Magnetic $\gamma$-Fe$_2$O$_3$/ZIF-7 Composite Particles and Their Application for Oily Water Treatment

Mozhgan Shahmirzaee,* Abdolhossein Hemmati-Sarapardeh, Maen M. Husein,* Mahin Schaffie, and Mohammad Ranjbar

1. INTRODUCTION

The global demand of oil prompts continued production of both light and heavy crude oils. Accidental oil spill into water bodies, on the other hand, poses catastrophic environmental problems, in addition to immeasurable financial challenges.\(^{1-3}\) For example, the biggest recorded crude oil spill released 4.9 million barrels of crude oil into the Gulf of Mexico over a short period of time and cost $30 billion in reclamation effort.\(^{4}\) Subsequently, continuous effort should be invested to develop feasible materials and protocols for oily water purification.\(^{5}\)

Nanomaterials have been widely used in the advancement of enhanced oil recovery processes.\(^{6}\) They were also explored as potential materials for advancing separation processes. Among other technologies, such as biological methods, sedimentation–coagulation, photocatalysts, and filtration,\(^{14}\) that have been used to remove organic/oily pollutants from water, adsorption is considered an effective technology owing to its simplicity, ease of handling, and favorable economy.\(^{11}\) Effective sorbents such as hybrid foams,\(^{12-14}\) sponges,\(^{1,5,16}\) activated carbon,\(^{17,18}\) fibers,\(^{19,20}\) aerogels,\(^{21}\) porous materials,\(^{22,23}\) and magnetic materials\(^{24}\) have been proposed over the past few decades. General attributes of ideal sorbents include super-hydrophobicity, excellent recyclability, and environmentally friendly chemical and physical nature. Accordingly, the high specific surface area, surface roughness, low density, and nontoxicity of adsorbents have been studied.\(^{25}\) Achieving these specifications for materials with effective magnetic properties provides the advantage of easily recoverable sorbents. Magnetic nanoparticles (NPs) such as Fe$_3$O$_4$/PS,\(^{25}\) Fe$_3$O$_4$/SiO$_2,^{26}$ and yeast magnetic bionanocomposites\(^{27}\) have been investigated. Rapid removal of oil-loaded sorbents through separation with permanent magnets has been reported. On the other hand, porous materials with a large specific surface area have been fabricated to serve oil/water separation.\(^{14,28,29}\) Metal–organic framework (MOF) porous materials in different shapes have shown good oily pollutant cleanup attributes due to their high surface area, hierarchical porous structure, and highly
precipitation coupled with in situ synthesis and coating operating conditions and a minimum number of precursors/reagents would involve a simple experimental protocol with mild structures over a magnetic core ideal for oil spill separation the need for meticulous surface premodification. In this study, we report the synthesis of a novel γ-Fe$_2$O$_3$/ZIF-7 composite with powerful magnetic properties can meet the formidable demand of oil spills. In addition, the superparamagnetic properties and superhydrophobicity of the sorbent are also reported.

Figure 1. Schematic preparation procedure of the γ-Fe$_2$O$_3$/ZIF-7 composite.

2. MATERIALS AND METHODS

2.1. Materials. Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, 99%), FeCl$_3$·4H$_2$O (98%), NH$_4$OH (ammonium hydroxide, 25–30% of ammonia), N,N-dimethylformamide [DMF, HCON(CH$_3$)$_2$, 99.8%], methanol (CH$_3$OH, 99.8%), and ethanol (CH$_3$CH$_2$OH, 99.9%) were purchased from Sigma-Aldrich (Darmstadt, Germany). Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, 98% pure), benzimidazole (C$_7$H$_6$N$_2$, 98%), and HCl (hydrochloric acid, 37%) were purchased from Merck (Darmstadt, Germany). Heavy crude oil was prepared from a well in the south of Iran with viscosity of 415.4 cP at 60 °C and an oil API gravity of 19. Toluene and acetone were obtained from Merck (99% pure, Darmstadt, Germany). All above materials were utilized as received without additional purification. Deionized (DI) water was used throughout the tests.

