# Highly hydrophobic ZIF-8 particles and application for oil-water separation

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ABSTRACT

ZIF-8(zinc-methylimidazolate framework-8), one of the zeolitic imidazolate frameworks (ZIFs), was put into a tea bag for selective removal of oils from water surface, and exhibits strong hydrophobicity with a water contact angle of 142°, ZIF-8 particles combined with highly hydrophobic and superoleophilic properties. Our Experiment results showed that the highly hydrophobic ZIF-8 particles and the ZIF-8/tea bag could be reused in oil-water separation for twenty cycles. More importantly, the oil could be readily removed from the surfaces of particles by heating combined with reduced pressure treatment whereas the particles still kept highly hydrophobic and superolephilic characteristics, which render its potential applications in the cleanup of oil spills and the removal of organic pollutants on water surface.

## 1. Introduction

Oil pollution has become one of the most serious global environmental issues today. A large amount of oil pollution exists in different forms and is generated by various sources: the major sources of oil spill pollution in the ocean include the runoff of oil and fuel from land-based sources and accidental spills [1]. Major industrial sources of oil waste include petroleum refining and petrochemical plants [2], steel manufacturing and metal working [3], vehicle repair, and other manufacturing plants. Major municipal sources of oil, which contain up to 36% oily substances, are derived from vegetable and animal oils in kitchen and human wastes [4]. Large amounts of oil discharged into the aquatic ecosystem can cause serious environmental problems, including clogging of sewage treatment plants, an adverse effect on the aquatic biota, and increasing biochemical oxygen demand due to the large amount of bacteria necessary to decompose the oil.

In recently, Physical adsorption using porous materials as adsorbents has been proved to be a very promising way to clean-up water [5], Absorbents collect the oil and separate it from the water by absorption. The use of absorbent materials is more popular owing to simplicity, low cost in operation and ready availability. Generally, an ideal absorbent material should have properties such as high oil-absorption capacity, high selectivity, low density, better recyclability, environmental friendliness, and so on. Several types of porous materials have been widely explored including activated carbon [6], zeolites [7], and natural fibers [8], silica [9], organophilic clays [10] and synthetic polymers [7], suffer from low separation selectivity and low absorption capacity. A number of advanced materials have been developed and suggested to overcome these principal drawbacks, but they still show unsatisfactory regeneration and cycling ability [11–14].

Here, we reported a kind of low-cost, effective, thermally stable, recyclable, excellent cycling ability, environmentally friend, and highly selective oil-absorbent porous materials based on MOF particles. As a unique class of porous materials, Metal-organic frameworks (MOFs) are materials which consist of metal ions or clusters connected by organic linker groups, and have attracted considerable interest in recent years owing to their potential in gas storage and separation, catalysis, and other emerging applications [15–18]. Zeolitic imidazolate frameworks (ZIFs) are a sub-family of MOFs that also have tunable pore sizes and chemical functionality [19]. ZIFs are based on metal imidazolates, and their structures are similar to the $SiO_2$ frameworks of silicate zeolites [20]. A new type of zeolitic imidazolate framework that has a zeolite topology is ZIF-8. The five-membered imidazolate ring creates a framework by bridging the Zn(II) centers to the N-atoms in the 1,3-positions of the ring. The zeolite topology formed is sodalite (SOD). The 145° angle made by the metal-imidazolate-metal bond is similar to the Si—O—Si bond angle of zeolites [21,22]. ZIF-8 possess the exceptional chemical stability and rich structural diversity found in zeolites. Its high chemical and thermal stability also suggests that recycling could be easily achieved. As expected, the resulted material named ZIF-8 possesses a large surface area, strong hydrophobicity and exhibits superoleophilic properties. Which offers a possibility to fast removal oils or organic solvents from water surface. The ZIF-8 particles also showed good structural stability and exhibited good recyclability in water and

oil separation. Few studies applied the highly hydrophobic MOF particles in the water-oil separation technology. In our work, the absorbent ZIF-8 was prepared by a routine method without any modification and reported in several literature [23–25], but we overcame the defects of ZIF porous materials for oil-water separation by using a ZIF-8/tea bag, which has not yet been reported. There are several advantages offered by the ZIF-8/tea bag strategy for oil-water separation. Firstly, it is easy to collect and recover ZIF porous materials after the oil-water separation experiments using a ZIF-8/tea bag. Secondly, after 20 consecutive cycles of oil absorption, the quality of the ZIF-8/tea bag almost has not changed and the oil-absorption capacity of the ZIF-8/tea bag differs almost negligibly. What's more, the ZIF-8/tea bag could be regenerated by heating combined with reduced pressure treatment, instead of solvent extraction. This would significantly reduce waste and operation cost associated with the manufacture of ZIF materials.

