Zeolitic imidazolate framework dispersions for the fast and highly efficient extraction of organic micropollutants

*Fernando Maya, Carlos Palomino Cabello, Sabrina Clavijo, José M. Estela, Víctor Cerdà, Gemma Turnes Palomino**

Department of Chemistry, University of the Balearic Islands, Cra. de Valldemossa km 7.5, Palma de Mallorca, E-07122, Spain.

Keywords: zeolitic-imidazolate frameworks, nanoporous materials, nanocrystal dispersions, micropollutants, phthalate esters.

Abstract: Development of advanced strategies for the extraction and preconcentration of trace levels of pollutants is essential for the quality control of water resources. A new procedure for the fast and highly efficient extraction of organic micropollutants from water using dispersions of zeolitc imidazolate framework-8 (ZIF-8) crystals in a mixture of solvents is reported. The synergistic effect of using ZIF-8 dispersions in mixtures of water miscible and immiscible solvents enhances mass transfer and greatly improves extraction kinetics and capacity in

comparison with the use of porous crystals or solvent microextraction separately. The effect of the ZIF-8 crystal size and surface composition has been evaluated using four different ZIF-8 samples spanning the micro- and nanometer range. The relevant parameters involved in the extraction such as the composition of the dispersion medium, the amount of ZIF-8 crystals, the extraction time, or the volume of dispersion required to ensure the maximum extraction efficiency, has also been studied using diethyl phthalate as a model compound. The use of 26 nm ZIF-8 crystals obtained using *n*-butylamine modulated synthesis has shown very fast extraction kinetics and excellent enrichment factors ranging from 150 to 380 for a mixture of six phthalate esters listed as priority pollutants by the United States EPA, allowing to reach detection limits below the ng/L.

1. Introduction

Water is one of the human basic needs,[1] and the quality control of water resources is crucial in order to avoid short- or long-term problems derived from water pollution.[2,3] The quality control of water often involves the use of advanced materials for the efficient enrichment of toxic micropollutants present on the environment at very low levels prior to their detection and quantification.[4,5] In this sense, porous materials, like porous carbons,[6] surface-modified silica,[7] porous polymers,[8] and metal-organic frameworks (MOFs) and related compounds,[9-12] are currently under active investigation as advanced sorbents for pollutant extraction and preconcentration.

MOFs, obtained by linking metal cations (or cationic metal clusters) with organic linkers, have attracted significant interest in the last years mainly due to the advantage of showing a large variety of structural types and chemical compositions, high surface area and permanent nanoscale porosity.[13,14] MOFs have been widely studied as materials for catalysis,[15,16] gas storage and separation,[17,18] sensing and drug delivery,[19] and, more recently, the first analytical applications of MOFs have emerged.[20] In this field, MOFs have shown to be promising materials as sorbents for sample preparation,[21-23] as chromatographic stationary phases,[24-29] as well as for the development of improved detection systems[29,30] and sensors.[31-33] However, MOFs crystalline powders generally possess a random crystal size and shape, which makes troublesome their direct application and have led to engineer hybrid materials containing them, such as flow through supports,[34] magnetic beads,[35] beads coated with a MOF shell[36], or MOF crystals entrapped on a porous monolith[37].

Among the different types of MOFs, zeolitic imidazolate frameworks (ZIFs)[38-40] are a subclass of MOFs with zeolite-type topologies composed of four-coordinated transition metal cations linked by imidazole ligands. The ZIF-8,[41,42] with a cubic sodalite-related framework obtained by linking zinc atoms through 2-methylimidazole ligands (Fig. S1), is a very attractive candidate for analytical applications because of its high surface area, hydrophobicity and exceptional chemical and thermal stability. The synthesis of ZIF-8 is highly versatile facilitating the integration of this material into sensors or devices.[31] However, the direct use of ZIF-8 crystals as sorbents is troublesome due to the difficulty to prepare packed beds with irregularly shaped crystals, and to the poor contact between phases when the hydrophobic crystals are directly added to an aqueous phase. By the former reasons, the reported applications of as-synthesized ZIF-8 crystals for the extraction of pollutants from water require of long extraction times,[43,44] the fabrication of ZIF-8 extraction containers,[45-47] or the use of engineered hybrid ZIF-8 supports.[48]

Herein we report on the use of dispersions of ZIF-8 crystals in binary water miscible and inmiscible solvent mixtures as a high-performance synergetic approach for the extraction and preconcentration of environmental pollutants such as the rhodamine B dye, one of the most important xanthene dyes and dye pollutants from the textile industry,[49] and a mixture of six phthalate esters listed as priority pollutants by the European Environmental Agency and the US Environmental Protection Agency (EPA)[50] (chemical structures showed in Fig. S2). The influence on the extraction performance of the ZIF-8 crystal size and surface composition as well as other relevant parameters, such as the composition of the dispersion medium, the amount of ZIF-8 crystals, the extraction time, or the volume of dispersion required to ensure the maximum extraction efficiency, has also been evaluated. The reported procedure, once optimized, has allowed to obtain very high enrichment factors for phthalate esters in a very short time and could be easily extended to other families of organic pollutants.

2. Experimental

2.1. Chemicals. Methanol (≥ 99.8%), dichloromethane (≥ 99.9%), acetonitrile (≥ 99.9%), ethyl acetate (≥ 99.9%), hexane (≥ 96%), $Zn(NO_3)_2.6H_2O$ (98%), 2-methylimidazole (99%), *n*-butylamine (≥ 99.5%), sodium formate (99%), Rhodamine B (≥ 95%) and diethyl phthalate (99.5%), were purchased from Sigma-Aldrich and used as received. A 2000 µg/mL EPA phthalates esters mix analytical standard in hexane was purchased from Supelco, containing dimethyl phthalate (DMP); diethyl phthalate (DEP); di-n-butyl phthalate (DBP); Bis(2-ethylhexyl) phthalate (DEHP); butyl benzyl phthalate (BBP); di-*n*-octyl phthalate (DNOP).

2.2. Synthesis. ZIF-8 samples of different crystal size were synthesized following procedures reported in the literature.[51,52]

For ZIF-8 nanocrystals (ZIF-NC) synthesis two solutions, one of 810.6 mg (9.874 mmol) of 2-methylimidazole (Hmim) in 50 mL of methanol and another one of 734.4 mg (2.469 mmol) of $Zn(NO_3)_2.6H_2O$ in 50 mL of the same solvent, were prepared. The solution containing the organic ligand was slowly poured into the other one under stirring. The solution mixture was left, without stirring, at room temperature for 24 h. The resulting white solid was separated by centrifugation, washed three times with fresh methanol and dried at room temperature.