2.2. Preparation of the Absorbent. 2.2.1. Synthesis of the γ-Fe$_2$O$_3$ NPs. The γ-Fe$_2$O$_3$ NPs were synthesized by a wet chemical method at room temperature. Solutions of 2 M FeCl$_2$ and 1 M FeCl$_3$ in 2 M HCl were prepared under continuous magnetic stirring. Drops of a 2 M NH$_4$OH solution were added, and the pH of the aqueous solution was adjusted to 9.73. After stirring for 2 h, a brown precipitate was obtained, which was filtered and washed several times with ethanol and DI water. The gathered precipitate was dried in an oven at 70 °C for 12 h.

2.2.2. Synthesis of the γ-Fe$_2$O$_3$/ZIF-7 Composite. The in situ synthesis of the ZIF-7 nanostructure onto the γ-Fe$_2$O$_3$ NP utilized the precipitation method reported in the literature with slight modifications, as illustrated in Figure 1. In brief, 0.0500 g of the γ-Fe$_2$O$_3$ NPs and 0.2347 g benzimidazole were dispersed in 30 mL of DMF using ultrasonication for 30 min. A mass of 0.8025 g of Zn(NO$_3$)$_2$·6H$_2$O was dissolved into 30 mL of DMF and slowly added to the sonicated suspension over 5 min at room temperature. The mixture was transformed into a water bath maintained at 60 °C. The in situ synthesis was carried out for different times of 1, 2, and 3 h in order to investigate the effect of the precipitation time on the sorption properties. During this time, ZIF-7 nanostructures emerged on the surface of the magnetic γ-Fe$_2$O$_3$ NPs. The resultant composite was collected by filtration and washed several times with ethanol and finally dried at 60 °C for 12 h.

2.3. Characterization. The X-ray diffraction pattern of the synthesized products was collected on an X’Pert diffractometer (model, Vendor, Country) with Cu Kα radiation and 2θ ranging from 0 to 60° at 40 kV and 20 mA. The XRD pattern was compared with the standard patterns in X-pert HighScore software in order to identify the particles. The crystal size was determined using Scherrer eq 1.
D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (E1)

where D is the crystal size (nm), \lambda is the X-ray radiation wavelength (nm), \theta is the Bragg angle, and \beta is the full width at half-maximum peak (radians). The Bragg angle, 2\theta = 21.211^\circ, was selected for these calculations since it corresponded to the most pronounced peak. The morphology of the product particles was investigated by field-emission scanning electron microscopy (FE-SEM, Hitachi S4160, Tokyo, Japan) equipped with an energy-dispersive X-ray (EDX) probe. The magnetic properties of the NPs and the composite at different preparation times were measured on a vibrating sample magnetometer (model of LBKF, Meghnatis Daghhigh Kavir, Iran). The N2 adsorption–desorption isotherms of the NPs and the nano-structural composite were determined using an automated surface area analyzer (model of Sorptometer Kelvin 1042). The surface area and pore volume were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) equations, respectively.

Thermogravimetric analysis (TGA) of the samples was carried out on a thermoanalyzer (TG NETZSCH 209F3, Germany) under 50 cm3/min of flowing argon from room temperature to 1000 °C at a 10 °C/min of heating rate. The different functional groups and anchoring sites were assigned with the aid of a Fourier transform infrared (FT-IR) spectrometer (Tensor 27 model, Bruker Co, Germany) under ambient conditions for wave numbers ranging from 400 to 4000 cm\(^{-1}\). The powder was compressed into a tablet by applying pressure. A sessile droplet was placed on top of the tablet, and the image of the droplet was analyzed by fitting the Laplace equation to the shape with the aid of a contact-angle measuring system (G10 model, Kruss, Germany).

### 2.4. Oil and Hydrocarbon Removal

Oil/hydrocarbon sorption by the \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) particles was estimated based on a UV–vis spectrophotometer (CARY-100, Varian Australia Pty Ltd., Australia) measurements of the oil/hydrocarbon content. The samples of oily water models were prepared with different contents of crude oil, acetone, toluene, and a 50/50 mixture of toluene/acetone in water, including 250, 500, 1000, 2000, and 3000 mg/L. The samples were prepared under sonication for 30 min. Then, 0.5 g of \(\gamma\text{-Fe}_{2}O_{3}\) or \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) particles was added to the 1000 mL mixture containing the oil. Five samples were collected every 5 min based on the equilibrium time (25 min) over 30 min under sonication. The maximum wavelength was obtained under an intermediate concentration of the oily water sample (1000 mg/L), and a linear calibration curve was constructed. The particles, together with the sorbed oil, were collected by a permanent magnet at the end of every time interval (5 min). The concentration of the remaining oil was measured using UV–vis spectroscopy. A plot of C/C0 versus sorption time was used to study the sorption process of oily pollutants using \(\gamma\text{-Fe}_{2}O_{3}\) NPs and the \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) composite. The percent removal of the oil/hydrocarbon was determined as follows (eq E2).

