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Cu$^{II}$-based metal-organic nanoballs for very rapid adsorption of dyes and iodine

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Cu$^{II}$-nanoballs have been determined to be among the best MOPs (Metal-Organic Polyhedra) reported so far for the adsorption of small molecules, with the highlighting advantage of the rapid kinetics, which focuses applicability to the removal of emergent pollutants.

Organic dyes are nowadays widely used in many industries including medicine, textile, leather, printing and plastic.$^1$ The consequence of this fact is that dyes are present as emergent pollutants in soils and water where remain for large periods of time due to their high stability,$^2$ with potential risk of toxicity in wildlife and in humans.$^3$ On the other hand, the presence of iodine in soils, water and gas as nuclear activity pollutant product$^4$ or due to its extended use as germicide,$^5$ is still being a problem in many countries, which remembers the imperative need of its removal. Accordingly, several attempts to remove pollutants are being studied, such as the use of activated carbon,$^6a$ coagulation,$^6b$ photocatalysis$^6c$ or adsorption.$^6d$ This last method rose as one of the most feasible methods thanks to its efficiency and economic competitiveness.$^7$

In this area, Metal-Organic Frameworks (MOF) have attracted great interest in recent years, taking a leading role in the field of catalysis,$^{8a}$ drug delivery,$^{8b}$ sensors,$^{8c}$ and absorption.$^{8d}$ In the last decade, promising results have been reported specifically in the field of adsorption, based in the topology and chemical features of this type of porous materials.$^9$ Those are formed binding metal nodes with organic linkers generating porous networks, where the guest molecules accommodate when adsorption takes place. Many times these pores are originally occupied by solvent molecules that must be displaced, for efficient adsorption. Thus, it is common the activation of MOF with temperature to obtain an adsorbent material.$^{10}$ Therefore, an accurate characterization of the original compound as well as the activated one ensures greater efficiency of the adsorption process. In this context, this work presents the characterization of the activated compound $\alpha$MOP@Ei2-1 obtained from the already reported$^{11}$ $[\text{Cu}_{24}(m\text{-BDC})_{24} (\text{DMF})_{20} (\text{H}_{2}\text{O})_{4} ] \cdot 24\text{DMF} \cdot 40\text{H}_{2}\text{O}$ ($\text{MOP@Ei2-1}$), where $m$-BDC is 1,3-benzenedicarboxylic ligand and DMF is $N,N'$-dimethylformamide, as well as an study of dyes and iodine adsorption as pollutant examples, focusing on the kinetics of the rapid process.

Compound MOP@Ei2-1 consists of a MOP formed by 24 Cu$^{II}$ atoms grouped in 12 paddle-wheels linked by $m$-BDC. This arrangement generates a cuboctahedron structure with a large cavity within (1.6 nm of diameter), where crystallization and coordination H$_2$O and DMF molecules occupied the internal cavity, as well as the interstitial voids (Fig. 1). These structural units are nanoballs with a diameter of 2.4 nm. These nanoballs show two types of crevices: 8 triangular-like and 6 square-like ones (Fig. 1).

Fig 1. (a) View of the original MOP@Ei2-1 (coordination and crystallization solvent molecules can be seen), (b) activated $\alpha$MOP@Ei2-1 and (c) geometry and dimensions of the two types of crevices.
Thermal characterization of MOP@Ei2-1 was reported previously. The powdered compound maintains crystallinity up to 165 °C. However, nanoballs remain stable up to 280 °C (Fig. S1, ESI), when the CuO residue begins to form. The amorphous phase occurs in the temperature range in which the m-BDC organic ligand still has not been degraded, according to thermovgravimetry. Having taking into account the latter, αMOP@Ei2-1 was produced by heating MOP@Ei2-1 at 240 °C during 1h (heating rate was 3 °C/min). This way, the adsorption capacity of the network was expected to be optimized.