ZIF-8 crystal size can be controlled by the addition of a modulator agent into the organic ligand solution.[51] Following this approach, smaller ZIF-8 nanocrystals (ZIF-NCB) were obtained by addition of 0.975 mL (9.874 mmol) of *n*-butylamine to the Hmim solution. Micro-sized ZIF-8 crystals (ZIF-MC) were prepared by adding 671.5 mg (9.874 mmol) of sodium formate to the Hmim solution. The rest of synthesis conditions were kept the same as in the preparation of ZIF-NC sample.

Larger ZIF-8 microcrystals (ZIF-C) were obtained using the same reaction mixture as that used in the formate-modulated microcrystal synthesis. The reaction solution was then transferred to a closed vessel and heated in a microwave oven at 373 K for 4 h.

2.3. Sample characterization. Powder X-ray diffraction data were collected using CuKα (λ = 1.54056 Å) radiation on a Siemens D5000 diffractometer. Particle morphology was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using a

Hitachi S-3400N microscope operated at 15 kV and a Hitachi ABS microscope operated at 100 kV, respectively.

2.4. Micropollutant extraction using ZIF-8 crystals dispersions. Unless stated, a typical extraction procedure was as follows. A binary solvent mixture of dichloromethane and methanol (20/80, v/v %) was prepared. ZIF-8 crystals were added to a final concentration of 5 mg of ZIF-8 per mL of solvent mixture, and re-dispersed in it by sonication for 30 min. 9 mL of an aqueous sample containing the organic pollutant were placed in a screw-capped glass vial of the appropriate size and 1 mL of the ZIF-8 crystals dispersion was rapidly injected in it using a 1 mL glass syringe with a metallic needle. The mixture was vortexed for 1 min, and centrifuged for another 1 min at 4000 rpm. The aqueous phase was finally separated from the dichloromethane soaked ZIF-8 crystals by decantation. The quantification of the remaining amount of pollutant in the aqueous phase was determined by direct UV-vis spectrophotometry. Rhodamine B absorbance was measured at 553 nm. DEP absorbance was measured at 275 nm.

For the enrichment of pollutants prior to GC-MS analysis (see detailed GC-MS analysis conditions in the supplementary information), the sediment containing the ZIF-8 crystals after centrifugation was dried under a gentle steam of nitrogen in order to remove the dichloromethane soaking the crystals, as well as the undesired remaining water. Extracted species were desorbed using 0.25 mL of ethyl acetate under sonication for 5 min. Finally, the extract was centrifuged for 2 min at 4000 rpm and most of the solvent was retrieved with a microsyringe and placed in a small-volume vial for the subsequent gas chromatography – mass spectrometry analysis.

3. Results and discussion

3.1. Extraction procedure

The basis of the developed new extraction procedure using ZIF-8 dispersions in solvent mixtures is similar to that of the dispersive liquid-phase microextraction technique.[53] In a typical extraction experiment, ZIF-8 crystals were dispersed in a homogeneous binary solvent mixture composed by a water miscible solvent (methanol), and containing a smaller amount of a water non-miscible solvent (dichloromethane, 5-25%). The solvent mixture containing the dispersed ZIF-8 crystals was rapidly injected into an aqueous solution containing the organic pollutant, and the non-miscible solvent was phase separated releasing small droplets which were dispersed throughout the aqueous phase due to the action of the water miscible solvent. The ZIF-8 crystals due to the hydrophobic character of their surface tend to confine in the water non-miscible solvent droplets, which gradually settle down due to its higher density regarding to water. To illustrate the operation of the developed procedure, Fig. 1 shows its application for the extraction of rhodamine B. The direct addition of ZIF-8 nanocrystals into the rhodamine B aqueous solution does not allow good contact between phases (Fig. 1a) and complete extraction was not achieved even after 24 hours under stirring conditions (Fig. 1b). However, using the developed procedure the organic molecule was completely extracted after only 1 min of vortex mixing and 1 min of centrifugation (at 4000 rpm) (Fig. 1c), which proves that the described solvent-assisted solid-phase extraction synergistic approach allows the rapid and efficient extraction of organic pollutants. In the case of pure solvent extraction, using an identical mixture of solvents and extraction conditions in the absence of ZIF-8 crystals, the extraction of the organic pollutant was also incomplete (Fig. 1d).

3.2. Synthesis and characterization of ZIF-8 crystals

An interesting method to control the size and shape of some MOFs is the addition of monodentate ligands, named modulators, which compete with the bridging multidentate linkers for coordination to the metal. This competition regulates the nucleation and growth rates and the final crystal size.[51,52,54] Following this approach, four ZIF-8 samples with different crystal sizes were prepared in order to evaluate the influence of the crystal size on the extraction performance (see experimental section for synthesis details).

Fig. 2a shows the X-ray powder diffraction patterns of the synthesized samples. All diffraction lines of the diffractograms can be assigned to a ZIF-8 structure type, indicating that in all cases pure-phase ZIF-8 crystals were obtained without the occurrence of any other transient crystalline phase. Successful synthesis of ZIF-8 was also checked by FT-IR spectroscopy (Fig. S3). All the spectra show the typical bands of the ZIF-8 metal-organic framework.[38,51,52] No significant differences were observed among the different ZIF-8 samples prepared.

The morphology and crystal size of the prepared materials were studied by Scanning Electron Microscopy (SEM) (Fig. 2c to 2e) except in the case of the smallest nanocrystals prepared using *n*-butylamine as modulator, which were examined by Transmission Electronic Microscopy (TEM) (Fig. 2b). Statistical analysis performed on several electronic micrographs showed that room temperature synthesis performed in the absence of modulator ligand (ZIF-NC) or in the presence of n-butylamine (ZIF-NCB) (Fig. 2c, 2b, and S4) produced nanoparticles with globular shape and a mean particle size of about 148 and 26 nm, respectively, probably due to the early termination of the crystal growth. In the case of formate-modulated synthesis, individual microcrystals with rhombic dodecahedral morphology with an average size of 3 and 12 μm, respectively, were obtained (Fig. 2d, 2e, S5 and S6).