\[
\% R = \frac{C_0 - C}{C_0} \times 100 \quad (E2)
\]

where \(C_0\) is the initial concentration of the oil/hydrocarbon in the mixture and \(C\) is the residual concentration after sorption. The \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) particles were washed three times with ethanol before they could be reused. The recyclability of the particles was assessed by reusing the particles to separate the oil from water 15 times.

For the regeneration process, the \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) particles together with the sorbed oil were mixed with ethanol and sonicated for 30 min. Then, the \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) particles were removed using a permanent magnet and dried at 60 °C for 6 h before being reused. The reduction in the sorption efficiency is expressed as

\[
\eta = \frac{\% R_1 - \% R_2}{\% R_1} \times 100 \quad (E3)
\]

where \(\% R_1\) is the removal of oil/hydrocarbon by the \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) particles prepared freshly and \(\% R_2\) is the removal by the recycled particles, as defined by eq E2. It is noted that oily water mixtures were prepared at the same \(C_0\) concentration and 30 min of sorption was used.

**Figure 2.** XRD patterns for (a) \(\gamma\text{-Fe}_{2}O_{3}\), (b) freshly prepared \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) composite particles, and (c) \(\gamma\text{-Fe}_{2}O_{3}/\text{ZIF-7}\) composite particles after 15 cycles of oil separation. Blue circles highlight the ZIF-7 structure.

### 2.5. Kinetic Study

The kinetics of oil/hydrocarbon sorption was studied by collecting samples every 5 min from the oily water mixtures over 25 min at 25 °C. First- and second-order kinetic models were fitted to the results. Firstly, the mass of the pollutant sorbed per mass of the sorbent was defined as follows.

\[
q_t = \frac{C_0 - C_t}{M} \times V \quad (E4)
\]

where \(q_t\) is the mass of the sorbed pollutant per mass of the sorbent at any instant in time (mg/g), \(C_0\) presents the initial concentration of the pollutant solution (mg/L), \(C_t\) is the concentration of the pollutant at any time (mg/L), \(M\) is the amount of the sorbent added (g), and \(V\) presents the volume of the solution (L). The linear form of the first-order kinetics is given in eq E5.

\[
\ln(q_e - q_t) = \ln(q_e) - k_t t \quad (E5)
\]

where \(q_e\) denotes the mass of the sorbed pollutant per mass of the sorbent at equilibrium, and \(k_t\) is the rate constant of first-
order sorption (1/min). A plot of $\ln(q_e - qt)$ versus $t$ should give a straight line with a slope of $-k_1$ and intercept of $\ln(q_e)$. Accordingly, $k_1$ and $q_e$ can be evaluated from the slope and the intercept. The linear form of the pseudo-second-order kinetics is given in eq E6.63

$$
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}
$$

(E6)

where $k_2$ denotes the pseudo-second-order rate constant of sorption (g/mg min). A plot of $t/q_t$ versus $t$ gives a straight line with a slope of $1/k_2q_e^2$ and intercept of $1/q_e$. Accordingly, $k_2$ and $q_e$ can be evaluated from the slope and the intercept.

3. RESULTS AND DISCUSSION

3.1. Particle Characterization. Figure 2 shows the XRD pattern of the $\gamma$-Fe$_2$O$_3$ NPs and the $\gamma$-Fe$_2$O$_3$/ZIF-7 composite. The XRD fingerprint of the $\gamma$-Fe$_2$O$_3$ matches a cubic structure of pure magnetic $\gamma$-Fe$_2$O$_3$ indexed with JCPDS no 00-039-1346, as shown in Figure 2a. According to Scherrer eq E1, the average crystallite size of the $\gamma$-Fe$_2$O$_3$ is 13 nm. The XRD pattern of $\gamma$-Fe$_2$O$_3$/ZIF-7 shows the peak positions of the porous ZIF-7 nanostructure with crystallite planes (011), (002), (022), (013), (222), (114), (233), (134), (044), and (244).64 The ZIF-7 nanostructures do not have an effect on the crystallinity of the $\gamma$-Fe$_2$O$_3$ NPs, as depicted in Figure 2b. In addition, a simple comparison between XRD patterns after 15 recycle runs (Figure 2c) confirms a similar composite structure as the freshly

