hydrolysis of toxic methyl paraoxon (oral rat LD₅₀ = 3.27 mg kg⁻¹)²⁴ into 4-nitrophenol (oral rat LD₅₀ = 667 mg kg⁻¹)²⁵ and dimethylphosphate (oral rat LD₅₀ = 3283 mg kg⁻¹)²⁶ in unbuffered aqueous solution. All assayed MOF-808 materials lead to a significant hydrolysis of the ester P-O bond after 24 hours (MOF-808_15: $92.8 \pm 0.9\%$; MOF-808_60: $91.1 \pm 6.4\%$; MOF-808_120: $86.0 \pm 5.8\%$) (Fig. 2b). The degradation profiles can be fitted to a second-order kinetics model, with half-life times of 113 min, 137 min and 231 min, for MOF-808_15, MOF-808_60 and MOF-808_120, respectively (Table S3[†]). These results demonstrate the detrimental impact of crystal size on catalytic activity, with the MOF-808_120 material exhibiting the worst performance in the assayed series. These results are in line with previously

published studies on MP hydrolysis by MOF-808 in pure water ($t_{1/2}$ = 300 min).¹⁵

Interestingly, these porous materials were also able to simultaneously degrade methyl paraoxon and capture

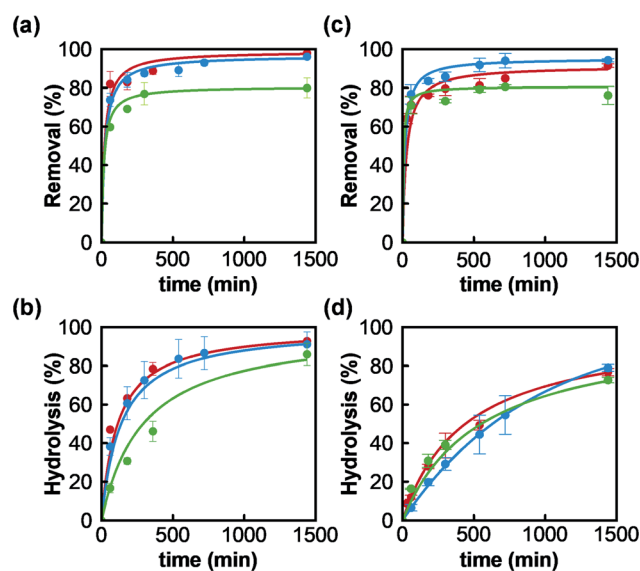


Fig. 2 (a) Adsorption kinetics of phosphate. (b) Degradation kinetics of methyl paraoxon. (c) Adsorption kinetics of phosphate in the presence of methyl paraoxon. (d) Degradation kinetics of methyl paraoxon in the presence of phosphate. Experimental conditions: unbuffered aqueous solutions at 25 °C (1 mL), 0.08 μmol of MOF-808, [MP] = 0.08 mM, and [PO₄³⁻] = 0.08 mM (MOF-808_15: red, MOF-808_60: blue and MOF-808_120: green).



In order to prove this hypothesis, we carried out UV-vis studies which revealed that pesticide concentration in the supernatants decreased at the same rate as the concentration of *p*-nitrophenol (one of the degradation products) increased. Interestingly, an isosbestic point was observed at 297 nm, pointing out that neither methyl paraoxon nor *p*-nitrophenol is incorporated into the porous matrixes (Fig. 3b). Furthermore, suspensions of MOF-808_60 (5.6 μ mol) and methyl paraoxon (5.6 mM) were incubated in 1 mL of D₂O for 24 h at room temperature in the presence and absence of phosphate (5.6 mM). The supernatants were analysed by means of ¹H and ³¹P NMR spectroscopy using glyphosate as an internal reference. Both the pesticide and its degradation products (*p*-nitrophenol and dimethylphosphate) were successfully identified in ¹H and