3.3. Application to the extraction of rhodamine B

To check the solvent-assisted solid-phase extraction procedure developed, an initial test for the extraction of the dye rhodamine B was conducted (see experimental section for extraction procedure details). Rhodamine B is a well-known water tracer fluorescent and is widely used as a colorant in textiles and food,[55] being one of the most important dye pollutants of textile industry.[56]

Results obtained using dispersions in methanol/dichloromethane of the four different ZIF-8 samples prepared, together with those obtained using only the solvent mixture (in absence of ZIF crystals) or only the ZIF crystals (in absence of the dichloromethane/methanol mixture), are shown in Fig. 3. It can be observed that the uptake of rhodamine B increases while the size of the ZIF-8 crystal decreases, and that a remarkable increase was obtained when using the smallest ZIF-8 crystals (26 nm). Besides that, results depicted in Fig. 3 show that the combined action of the dispersed ZIF-8 crystals in the binary solvent mixture provided, in all cases, at least a 4-5 fold enhancement of the uptake of rhodamine B compared to the sum of the uptake values obtained using separately either the solvent mixture or the ZIF crystals, showing a synergetic effect. The best results were obtained when using the butylamine-modulated ZIF-8 nanocrystals as solid sorbent, which results in a 23-fold increase for the extraction of rhodamine B. The significant increase in the uptake of rhodamine B is probably due to the smaller crystal size and concomitant increase of the effective surface area for extraction, although the contribution of other factors, such as the presence of dual micro- and mesoporosity, as previouly reported by other authors,[52] the incorporation of n-butylamine molecules on the crystal surface (with the subsequent modification of surface properties, *vide infra*) or the fact that smaller crystals can generate smaller droplets of the hypdrophobic solvent, enhancing the effective contact area between the aqueous and the organic phase, cannot be discarded.

To assess the extraction performance of ZIF-8 in comparison with other materials typically used for the extraction of organic compounds, a comparison with two of the most commonly used solid sorbents, silica-C18 beads and activated carbon, was performed following the same procedure used in the case of ZIF-8 crystals (Fig. 3). The extraction ability of the dispersions of ZIF-8 crystals was always higher than that of activated carbon (DISP-AC). In the case of the dispersion of silica-C18 beads (DISP-C18), the rhodamine B uptake was similar to those of ZIF-8 microcrystals and lower to those of ZIF-8 nanocrystals, especially to those prepared using *n*-butylamine as modulator, which showed a 5-fold higher uptake in comparison with commercial silica-C18 beads, and a 12-fold increase in comparison with activated carbon.

3.4. Application to the extraction of diethyl phthalate. Extraction conditions optimization

Phthalate esters are widely used as additives to reinforce the properties of plastic materials. When plastic is degraded phtalates can be released to the environment. Human exposure to phthalates is because of direct use of plastic products containing them, or indirectly due to general environmental contamination. For example, the diethyl phtalate (DEP) is a commonly used phthalate ester, which is suspected to cause damage to the nervous system as well as to the reproductive organs.[56,57] For this, DEP and other commonly occurring phtalates have been classified as priority pollutants by the European Environmental Agency and the US Environmental Protection Agency (EPA).[44,50]

The uptake of DEP using alkylamine-modulated ZIF-8 crystals, a dispersion of dichloromethane in methanol, and the combined action of both using ZIF-8 crystals of different sizes was studied measuring the UV absorption of the remaining DEP in the aqueous phase after extraction (Fig. 4a). DEP uptake using only the alkylamine-modulated ZIF-8 nanocrystals was almost negligible in the short extraction time used (1 min). As in the case of rhodamine B extraction, the DEP uptake increased when using under the same conditions ZIF crystals dispersed in the solvent mixture, reaching its maximum value (approximately 370 mg DEP/g ZIF-8) when using the alkylamine-modulated ZIF-8 nanocrystals (Fig. 4b). However, in contrast with rhodamine B extraction, dispersions of ZIF-8 nanocrystals prepared in the absence of a modulator agent showed the lowest DEP uptake, suggesting that, in this case, the adsorption phenomenon depends on other factors apart from the surface area. An explanation could be that the presence during the synthesis of modulator agents which can be incorporated on crystals surface, as already reported by other authors,[53,58,59] may result in crystals with different surface properties and, as consequence, different surface affinity to DEP molecules. The incorporation of *n*-butylamine on ZIF-NCB nanocrystals was demostrated by the presence of *n*-butylamine signals in the ^{1}H NMR spectrum of the solution obtained by acid mineralization of the crystals in deuterium chloride (Fig. S7). From this spectrum a 2-methylmidazole/n-butylamine ratio of approximately 20/1 was determined, which is significant since the *n*-butylamine should be only present on the surface of the crystals. However, the amount of *n*-butylamine released when the ZIF-NCB nanocrystals were dispersed in the solvent mixture was almost negligible, since it was detected at trace level using GC-MS (Fig. S8). This fact reinforces the hypothesis that the *n*-

butylamine present in the crystal is coordinated to the surface modifying its properties and facilitating the extraction of hydrophobic organic molecules.

As the surface charge of ZIF-8 can be affected by the pH of the extraction medium,[41] its effect on the DEP adsorption was studied in the pH range from 2 to 12 for solvent-assisted solid-phase extraction using nanocrystals obtained in both, presence or absence of a modulator agent. The DEP uptake was not significantly influenced by the pH of the medium when the extraction was carried out using ZIF-8 nanocrystals prepared in the presence of *n*-butylamine (Fig. S9). In the case of ZIF-8 nanocrystals prepared in the absence of the modulator agent (Fig. S10), the extraction of DEP was highly influenced by the pH, obtaining the best results at pH≤ 4, a value lower than that used in the previous discussed extraction studies, which were conducted at a sligthly basic pH (7-8). However, although the DEP amount extracted by ZIF-8 nanocrystals obtained in absence of modulator molecules increases when pH decreases, it is necessary to work at pH lower than 4 and to increase the extraction time by a factor of ten to reach an uptake similar to that of *n*-butylamine modulated ZIF nanocrystals. Because of the much higher adsorption capacity shown by the alkylamine-modulated ZIF-8 nanocrystals, they were selected for further studies aimed to stablish the best extraction conditions.