![Figure 3. (a) Schematic representation of the buildup stages of the porous $\gamma$-Fe$_2$O$_3$/ZIF-7 composite nanostructure, (b) chemical structure, and (c) unit cell of the crystalline structure of ZIF-7.](image)

![Figure 4. FE-SEM micrographs of (a,b) $\gamma$-Fe$_2$O$_3$ NPs and (c–f) $\gamma$-Fe$_2$O$_3$/ZIF-7 composite nanostructures with a growth time of 1 h at different magnifications.](image)
prepared particles (Figure 2b). The XRD pattern of recycled $\gamma$-Fe$_2$O$_3$/ZIF-7 displays sharper peaks likely due to heating during recycling, which increases the crystallinity. According to Figure 2, no leftover impurity due to the preparation procedure appears in both the $\gamma$-Fe$_2$O$_3$ NPs or the $\gamma$-Fe$_2$O$_3$/ZIF-7 particles.

The mechanism of nucleation and deposition of ZIF-7 rods onto the magnetic NPs is schematically described in Figure 3. It can be noted that the coating process was carried out without surface modification of the $\gamma$-Fe$_2$O$_3$ NPs. The chemical structure shows the binding of Zn agents and benzimidazole ligands with a central porosity and crystal structure illustrated by the unit cell of ZIF-7 with sodalite topology. The schematic of the hierarchical porous structure of ZIF-7 is shown in Figure 3b,c.

The morphology of the $\gamma$-Fe$_2$O$_3$ NPs and the $\gamma$-Fe$_2$O$_3$/ZIF-7 particles is shown in Figure 4a,b,c−g, respectively. The $\gamma$-Fe$_2$O$_3$ NPs display a spherical morphology with an average diameter of 18 ± 0.9 nm, as estimated by Image J software (Figure 4b). This particle size is close the XRD estimate. Figure 4c−f shows the hexagonal rod morphology of ZIF-7 structures with a uniform thickness (Figure 4c−d) that, on a closer look (Figure 4e−f), roughly ranges in length from 0.5 to 1 μm. These hexagonal rods most likely coat agglomerated $\gamma$-Fe$_2$O$_3$ NPs. As evident with increasing magnification, the ZIF-7 rods having hexagonal surface morphology with ranging of 10−100 nm diameter grew onto the $\gamma$-Fe$_2$O$_3$ NPs in the C direction. It is likely that the $\gamma$-Fe$_2$O$_3$ NPs were agglomerated during the synthesis of the composite structure due to the absence of any capping agents in our synthesis protocol.

The effect of the growth time of the ZIF-7 coating is depicted in Figure 5. Upon increasing the deposition time from 1 to 3 h, an elongated ZIF-7 hexagonal nanorod structure appeared under SEM imaging. Figure 5 shows that the ZIF-7 nanorods grow in both lengths (0.5−1 and 1−2 to 3−6 μm) and diameters (10−100 and 30−120 to 50−200 nm) with increased coating time (1 and 2−3 h), respectively. Furthermore, EDX analysis provides the elemental composition of the $\gamma$-Fe$_2$O$_3$ NPs (Figure 6a) and the $\gamma$-Fe$_2$O$_3$/ZIF-7 composite particles (Figure 6b), which reveals Zn and N together with Fe within the composite nanostructure. The quantitative analysis of $\gamma$-Fe$_2$O$_3$ gives the mass ratios of Fe (71.5%) and O (28.5%), which correspond to Fe$_2$O$_3$, while the mass ratios obtained from the $\gamma$-Fe$_2$O$_3$/ZIF-7 were Fe (24.4%), O (12.6%), Zn (20.1%), N (15.6%), and C (27.3%).