## 2. Experimental section

### 2.1. Materials and physical measurements

Zinc nitrate hexahydrate ($Zn(NO_3)_2$·$6H_2O$) (purity 99.8%, Sigma-Aldrich), 2-methylimidazole (purity 99.8%, Sigma–Aldrich), Deionized water ($H_2O$, home-made), polydimethylsiloxane (purity 99.8%, Sigma-Aldrich), were used as obtained from commercial sources and used without further purification.

Powder X-ray diffraction (PXRD) spectra were recorded with a Rigaku 2500 VBZ + /PC. The X-ray generated from a sealed Cu tube was monochromated by a graphite crystal and collimated by a 0.5 mm MONOCAP (λ Cu-Kα = 1.54178 Å). The tube voltage and current were 40 kV and 40 mA, respectively. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris Diamond TG Thermogravimetric Analyzer at a heating rate of $10\,°C\,min^{-1}$ under a nitrogen gas flow in an $Al_2O_3$ pan. Nitrogen physisorption isotherms were measured at 77 K, on a Quantachrome Autosorb Automated Gas Sorption instrument. Infrared spectra were acquired from a Nicolet 6700 FTIR-ATR (Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance) spectrophotometer. The scanning electron microscopy (SEM) image was recorded on a Nova Nano SEM 430 field emission gun scanning electron microscope (FEI, Hillsboro, Oregon, USA).

### 2.2. Synthesis of adsorbents

ZIF-8 was synthesized using 2-methylimidazole as a linker according to the previously reported protocol [26,27]. The synthesis solution, which had a molar ratio of $Zn^{2+}$:2-methylimidazole:$H_2O$ = 1:8:1000, was prepared as follows: First, 6.56 g of 2-methylimidazole was dissolved in 120 mL of deionized (DI) water, and the pH of the solution was adjusted to approximately 9.5 using TEA. Second, 2.95 g of Zn $(NO_3)_2$·$6H_2O$ was dissolved in 60 mL of DI water. Then, the Zinc nitrate solution was mixed with the 2-methylimidazole solution under stirring. All of the operations were performed at room temperature (20 ± 2 °C). After stirring for 20 min, the reaction solution was delivered to a filter using an air compressor. Then, the solution was filtered and washed with DI water several times. To accelerate the filtration rate of the entire process, the system was pressurized using nitrogen. Finally, a product was obtained. The as-synthesized product contains large amounts of 2-methylimidazole and water. The activation procedure leading to a clean, empty and stable material was achieved using the following in-house procedure. Excess 2-methylimidazole and pore-occluded water were completely removed by sonification of the microcrystalline product three times in DI water for 2 h. Then, the ZIF-8 sample was heated to 120 °C under vacuum for 3 days to remove the solvents and other guest molecules in the pores. The yield of ZIF-8 was 1.804 g. The resulting void-cleaned sample is referred to as the "activated sample".

### 2.3. Measurement of water contact angle

For contact angle measurement the substrates were prepared following the procedure reported earlier [28–30]. Before the measurements, ZIF-8 were dried in a 120 °C vacuum oven for 24 h. The finely ZIF-8 powders were pressed between two Silicon (1 0 0) slides that had been previously rinsed with absolute EtOH and dried with a stream of nitrogen gas. After removing the upper slide, the exposed powder surface was used for conducting contact angle measurements. A Kruss G10 Drop Shape Analyzer Goniometer was employed to measure the contact angle of $H_2O$ and n-hexadecane on the ZIF-8. The image of the water drop on the surface was captured. Contact angles were determined by drawing a tangent close to the edge of the droplet. The contact angle values reported were an average of three separate measurements carried out at three different locations on the surface.