Dichloromethane is required to disperse the crystals throughout the aqueous phase. To assess the influence on the extraction efficiency of the amount of dichloromethane present in the solvent mixture, solutions containing different concentrations (from 10 to 25%) of dichloromethane were tested. Results depicted in Fig. 5a show that to achieve a good dispersion and a high DEP extraction yield a minimun concentration of 17% of dichloromethane is needed. In order to obtain a high uptake of DEP and concomitantly use the smallest possible volume of solvent we selected a concentration of 20% of dichloromethane for further studies.

Fig. 5b shows the effect of ZIF-8 concentration on the extraction performance. The addition of just 1 mg of ZIF-8 crystals per mL of dispersing solvent mixture enhanced the uptake of DEP by a factor of nearly 4. As expected, the amount of DEP extracted increases as the amount of ZIF-8 increases, reaching its maximum value at a concentration of approximately 10 mg of ZIF-8 crystals per ml of solvent mixture.

Fig. 5c shows the effect of the mixing time on the percentage of DEP extracted. Extraction using the developed procedure was very fast and an 80% of recovery was attained after just 1 min of mixing. This fact is attributed to the enhanced contact between phases when dispersions of ZIF-8 nanocrystals in dichloromethane/methanol mixtures are used.

Finally, Fig. 5d shows the influence of the volume ratio between the organic phase containing the ZIF-8 crystals and the aqueous phase. Best results were obtained by the addition of 1 mL of dispersion to a volume of 9 mL of aqueous sample.

3.5. Application to the enrichment of phthalate esters at trace levels

Under the previously optimized experimental conditions, the performance of the different ZIF-8 samples prepared was evaluated for the enrichment of trace levels of 6 phthalate esters, catalogued by the US Environmental Protection Agency as priority environmental pollutants. For that, 9 ml of a 20 μg/L phtalates mix standard aqueous solution was vortexed for 1 min with 1 ml of a dichloromethane/methanol solvent mixture (20/80, v/v%) containing 5 mg of ZIF-8 crystals. After extraction, the phthalate esters retained by the solid were desorbed using an appropriate solvent, and a small amount of the solvent used for desorption was injected into a GC-MS (see experimental section and supplementary information for details). Fig. 6 shows the chromatograms obtained for the phtalates mix standard solution, before and after solvent-assisted solid-phase extraction**.** The intensity of the 6 phthalate peaks markedly increased after extraction, showing the efficiency of the developed approach.

Fig. 7 compares the enrichment factors calculated from the ratio of the peak areas obtained from the GC-MS chromatograms with and without extraction. In agreement with results described for DEP extraction (*vide supra*) and with data previously reported by other authors,[44] very low enrichment factors, between 3 and 9, were obtained for all six phthalate esters when using ZIF-8 nanocrystals prepared in the absence of modulator agent as solid sorbent. Better results, with enrichment factors between 18 and 177, were obtained in the case of formate-modulated ZIF-8 microcrystals. As in the case of rhodamine B and DEP, the best results were achieved when the extraction is perfomed using *n*-butylamine-modulated ZIF-8 nanocrystals. The high enrichment factors obtained in this last case (between 150 and 380) demonstrate the feasibility and the high performance of the developed procedure for extraction and preconcentration of phtalates esters present in water even at very low levels. In fact, using *n*-butylamine-modulated ZIF-8 nanocrystals, the detection limits for the selected phthalate esters are below the ng/L for all 6 phthalate esters, a value much lower than those reported previously obtained using other extraction procedures (see Table S1).

4. Conclusions

This contribution presents a simple, rapid and highly efficient procedure for the enhanced extraction and preconcentration of organic environmental pollutants by using dispersions of porous solids in binary solvent mixtures, as exemplified using ZIF-8 crystals for the efficient adsorption of rhodamine B and phthalate esters. The binary solvent mixture, containing a dispersant water-miscible solvent and an extractant/ZIF-8 container solvent which is non-miscible with water, facilitates the use of porous ZIF-8 crystals for the extraction of micropollutants from water. The synergistic action of solvent extraction containing a porous solid allows to obtain excellent enrichment factors in a very short time in comparison with classical solvent extraction or direct extraction using only ZIF-8 crystals, specially in the case of *n*-butylamine modulated ZIF-8 nanocrystals. The superior performance of n-butylamine modulated ZIF-8 nanocrystals is attibutted mainly to their small crystal size and the more hydrophobic character of their surface. The simplicity of this approach can be extended to other MOFs and organic solvent mixtures, as well as applied to the extraction and preconcentration of different families of organic pollutants, enabling a plethora of new possibilities for chemical extraction.

Acknowledgments

The Spanish Ministerio de Economía y Competitividad (MINECO) and the European Funds for Regional Development (FEDER) are gratefully acknowledged for financial support through Project CTQ2013-47461-R. C.P. acknowledges the Spanish Ministerio de Educación y Ciencia (pre-doctoral fellowship) and F.M. that of the Government of the Balearic Islands and the European Social Fund (postdoctoral fellowship).