In order to properly characterize the thermally activated αMOP@Ei2-1, IR spectroscopy and UV-Vis analyses were carried out. IR spectra of MOP@Ei2-1 and αMOP@Ei2-1 (Fig. S2, ESI) are similar. This fact means that there are no significant structural changes except for two bands: 1627 cm⁻¹ and 3390 cm⁻¹. The intense band at 1627 cm⁻¹, which turns wider for the activated compound, corresponds to the elongation of C-N bonds (related to coordinated DMF molecules). Changes in the band at 3390 cm⁻¹ correspond to the disappearance of H-bonds. Diffuse reflectance UV-Vis measurements (Fig. S3, ESI) show similar spectra for the original and the activated samples, except for the loss of intensity in the band at 1913 nm which is related to the loss of coordination and crystallization water molecules inside and outside cuboctahedra. Therefore, the latter characterization confirms, as expected, that nanoballs keep integrity. Taking into account these facts, αMOP@Ei2-1 was activated at 240 °C by removing solvent molecules. Obviously, at 240 °C, loss of the long-range organization is expected to take place. On the other hand, the absence of H₂O and DMF molecules in the network means that the accessible volume in the internal cavity of the nanoballs increases from 0.90 nm³ to 2.14 nm³ (Fig. 1). As a result, the porous αMOP@Ei2-1 can exhibit adequate room to accommodate guest molecules.

Adsorption experiments were performed in aqueous and ethanol solution, after testing the stability of MOP@Ei2-1 in these solvents (Fig. S4, ESI). Several dyes were tested as adsorbates: cationic methylene blue (MB) and rhodamine 6G (R6G), anionic methyl orange (MO) and congo red (CR), and neutral dimethyl yellow (DY) (Fig S5, ESI). Besides, iodine (I₂) was also tested. Typically, 10 mg of αMOP@Ei2-1 was added into 4 mL glass beaker containing 1 x 10⁻⁴ mol·L⁻¹ of MB, RB, MO, or CR aqueous solution and DY and I₂ ethanol solution. After 7 days, the colors of the solutions became pale (Fig. 2), indicating the adsorption process having been occurred.

The adsorption of dyes was confirmed by IR spectroscopy for MB, CR and DY (Fig. S6, ESI). For samples of αMOP@Ei2-1 loaded with MB, CR and DY a band at 1690 cm⁻¹ can be observed, which can be assigned to C-N bonds. Additionally, for αMOP@Ei2-1 samples loaded with CR and MB, two bands are observed at 1310 and 3590 cm⁻¹ associated with C-S and N-H bonds, respectively. The observance of these bands in the IR spectra confirms the successful immobilization of MB, CR and DY molecules into αMOP@Ei2-1 nanoballs.

In order to quantify the process, previous calibration was carried out by means of UV-Vis absorption at selected wavelengths.
Due to the presence of two kinetic steps, adsorption rate constants were calculated for the first one where most of the adsorption has taken place. Thus, calculated adsorption rate constants for MB, CR, I$_2$ and DY are $4.8 \times 10^{-2}$, $2.1 \times 10^{-2}$, $1.2 \times 10^{-1}$ and $2 \times 10^{-1}$ min$^{-1}$, respectively (Fig. S15, ESI).

It is worth mentioning that the sizes of MB, CR and DY are in the range of the dimensions for the square crevices (Fig. 1). However, the different kinetics of dye adsorptions can be attributed to the synergy among the dimensions, shapes (Table S1, ESI) and ionic strength. Thus, although the size of CR is larger than DY, the ionic strength of CR solution is higher than DY. Therefore, adsorption kinetics of CR is more rapid than DY. On the other hand, MB is smaller than CR, and this makes possible its faster adsorption.

Comparison of the results herein presented with others reported elsewhere$^{17}$ indicates that aMOP@Ei2-1 is among the best of the adsorption MOPs. Moreover, the adsorption velocity is remarkable for three of the four studied adsorbates. In fact, just the compound reported by Zhu et. al.$^{17b}$ is clearly superior to aMOP@Ei2-1.

Dye release experiments were also carried out soaking dye charged samples into NaCl aqueous solution. After 24 h the adsorbent was removed from the solution and the concentration of the liquid was measured by UV-Vis. The results indicate that the desorbed amount for MB is significantly high ($2.6 \times 10^{-3}$ mmol·L$^{-1}$, 30% of the adsorbed dye). For the other dyes desorption rates are much lower: CR: $1.43 \times 10^{-2}$ mmol·L$^{-1}$ (0.1%), DY: $4.05 \times 10^{-2}$ mmol·L$^{-1}$ (5%), and iodine: $1.94 \times 10^{-2}$ mmol·L$^{-1}$ (2.5%).

In summary, a good thermal and structural characterization of the original MOP@Ei2-1 has been required to design an appropriate thermal activation focused to optimize the adsorption capacity while keeping integrity of the nanoballs in aMOP@Ei2-1. Preliminary investigations for aMOP@Ei2-1 indicate that adsorption is size-dependent which can be used for the removal of emergent pollutants from natural waters. Rapidness in adsorption is the most relevant feature of aMOP@Ei2-1.

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Notes and references


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