### 2.4. Oil-water separation experiments

ZIF-8 was used to Oil-water separation according to the previously reported method [31]. A commercially available tea bag was emptied, rinsed thoroughly with water and dried. This was then soaked in 20 mL methylbenzene solution which containing 1% polydimethylsiloxane (PDMS), sonicated for 15 min, and then kept overnight for drying. After evaporation of the solvent, the tea bag was filled with 1 g of the hydrophobic ZIF-8 sample to make a 'spill pouch'. About 1 mL oil dyed with traces of Sudan III dye was added to 10 mL distilled water in a Petri dish. The 'spill pouch' was then gently placed on the surface of the oil on the Petri dish. The oil was completely mopped up by the 'spill pouch' leaving behind just water.

## 3. Results and discussions

### 3.1. Characterization of the as-synthesized ZIF-8 adsorbents

ZIF-8 was synthesized from the reaction of $Zn(NO_3)_2$·$6H_2O$ with 2-methylimidazole in water at room temperature. The prepared ZIF-8 is water stable, and was characterized by PXRD, FT-IR, TGA and $N_2$ adsorption experiments. ZIF-8 particles were successfully prepared with pure phase as demonstrated by PXRD patterns in Fig. 1. The powder X-ray diffraction (PXRD) pattern of powder of ZIF-8 is in agreement with that of the simulated one, indicating its bulk phase purity. The IR data reveals that the bands at 3135 and 2929 $cm^{-1}$ are attributed to the aromatic and the aliphatic C-H stretch of the imidazole, respectively
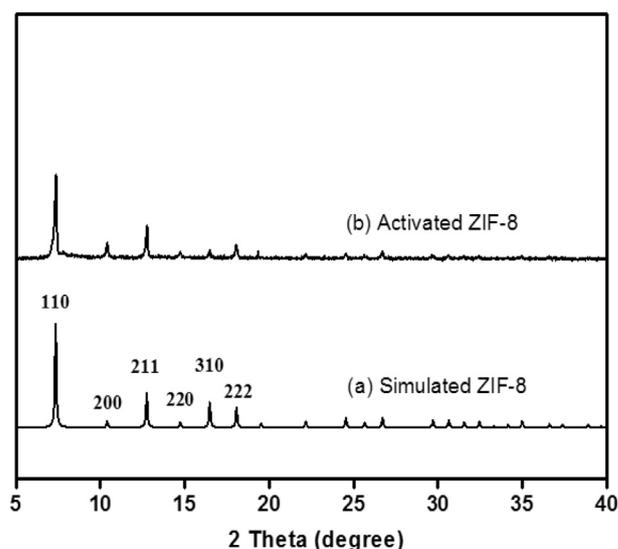


**Fig. 1.** XRD patterns of the as-synthesized ZIF-8 samples and the simulated one from ZIF-8.
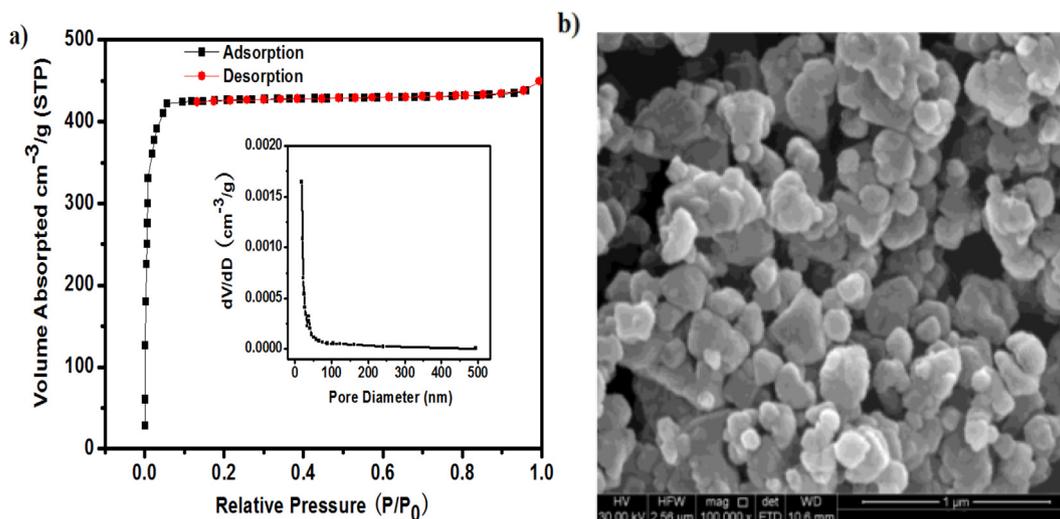
**Fig. 2.** (a) Nitrogen gas adsorption isotherm at 77 K for ZIF-8. $P/P_0$ is the ratio of gas pressure (P) to saturation pressure ($P_0$), with $P_0 = 740$ torr. Inset is the corresponding pore size distribution curves; (b) SEM images of the as-synthesized ZIF-8.