References

1 P. H. Gleick, *Water Int.*, 1996, **21**, 83.
2 R. P. Schwarzenbach, T. Egli, T. B. Hofstetter, U. von Gunten and B. Wehrli, *Annu. Rev. Environ. Resourc.*, 2010, **35**, 109.
3 M. Harada, *Critical Reviews in Toxicology*, 1995, **25**, 1.
4 Q. Liu, J. Shi, J. Sun, T. Wang, L. Zeng and G. Jiang, *Angew. Chem. Int. Ed.*, 2011, **50**, 5913.
5 L. Gao, C. Y. V. Li, K. Y. Chan and Z. N. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 7209.
6 A. Banerjee, R. Gokhale, S. Bhatnagar, J. Jog, M. Bhardwaj, B. Lefez, B. Hannoyer and S. Ogale, *J. Mater. Chem.*, 2012, **22**, 19694.
7 L. T. Gibson, *Chem. Soc. Rev.*, 2014, **43**, 5173.
8 H. Wang, H. Zhang, Y. Lv, F. Svec and T. Tan, *J. Chromatogr. A*, 2014, **1343**, 128.
9 S. Kitagawa, R. Kitaura and S. I. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334.
10 J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3.
11 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444-1.
12 S. T. Meek, J. A. Greathouse and M. D. Allendorf, *Adv. Mater.*, 2011, **23**, 249.
13 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
14 M. Eddaoudi, H. Li and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 1391.
15 J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
16 A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606.
17 J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
18 S. Ma and H. C. Zhou, *Chem. Commun.*, 2010, **46**, 44.
19 R. J. Kuppler, D. J. Timmons, Q-R. Fang, J-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang and H-C. Zhou, *Coord. Chem. Rev.*, 2009, **253**, 3042.
20 Z. Y. Gu, C. X. Yang, N. Chang and X. P. Yan, *Acc. Chem. Res.*, 2012, **45**, 734.
21 Y. Hu, C. Song, J. Liao, Z. Huang and G. Li, *J. Chromatogr. A*, 2013, **1294**, 17.
22 X. Li, J. Xing, C. Chang, X. Wang, Y. Bai, X. Yan and H. Liu, *J. Sep. Sci.*, 2014, **37**, 1489.
23 Z. Y. Gu, G. Wang and X. P. Yan, *Anal. Chem.*, 2010, **82**, 1365.
24 A. Centrone, E. E. Santiso and T. A. Hatton, *Small*, 2011, **7**, 2356.
25 C. X. Yang, Y. J. Chen, H. F. Wang and X. P. Yan, *Chem. Eur. J.*, 2011, **17**, 11734.
26 C. X. Yang and X. P. Yan, *Anal. Chem.*, 2011, **83**, 7144.
27 Z. Y. Gu and X. P. Yan, *Angew. Chem. Int. Ed.*, 2010, **49**, 1477.
28 S. M. Xie, Z. J. Zhang, Z. Y. Wang and L. M. Yuan, *J. Am. Chem. Soc.*, 2011, **133**, 11892.
29 K. Sugikawa, S. Nagata, Y. Furukawa, K. Kokado and K. Sada, *Chem. Mater.*, 2013, **25**, 2565.
30 L. E. Kreno, N. G. Greeneltch, O. K. Farha, J. T. Hupp and R. P. Van Duyne, *Analyst*, 2014, **139**, 4073.
31 G. Lu and J. T. Hupp, *J. Am. Chem. Soc.*, 2010, **132**, 7832.
32 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105.
33 C. Cui, Y. Liu, H. Xu, S. Li, W. Zhang, P. Cui and F. Huo, *Small*, 2014, **10**, 3672.
34 A. Saeed, F. Maya, D. J. Xiao, M. Najam-ul-Haq, F. Svec and D. K. Britt, *Adv. Funct. Mater.*, 2014, **24**, 5790.
35 Z. Xiong, Y. Ji, C. Fang, Q. Zhang, L. Zhang, M. Ye, W. Zhang and H. Zou, *Chem. Eur. J.*, 2014, **20**, 7389.

36 Y. Y. Fu, C. X. Yang and X. P. Yan, *Chem. Eur. J.*, 2013, **19**, 13484.
37 Y. Y. Fu, C. X. Yang and X. P. Yan, *Chem. Commun.*, 2013, **49**, 7162.
38 K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *P. Natl. Acad. Sci. USA*, 2006, **103**, 10186.
39 A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe, and O. M. Yaghi, *Acc. Chem. Res.*, 2010, **43**, 58.
40 R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875.
41 H. Wu, W. Zhou and T. Yildirim, *J. Am. Chem. Soc.*, 2007, **129**, 5314.
42 D. W. Lewis, A. R. Ruiz-Salvador, A. Gómez, L. M. Rodriguez-Albelo, F. –X. Coudert, B. Slater, A. K. Cheetham and C. Mellot-Draznieks, *CrystEngComm.*, 2009, **11**, 2272.
43 J. Q. Jiang, C. X. Yang and X. P. Yan, *ACS Appl. Mater. Inter.*, 2013, **5**, 9837.
44 N. A. Khan, B. K. Jung, Z. Hasan and S. H. Jhung, *J. Hazard. Mater.*, 2015, **282**, 194.
45 D. Ge and H. K. Lee, *J. Chromatogr. A*, 2011, **1218**, 8490.
46 D. Ge and H. K. Lee, *J. Chromatogr. A*, 2012, **1263**, 1.
47 D. Ge and H. K. Lee, *J. Chromatogr. A*, 2012, **1257**, 19.
48 N. Chang, Z. Y. Gu, H. F. Wang and X. P. Yan, *Anal. Chem.*, 2011, **83**, 7094.
49 P. Wilhelm and D. Stephan, *J. Photochem. Photobiol. A*, 2007, **185**, 19.
50 http://water.epa.gov/scitech/methods/cwa/organics/upload/2007_07_10_methods_method_organics_606.pdf.
51 J. Cravillon, S. Munzer, S. J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2009, **21**, 1410.
52 J. Cravillon, R. Nayuk, S. Springer, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2011, **23**, 2130.
53 M. Rezaee, Y. Yamini and M. Faraji, *J. Chromatogr. A*, 2010, **1217**, 2342.
54 M. Sindoro, N. Yanai, A. -Y. Jee and S. Granick, *Acc. Chem. Res.,* 2014, **47**, 459.
55 R. Jain, M. Mathur, S. Sikarwar and A. Mittal, *J. Environ. Manag.*, 2007, **85**, 956.
56 https://www.fishersci.ca/viewmsds.do?catNo=AC419000010.
57 I. Colón, D. Caro, C. J. Bourdony and O. Rosario, *Environ. Health Perspect.*, 2000, **108**, 895.
58 S. H. Swan, *Environ. Res.*, 2008, **108**, 177.
59 A. Umemura, S. Diring, S. Furukawa, H. Uehara, T. Tsuruoka and S. Kitagawa, *J. Am. Chem. Soc.*, 2011, **133**, 15506.
60 M. Sindoro, A-Y. Jee and S. Granick, *Chem. Commun.*, 2013, **49**, 9576.