The magnetic properties of the $\gamma$-Fe$_2$O$_3$ NPs and the $\gamma$-Fe$_2$O$_3$/ZIF-7 composite particles collected on the vibrating sample magnetometer at room temperature are given in Figure 7. The saturation magnetization of $\gamma$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$/ZIF-7 at an external field of 5 KOe is 63 and 45 emu/g, respectively, without magnetic hysteresis, suggesting superparamagnetic behavior. Generally, for coated particles, the magnetic properties depend on the particle size, specific surface area coverage, the degree of interaction of ZIFs with the $\gamma$-Fe$_2$O$_3$ NP, and the extent of the order of the ZIF coat. Hence, with more loading of porous ZIF-7 nanorods, the magnetic properties of the $\gamma$-Fe$_2$O$_3$ weakened from 45 to 33 emu/g due to increased length and agglomeration. Therefore, the above results suggest that $\gamma$-Fe$_2$O$_3$/ZIF-7 prepared after 1 h precipitation time exhibits superparamagnetic properties and can be effectively removed by
magnetic separation. Accordingly, this composite structure which can be easily removed by a magnet and display proper coverage of absorbent material is selected to perform further separation.

The surface area analysis of the \( \gamma\)-Fe\(_2\)O\(_3\) NPs and the \( \gamma\)-Fe\(_2\)O\(_3\)/ZIF-7 particles are shown in Figure 8. Figure 8a reveals a H3-type hysteresis, which suggests that the \( \gamma\)-Fe\(_2\)O\(_3\) NPs have negligible pore volume and almost all the 55 m\(^2\)/g surface area, as calculated based on the BET equation, is externally exposed. Assuming spherical particles, as suggested by SEM results in Figure 4a,b, this surface area corresponds to an average particles size of 20 nm, which is not very different from the SEM-obtained amounts. The \( \gamma\)-Fe\(_2\)O\(_3\)/ZIF-7 particles, on the other hand, display a H4-type hysteresis, which suggests type I and II isotherms with noticeable adsorption at low \( \frac{P}{P_0} \) and a large specific surface area of 647 m\(^2\)/g, as calculated using the BET equation. The difference in surface area estimated between \( \gamma\)-Fe\(_2\)O\(_3\) and \( \gamma\)-Fe\(_2\)O\(_3\)/ZIF-7 can be explained in light of the SEM results. The huge increase of the surface area corresponds to the ZIF-7 nanorods loaded onto the magnetic particles with microporous and mesoporous structures having average sizes of 1.8 and 4.5 nm, respectively, as confirmed by the pore volume curve in Figure 8b.

**Figure 8.** \( \text{N}_2 \) adsorption–desorption isotherms and BJH of (a) \( \gamma\)-Fe\(_2\)O\(_3\) NPs and (b) \( \gamma\)-Fe\(_2\)O\(_3\)/ZIF-7 composite measured at 77 K.

**Figure 9.** TGA profiles under an inert atmosphere for \( \gamma\)-Fe\(_2\)O\(_3\) NPs, ZIF-7, and \( \gamma\)-Fe\(_2\)O\(_3\)/ZIF-7.

**Figure 10.** FTIR spectra of benzimidazole, \( \gamma\)-Fe\(_2\)O\(_3\) NPs, ZIF-7, and \( \gamma\)-Fe\(_2\)O\(_3\)/ZIF-7.

**Figure 11.** Images of the \( \gamma\)-Fe\(_2\)O\(_3\)/ZIF-7 particles dispersed into DI water after (a) 0, (b) 12, and (c) 24 h.
The thermal stability of γ-Fe₂O₃, ZIF-7, and γ-Fe₂O₃/ZIF-7 was studied using their TGA profiles under an inert atmosphere. Figure 9 confirms that γ-Fe₂O₃ particles display excellent thermal stability with no weight loss up to 1000 °C, as also reported in the literature. Accordingly, γ-Fe₂O₃ NPs make a reliable support material. The TGA profile for ZIF-7, on the other hand, displays a three-step mass loss of 6 wt % (50–300 °C), 10 wt % (590–700 °C), and 40 wt % (700–900 °C). The first two steps are attributed to the removal of free and terminal H₂O and DMF molecules, while the last step relates to the decomposition of the ZIF-7 framework. Some literature pointed to the formation of ZnO as a decomposition product of ZIF-7, which is doubtful under an inert atmosphere, especially since no oxygen atoms exist in the structure of ZIF-7.