³¹P spectra. In particular, the ¹H NMR spectra confirm that 62.0 and 48.0% of methyl paraoxon was hydrolysed after 24 h in the absence and presence of phosphate, respectively. These conversion values were appreciably lower than those obtained in the batch experiments, which could be attributed to kinetic issues related to the use of deuterated water. Noteworthy, the comparison of the integrated H signals of non-degraded methyl paraoxon and *p*-nitrophenol with the internal reference (glyphosate) indicated that neither the pesticide nor *p*-nitrophenol was incorporated into the porous matrix (Fig. 3c, S5 and S6†). Conversely, dimethylphosphate (the other degradation product) was partially encapsulated inside the MOF (76.6% in the absence of phosphate vs. 44.4% in the presence of this anion) (Fig. S5 and S6†). Despite this fact, it seems that dimethylphosphate does not really compete with phosphate during the adsorption process, as corroborated by the previously discussed kinetic studies where phosphate uptake after 24 h was not affected by the presence of methyl paraoxon (see above). ³¹P spectra further supported these experimental results, confirming the generation and partial encapsulation of dimethylphosphate molecules as well as the almost complete encapsulation of phosphate ions after 24 h of incubation (Fig. S7 and S8†). In summary, pesticide degradation seems to take place on the particle surface and, consequently, the high surface area of the pores is available for the adsorption of phosphate ions. In contrast, methyl paraoxon molecules compete with phosphate ions for the active sites on the external particle surface, explaining the drop of about 10–15% in the hydrolytic efficiency when both P-pollutants are present.

To further explore the suitability of these materials as decontaminating agents, recyclability studies were carried out with MOF-808_60. After a first incubation of MOF-808_60 (0.08 μ mol) with equimolecular amounts of methyl paraoxon and

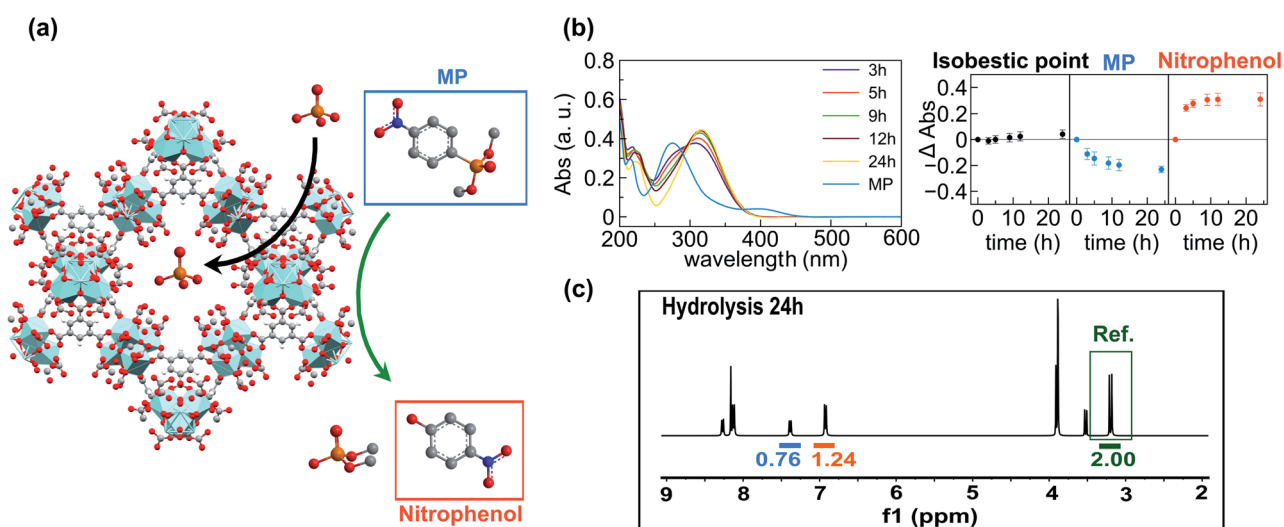


Fig. 3 (a) Schematic representation of phosphate encapsulation into the cavities of MOF-808 and degradation of methyl paraoxon taking place on the MOF surface. (b) UV-Vis spectra showing the degradation of methyl paraoxon by MOF-808_60. On the right, evolution of absorbance at 297 nm (isosbestic point, black), 274 nm (methyl paraoxon, blue) and 316 nm (*p*-nitrophenol, orange). (c) ^1H NMR of the supernatant after the hydrolysis of methyl paraoxon by MOF-808_60 after 24 h. The concentration of the internal reference (glyphosate) is the same as that of the total concentration of unreacted methyl paraoxon and generated *p*-nitrophenol, ruling out the encapsulation of the pesticide.