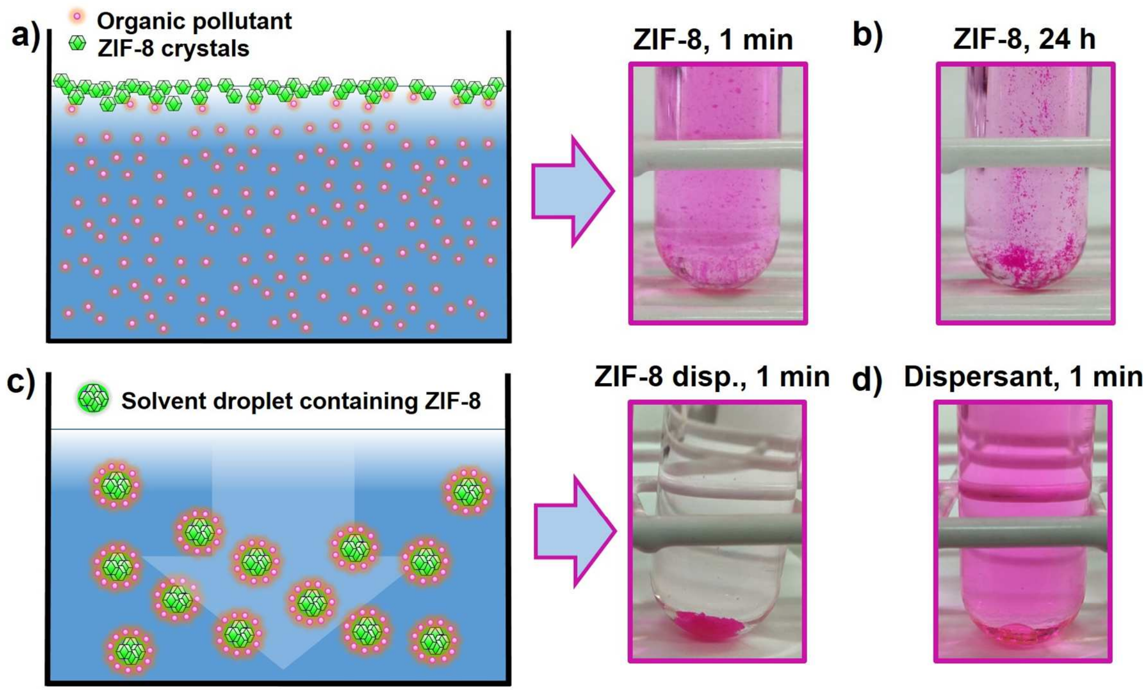

Fig. 1 Extraction of rhodamine B (10 µM, 9 mL) in water by direct addition of ZIF-8 crystals after a) 1 h and b) 24 h. Addition of c) an identical amount of ZIF-8 crystals dispersed in 1 mL of a dicholoromethane/methanol mixture (20/80, v/v%), and d) an identical solvent mixture in the absence of ZIF-8 crystals.

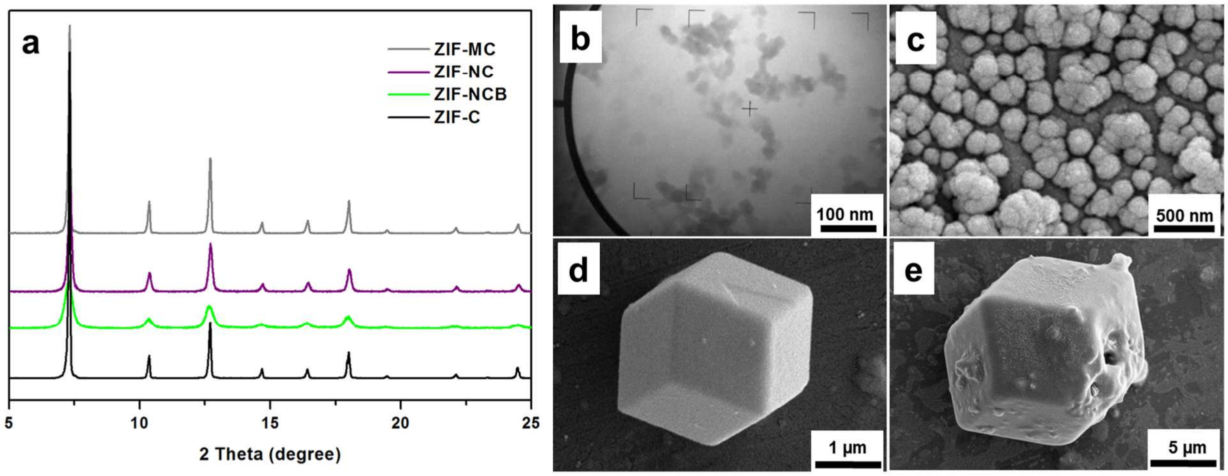

Fig. 2 a) Powder X-ray diffraction patterns of the different ZIF-8 samples synthesized: ZIF-NCB, *n*-butylamine modulated nanocrystals; ZIF-NC, nanocrystals; ZIF-MC, formate modulated microcrystals; and ZIF-C, formate modulated microcrystals prepared at 373 K. TEM image of ZIF-NCB (b). SEM images of ZIF-NC (c), ZIF-MC (d), and ZIF-C (e).

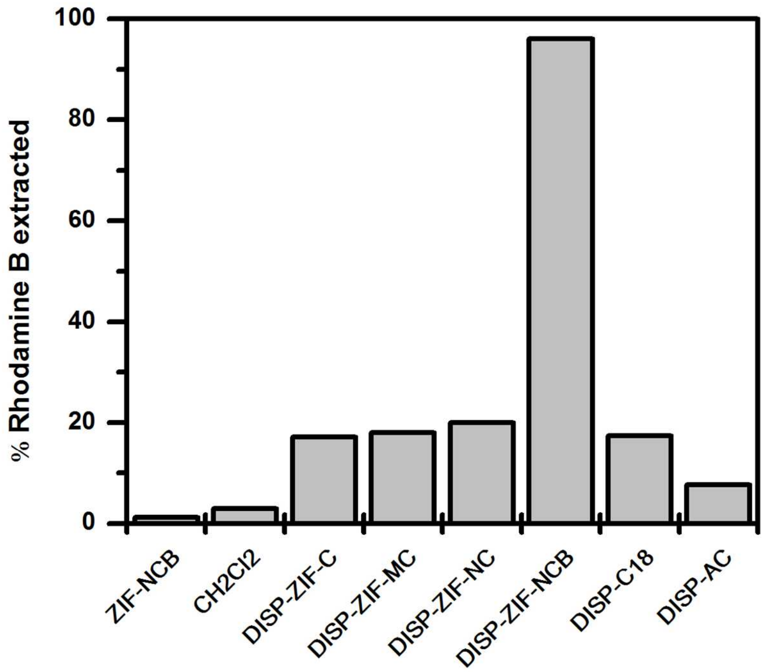

Fig. 3 Percentage of Rhodamine B extracted using dispersions of ZIF-8 crystals of different size. Results obtained using only the solvent mixture (CH2Cl2), only the butylamine-modulated ZIF-8 crystals (ZIF-NCB) and dispersions of activated carbon (DISP-AC) and silica-C18 beads (DISP-C18) are also shown for the sake of comparison. See experimental section for details on the extraction procedure.