(Supporting Information Fig. S1). The peak at $1584 \, cm^{-1}$ can be assigned as the C=N stretch mode specifically, whereas the intense and convoluted bands at $1350$–$1500 \, cm^{-1}$ are associated with the entire ring stretching. The bands in the spectral region of $900$–$1350 \, cm^{-1}$ are for the in-plane bending of the ring while those below $800 \, cm^{-1}$ are assigned as out-of-plane bending. The TGA traces in Fig. S2 reveals that the ZIF-8 is stable up to 500 °C. The BET surface area (pore volume) of framework was calculated with $N_2$ adsorption data in Fig. 2a, and found to be $1408 \, m^2/g$ ($0.627 \, cm^3/g$) (See Table S1), the pore size distribution (PSD) analyzed with HK method demonstrated the existence of microporous in ZIF-8 framework. As can be seen in Fig. 2b, SEM images and Fig. S3 revealed the formation of ZIF-8 particles with an average diameter of 238 nm.

### 3.2. Absorption of organic solvents

To further confirm the hydrophobicity of ZIF-8, the surface wettability of ZIF-8 was investigated by water contact angle (CA) measurements. It was observed that ZIF-8 is strongly hydrophobic with a water CA (5 μL) of $142 \pm 1.2°$ (Fig. 3a), which should mainly originate

from its hydrophobic compositions of conjugated imidazolate rings. In contrast, when a n-hexadecane droplet was placed on the surface of the ZIF-8 sample, the oil was quickly adsorbed and a CA with n-hexadecane of nearly 0° was obtained (Fig. 3b), indicating that ZIF-8 is super-oleophilic. We reasoned that the strong oleophilicity of ZIF-8 should be attributed to its hydrophobic surface and porous structure, rolling angle of a water (5 μL) is $12.3 \pm 1.8°$. Based on the above results, ZIF-8 is highly hydrophobic and superoleophilic, and exhibits the potential in oil/water separation.

The ZIF-8 powder was tested to determine the absorption capacities of different organic solvents, particularly hydrophobic ones, which are well-recognized as constituents of oil, such as hexadecane, decane, dodecane and tetradecane, methanol, Silicone oil 20, DMF, toluene (TL), $CCl_4$, $CH_2Cl_2$. To the best of our knowledge, this is the first report of any MOF powder material being exploited for oil/water separation purposes. In the Fig. 4, we could see that the recorded absorption capacity were about 70–250% (the relative adsorption capacity of the samples was calculated using the following equation ($W_{wet} - W_{initial}$)/ $W_{initial} \times 100\%$ where $W_{initial}$ and $W_{wet}$ are the masses of initial and wet samples). Although this absorption capacity is still slightly smaller than
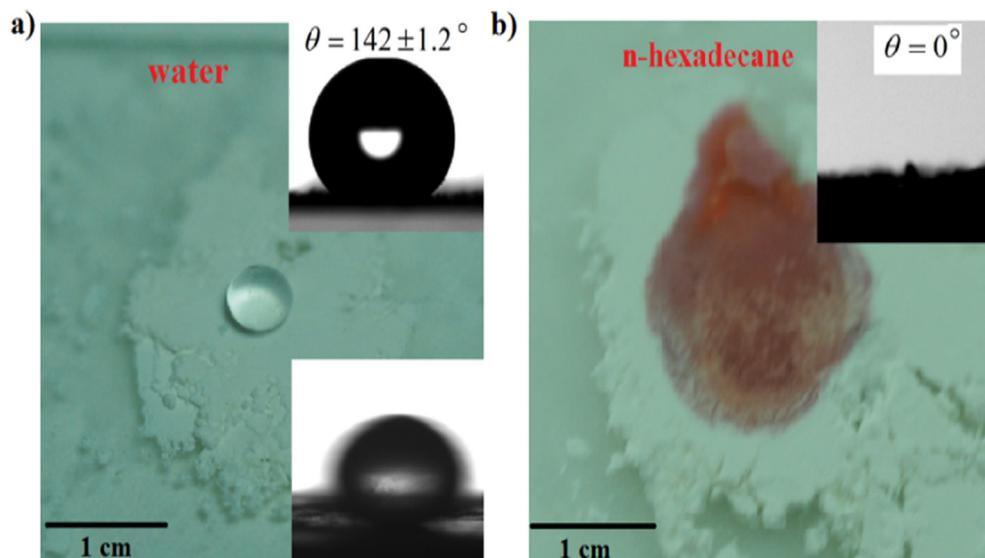