The TGA results of γ-Fe₂O₃/ZIF-7 display a shift toward higher temperatures relative of the ZIF-7 decomposition profile with the two major mass loss regions of 35 wt % shifting to 610–710 °C and 25 wt % shifting to 710–930 °C. This shift suggests a more stable ZIF-7 structure onto the γ-Fe₂O₃ particles than a standalone structure. The TGA profile of γ-Fe₂O₃/ZIF-7 helps determining the ZIF-7 content attached to the surface of the γ-Fe₂O₃ particles, especially since the mass loss profile displays the three step loss encountered for the standalone ZIF-7 structure. For the γ-Fe₂O₃/ZIF-7, ~45% of the mass remains, which could be attributed to the ZIF-7 pyrolysis product and the original γ-Fe₂O₃ particles.

Table 1. OCA of the γ-Fe₂O₃ NPs and γ-Fe₂O₃/ZIF-7 Composite

| sorbent          | OCA (deg) |
|------------------|-----------|
| γ-Fe₂O₃          | 3 ± 0.5   |
| γ-Fe₂O₃/ZIF-7    | 155 ± 0.5 |

Figure 12. OCA of (a) γ-Fe₂O₃ NPs and (b) γ-Fe₂O₃/ZIF-7 composite.

Figure 13. Images of (a) milky crude oil emulsion and (b–d) sorption and separation of the γ-Fe₂O₃/ZIF-7 particles.

Figure 14. Removal of (a) crude oil, (b) acetone, (c) toluene, and (d) 50/50 acetone/toluene mixture by the γ-Fe₂O₃ NPs.
According to the empirical formula, only 15% of this weight loss can be attributed to the removal of DMF solvent molecules. The mass losses indicate that the weight changed, mainly as a result of the removal of DMF (<200 °C) and thermal decomposition of the frameworks (>600 °C).

Figure 10 shows the FT-IR spectra of benzimidazole, ZIF-7 crystals, γ-Fe$_2$O$_3$ NPs, and γ-Fe$_2$O$_3$/ZIF-7 composite particles. In the FTIR spectra of benzimidazole, the peaks at 1500−1600 and 2500−3500 cm$^{-1}$ are identified as the C=C stretch band of the aromatic ring of benzimidazole and the stretch band of the N=H group, respectively. The C−H stretch vibration of benzimidazole occurs in the wavelength range of 3000−3100 cm$^{-1}$, while the peak in the range of 1580−1650 cm$^{-1}$ is attributed to the bending vibration of the N−H group. For the ZIF-7 spectrum, the disappearance of the strong and broad N−H band between 2500 and 3250 and 1580−1650 cm$^{-1}$ compared to benzimidazole suggests that benzimidazole has been fully deprotonated during the crystallization and leads to the formation of ZIF-7. The ZIF-7 peaks in the range of 700−1700 cm$^{-1}$ are attributed as follows. The peak at 777 cm$^{-1}$ corresponds to the C=O band, and the peak at 1455 cm$^{-1}$ is attributed to the C−C band arising from the benzene functional group of benzimidazole of the ZIF-7 crystals. For the γ-Fe$_2$O$_3$ NPs, the Fe−O vibration corresponds to the peak at 587 cm$^{-1}$. The other peaks at 632, 795, 892, and 1629 cm$^{-1}$ are attributed to the other peaks at pure maghemite. Absorption peaks at 3170 and 3408 cm$^{-1}$ are attributed to the hydroxyl group (−OH). The γ-Fe$_2$O$_3$/ZIF-7 peaks display a slightly different pattern from γ-Fe$_2$O$_3$ NPs, which depicts most of the major ZIF-7 peaks.

3.2. Oil/Water Separation. The γ-Fe$_2$O$_3$/ZIF-7 particles were dispersed into water by vigorous shaking but mostly separated at the surface over 24 h of sitting time (Figure 11), suggesting a highly hydrophobic material coupled with low particle density. The superhydrophobicity of a solid surface depends on its surface roughness and surface energy. In addition, the results of the oil contact angle (OCA) of γ-Fe$_2$O$_3$ NPs and γ-Fe$_2$O$_3$/ZIF-7 in Figure 12a,b, respectively, confirmed the oleophilicity (hydrophobicity) of γ-Fe$_2$O$_3$/ZIF-7. As shown, the OCA of γ-Fe$_2$O$_3$ NPs is higher than 150° with superhydrophilic properties and the γ-Fe$_2$O$_3$/ZIF-7 composite is oleophilic because the OCA is close to zero (Table 1). These results depict that the magnetic γ-Fe$_2$O$_3$ NP have been successfully coated with ZIF-7 structures as a hydrophobic layer. Consequently, the γ-Fe$_2$O$_3$/ZIF-7 composite can selectively sorb oil and repel water.