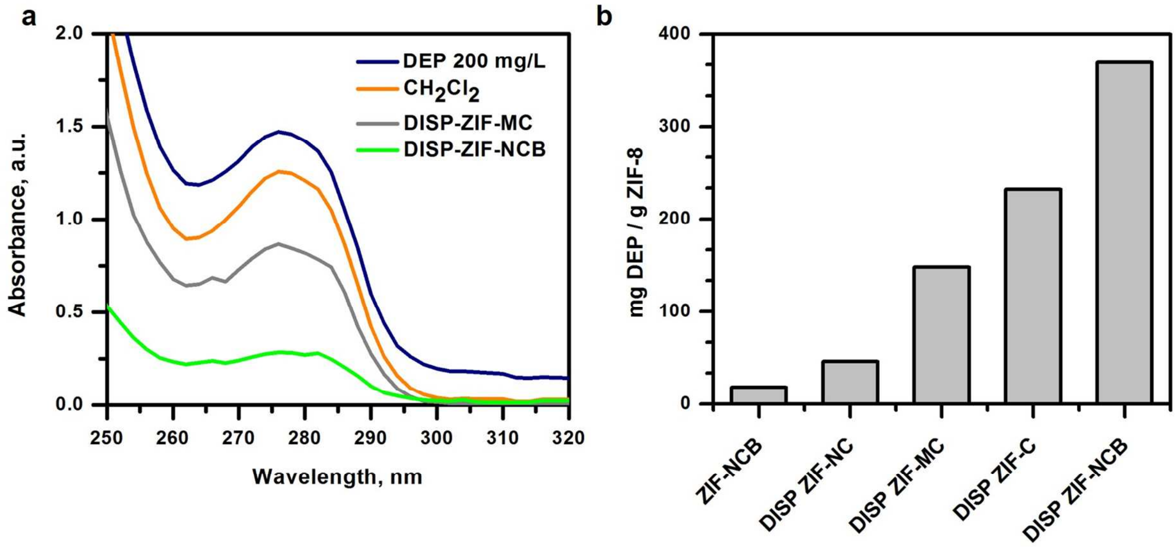

Fig. 4 a) UV-vis spectra of a 200 mg/L diethyl phthalate (DEP) solution before and after extraction with a dispersion without (CH2Cl2) and with 5 mg/mL of both ZIF-8 microcrystals (DISP-ZIF-MC) and ZIF-8 nanocrystals synthesized using *n*-butylamine as modulator agent (DISP-ZIF-NCB). b) Quantification of the amount of DEP extracted by using different ZIF-8 crystals. The contribution of DEP extraction by the dichloromethane/methanol mixture has been

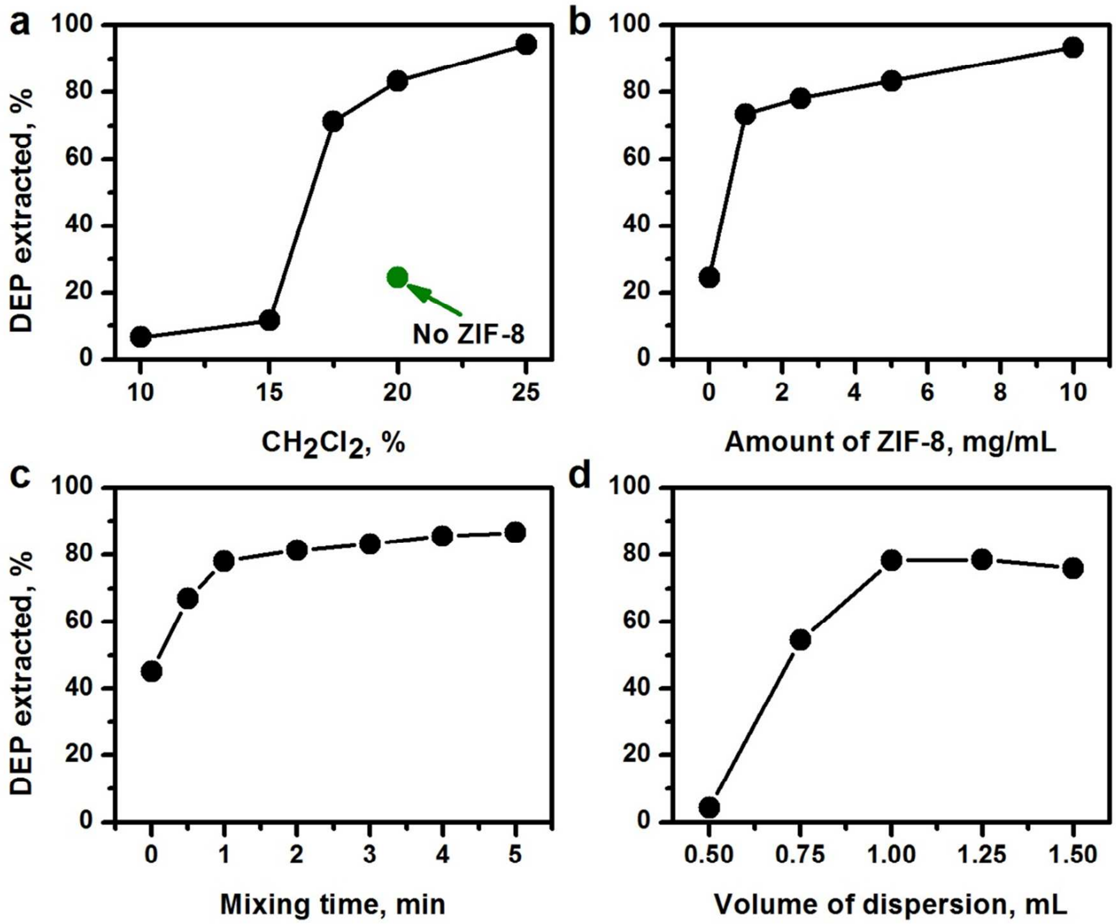

Fig. 5 Effect on the extraction of DEP of a) the amount of dichloromethane, b) the amount of ZIF-8 crystals, c) the vortex-assisted mixing time and d) the volume ratio between the methanol/dichloromethane mixture containing ZIF-8 crystals and the aqueous phase containing DEP. All the studies have been performed using *n*-butylamine-modulated ZIF-8 nanocrystals.