**Fig. 3.** Digital photographs of ZIF-8 (a) after a drop of water (5 μL) was placed onto the samples, Inset show contact angle measurement ($142 \pm 1.2°$) and rolling angle measurement ($12.3 \pm 1.8°$); (b) after a drop of n-hexadecane was placed onto the samples, Inset shows contact angle measurement (0°).
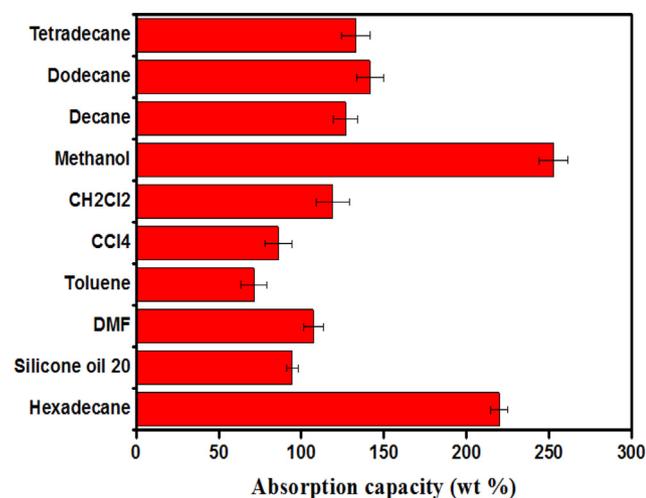
**Fig. 4.** Absorption capacities for a selection of organic solvents and oils in terms of its weight gain.



**Fig. 6.** The absorption capacity of ZIF-8 after twenty cycles.

fabric-based materials (300–500%) [32], it is much higher than have been reported Zeolite (5.5–10%) [33], Activated carbon (5–30%) [34-36], Bentonite (29–37%) [37], UHMOF-100 (40–70%) and reported membranes (45–80%) [38].

The hydrophobic ZIF-8 samples display high water contact angle and extremely low oil contact angle which make them ideal for selective absorption of oil spilled over water. The sample was also tested for real-time volumetric oil/water (1:10) separation, and showed its excellent oil-water separation capacity. To simulate an actual separation process, we carried out oil-water separation experiment using 'spill-pouch' filled with ZIF-8 particles that can mop up oil spilled over water surface. Each 'spill-pouch' contains 1 g of hydrophobic ZIF-8 particles. Also, the walls of the 'spill-pouch' are rendered hydrophobic and oleophilic through hydrophobization treatment. The 'spill-pouch' can be easily placed over the oil spillage region when it gradually absorbs all the oil leaving behind water (Fig. 5a–d). The kinetics of the oil absorption is relatively fast and the pouch readily absorbs the oil in less than 120 s by capillary effect due to the presence of superoleophilic ZIF-8 particles inside the pouch as well as on the walls (see Fig. 5e). After the oil-water separation experiments, the quality of water almost has

not changed, which indicates that the ZIF-8/tea bag only absorb oil over water.