phosphate (0.08 mM, 1 mL), the solid was filtered off and treated with a highly concentrated hydrogencarbonate solution (4 mM, 1 mL, pH = 8.3, 5 h) recovering a substantial amount of the previously adsorbed phosphate ($79.2 \pm 3.0\%$) (Fig. 4). Then, and in order to decompose the entrapped hydrogencarbonate anions, we proceeded to regenerate the MOF-808_60 matrix by suspending the solid with diluted hydrochloric acid (4 mM, 1 mL, 5 h). The recyclability was further evaluated over two additional cycles. The results revealed that the material maintained similar performances to the ones observed, in the first cycle, towards phosphate adsorption, pesticide degradation and phosphate recovery. A drop of only 10% occurred between the second and third cycles for methyl paraoxon hydrolysis (Fig. 4). To prove the impact of all these processes (catalysis and adsorption, subsequent desorption of phosphate and matrix regeneration) on the structural integrity of the dual material, both the MOF_808_60 solid and eluted solutions were analysed by XRPD and ICP-MS, respectively. Although a certain loss of crystallinity was observed after the different treatments (Fig. S9†), neither Zr nor trimesate linker leaching was observed, ruling out ligand exchange. Nevertheless, a partial displacement of the $-\text{COO}-$ sites of BTC linkers cannot be ruled out, as previously observed by Zhang, Chen *et al.*²⁷ In any case, this observed amorphization does not affect the final performances of our material, as demonstrated by its good recyclability.

Furthermore, the ability of MOF-808_60 to both decompose methyl paraoxon and capture phosphate in the presence of several interferents typically found in water, such as chloride, sulphate, nitrate and hydrogencarbonate ions (interference : pesticide : phosphate ratio 5 : 1 : 1), was investigated (Fig. S10†). Regarding pesticide hydrolysis, only the presence of sulphate and nitrate seemed to slightly decrease the total amount of degraded methyl paraoxon after 24 h (80.3 ± 1.5 and $71.2 \pm 2.1\%$, respectively). In contrast, the phosphate adsorption capacity of MOF-808_60 remained unaltered in all cases except when hydrogencarbonate was used as an interferent

(phosphate uptake dropped by up to $55.9 \pm 5.7\%$). Notwithstanding, the hydrogencarbonate to phosphate molar ratio used in these assays is much larger than that typically found in wastewaters (1.5 : 1).²⁸

Conclusions

We have demonstrated the feasibility of preparing high quality MOF-808 materials through a fast and environmentally friendly water-based microwave reaction. By modulating the heating ramp, highly crystalline and porous materials with homogeneous and tuned crystal size were obtained. Moreover, these matrixes have been proved to exhibit a good performance toward the capture of phosphate ions or the degradation of toxic methyl paraoxon pesticide in water. In mixtures containing both pollutants, these MOFs were also able to simultaneously decompose methyl paraoxon and capture phosphate ions without a significant detriment to the individual performance. UV-Vis and NMR spectroscopy analysis have demonstrated that while phosphate ions can be adsorbed inside the pores, pesticide degradation takes place mainly on the external particle surface. Furthermore, a strategy has been designed to regenerate the adsorbent and recover the trapped phosphate ions which may contribute to the P circular economy. Specifically, MOF-808_60 has been proved to exhibit good reusability maintaining a good performance over at least three degradation-adsorption-desorption cycles. These results represent a step forward in the application of MOF materials in wastewater treatment.

Author contributions

Lydia González: investigation, visualization. Rodrigo Gil-San Millán: investigation, methodology. Jorge A. R. Navarro: supervision, funding acquisition, writing – review & editing. Carmen R. Maldonado: project administration, supervision, funding acquisition, writing – original draft, writing – review & editing. Elisa Barea: project administration, supervision, funding acquisition, writing – original draft, writing – review & editing. Francisco J. Carmona: conceptualization, investigation, methodology, funding acquisition, writing – original draft, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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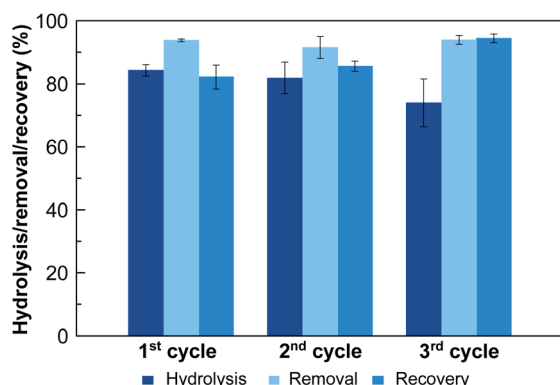


Fig. 4 Recyclability studies of MOF-808_60 along three successive cycles: (i) simultaneous hydrolysis of methyl paraoxon and removal of phosphate and (ii) subsequent recovery of phosphate by exchange with hydrogencarbonate anions. After each cycle, MOF-808_60 was regenerated by treatment with an aqueous solution of hydrochloric acid (2.5 mM).



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