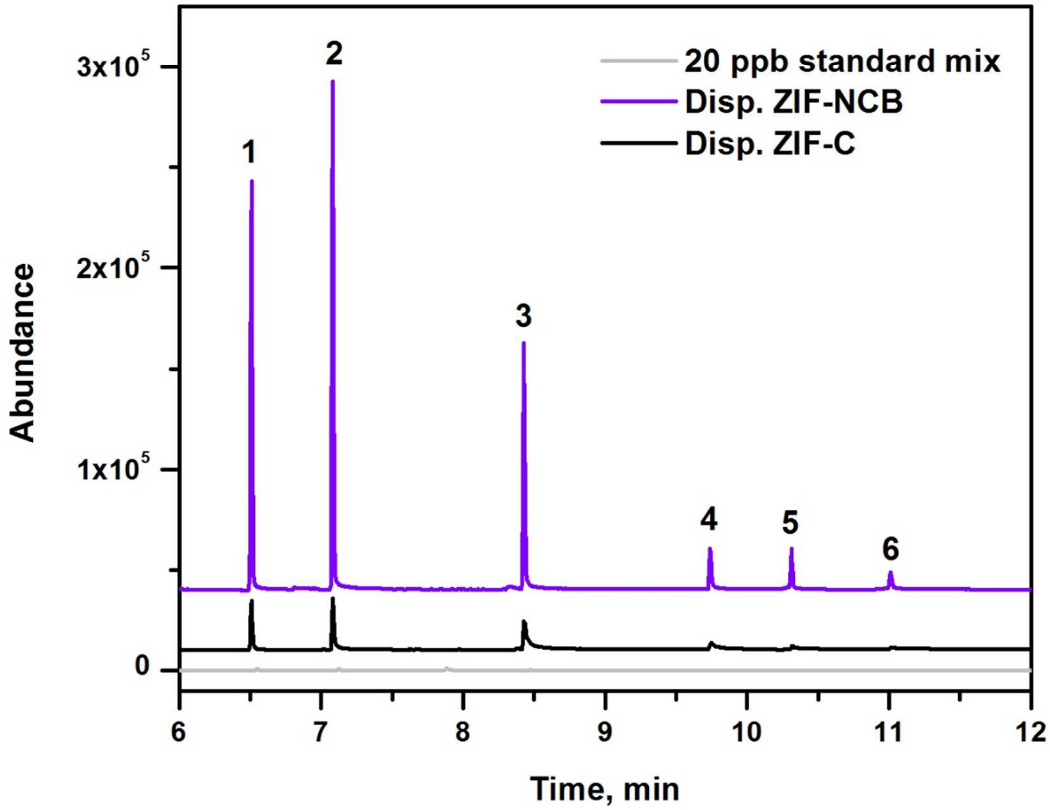

Fig. 6 GC-MS chromatograms of a mixture of 6 phthalate esters obtained by direct injection of a 20 µg/L standard and after solvent-assisted porous solid sorbent extraction using the larger ZIF-8 microcrystals (ZIF-C) and the ZIF-8 nanocrystals synthesized using *n*-butylamine as modulator agent (ZIF-NCB). Peaks: 1, DMP; 2, DEP; 3, DBP; 4, DEHP; 5, BBP; 6, DNOP.

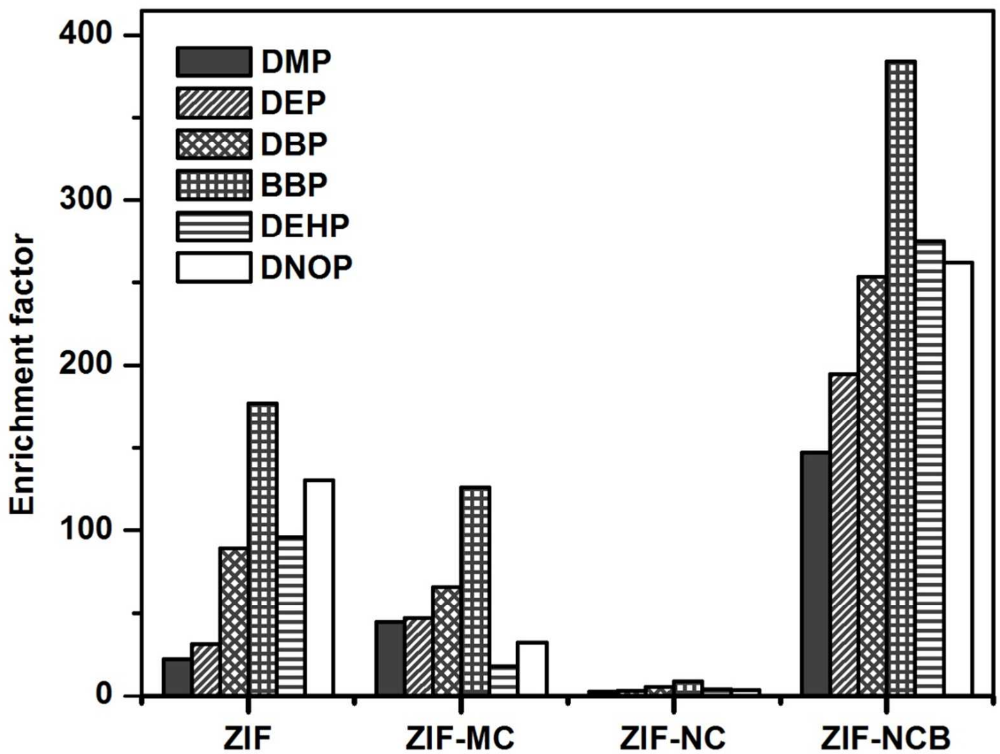

Fig. 7 Enrichment factors obtained for a mixture of six phthalate esters after solvent-assisted extraction using ZIF-8 crystals of different size.