Before the oil-water separation experiment, a tea bag was hydrophobically treated by polydimethylsiloxane (PDMS), which served to form a thin PDMS film to the tea bag. The hydrophobic film allowed oil molecule enter into tea bag, but water molecule couldn't go through [39,40], then oil molecule was absorbed by ZIF-8 particles through capillary force. Hydrophobicity of ZIF-8 is attributed to its chemical composition i.e. the methyl functionalized Im linkers as well as the coordinative saturation of the metal sites [41], which is the reason why the ZIF-8/tea bag could be used for oil-water separation.

### 3.3. The reusability and the regeneration of ZIF-8

In order to further evaluate the reusability, the recycling pollutants and the regeneration of ZIF-8 are illustrated in Fig. 6. It was verified that the prepared ZIF-8/Tea bag was reusable, and had an oil-absorption capacity that differed almost negligibly, even after 20 consecutive cycles of oil absorption. Heating combined with reduced pressure treatment can be applied, instead of solvent extraction which is complicated, and more expensive. The temperature required for vaporization can be controlled and kept around the boiling point of the
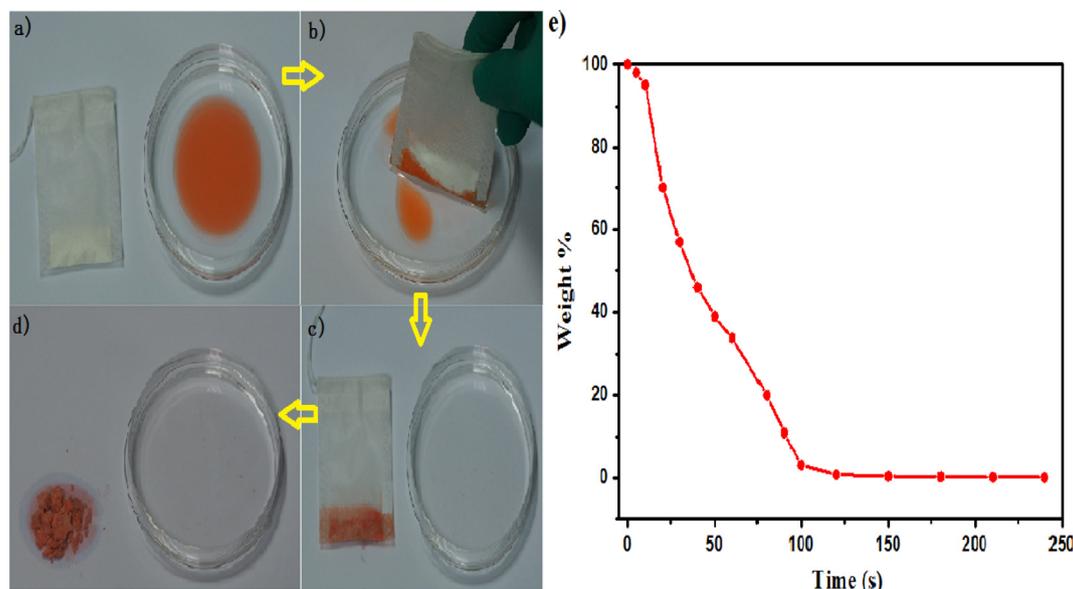


**Fig. 5.** Selective removal of oil from oil-water mixtures: in 'spill-pouch' format: (a) water contaminated with sunflower oil dyed with Sudan III dye, (b) oil mop-up by 'spill-pouch', and (c and d) clean water left behind, oil absorbed by 'spill-pouch', (e) Thermogravimetric analyses for hexadecane in water.
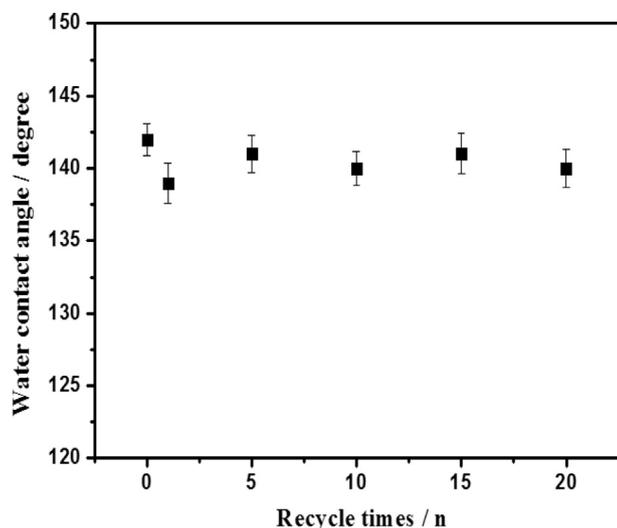
**Fig. 7.** Water contact angles of highly hydrophobic ZIF-8 particles after oil-water separation for twenty cycles.
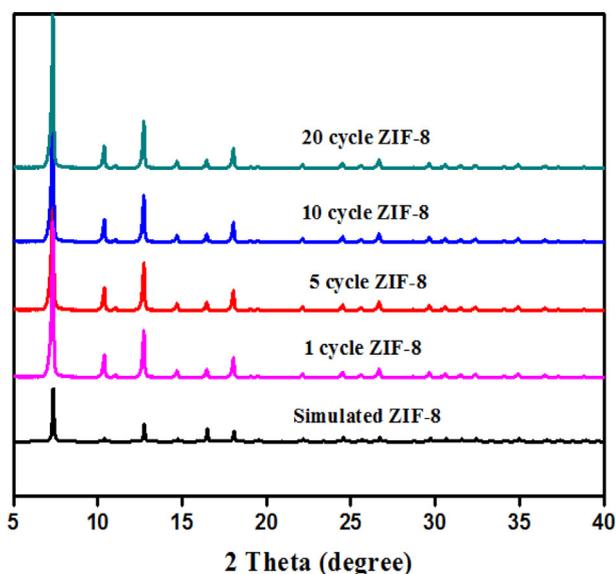


**Fig. 8.** XRD patterns of ZIF-8 before and after adsorption separation.

absorbates. The residual mass of dodecane in the ZIF-8/Tea bag was then weighed. This process was repeated 20 times to check the feasibility and completeness of recycling organics from a ZIF-8/Tea bag, followed by the regeneration of the ZIF-8/Tea bag.

Another feature of the highly hydrophobic particles was their excellent recyclability in the oil-absorbent capacity, which would significantly reduce the materials waste and operation cost. After absorbance, the ZIF-8/Tea bag could be regenerated by heating combined with reduced pressure treatment. Only slight changes in water contact angles were observed in each cycle (twenty times for the study shown in Fig. 7), as proven by keeping water contact angles above 139°. It should be noted that the highly hydrophobic and superoleophilic ZIF-8 could sustain a temperature up to 500 °C, indicating good thermal stability of the highly hydrophobic particles (see the Supporting Information, Fig. S2)

The structure of ZIF-8 before and after absorption separation was characterized by XRD, Fig. 8 shows the structures of ZIF-8 before and after the absorption separation experiments. Less than 1% residual weight remained in the ZIF-8 after each cycle for both absorbates of toluene and dodecane, indicating the highly stable recycling

performance. The absorption ability of ZIF-8 remained essentially identical after 20 cycles of testing. Meanwhile, the absorbed organics could be released by simply heating combined with reduced pressure the material and collecting the condensate. No damage to the ZIF-8 microstructure was observed after this process from Fig. 8. No combustion or structural damage occurs in whole treatments at moderate temperatures. Therefore, many pollutants, including heavy oil, could in principle be separated from ZIF-8 and further reused after heating combined with reduced pressure treatment. Heat treatment or vacuum treatment is necessary, instead of chemical extraction.

## 4. Conclusions

In summary, the idea of using strong hydrophobic and super-oleophilic powder as a selective oil sorbent against water was presented. The ZIF-8/Tea bag was found to be suitable for separating the oil from water surface and was able to achieve high separation efficiency. This low-cost, repeatable, effective and environmentally friendly material makes a potential candidate for oil spill clean-ups. The preparation method of the strong hydrophobic powder is simple, making the mass production of such powder possible.

## Acknowledgements

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.seppur.2018.04.027.

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