3.2.1. Oil and Hydrocarbon Removal. The removal of crude oil and different model pollutants, including toluene, acetone,
and a 50/50 mixture of toluene/acetone, using the γ-Fe₂O₃ NPs and γ-Fe₂O₃/ZIF-7 particles was evaluated. Emulsified droplets of the organic pollutants in DI water under 30 min sonication appeared milky (Figure 13a). The sorption of the pollutants was accomplished by adding 0.5 g of the γ-Fe₂O₃ NPs or γ-Fe₂O₃/ZIF-7 particles under the same sonication, followed by

Figure 17. Matching experimental sorption data of the removal of crude oil: acetone; toluene; and 50/50 acetone/toluene mixture by the γ-Fe₂O₃/ZIF-7 particles with (a,c,e,g) first- and (b,d,f,h) pseudo-second-order kinetic models.
The Sorption of Di... for the... rate for the... different pollutants with high pollutant content... showed the highest... a measurable drop in the... Figure... Table... Different Pollutants from Oily Water Samples Using... Sorption is rapid... The rate of sorption of the... different pollutants can be... Figure... ACS Omega http://pubs.acs.org/journal/acsodf

| sorbents                          | water contact angle (deg) | surface area (m²/g) | pollutant type                        | separation (wt %) | reference (year) |
|----------------------------------|---------------------------|---------------------|---------------------------------------|-------------------|------------------|
| γ-Fe₂O₃/ZIF-7 particles          |                           | 690                 | crude oil and hydrocarbons/water       | 600               | present work     |
| Fe₃O₄/PS magnetic NPs            | 131.2                     |                     | organic solvents                      | 240               | 25               |
| ZIF-8/carbon nitride foam        | 138                       | 211                 | different oils/water                   | 36–58             | 84               |
| HFGO@ZIF-8                       | 125                       | 590                 | nonpolar and polar organic solvents and oils | 150–600          | 83               |
| ZIF-8 particles                  | 142                       | 1408                | different oils                         | 70–250            | 81               |

Table 3. Kinetic Parameters of Pseudo-First-Order \( \left( R_1^2 \right) \) and Pseudo-Second-Order \( \left( R_2^2 \right) \) and \( k_1 \) (1/min) and \( k_2 \) (g/min) for the Sorption of Different Pollutants from Oily Water Samples Using γ-Fe₂O₃/ZIF-7 Particles

| C₀ (mg/L) | crude oil | acetone | toluene | 50/50 acetone/toluene mixture |
|-----------|-----------|---------|---------|-----------------------------|
|           | \( R_1^2 \) | \( R_2^2 \) | \( k_1 \) | \( k_2 \) | \( R_1^2 \) | \( R_2^2 \) | \( k_1 \) | \( k_2 \) | \( R_1^2 \) | \( R_2^2 \) | \( k_1 \) | \( k_2 \) |
| 250       | 0.924     | 0.992   | 0.131   | 0.020                       | 0.936       | 0.993   | 0.097   | 0.020       | 0.966       | 0.990   | 0.056   | 0.020       | 0.979       | 0.993   | 0.066   | 0.020       |
| 500       | 0.959     | 0.999   | 0.101   | 0.013                       | 0.939       | 0.989   | 0.074   | 0.010       | 0.936       | 0.989   | 0.050   | 0.010       | 0.942       | 0.990   | 0.082   | 0.010       |
| 1000      | 0.931     | 0.964   | 0.094   | 0.005                       | 0.963       | 0.983   | 0.088   | 0.005       | 0.945       | 0.989   | 0.072   | 0.005       | 0.982       | 0.993   | 0.072   | 0.005       |
| 2000      | 0.937     | 0.982   | 0.085   | 0.003                       | 0.971       | 0.978   | 0.095   | 0.002       | 0.966       | 0.987   | 0.104   | 0.002       | 0.951       | 0.988   | 0.084   | 0.002       |
| 3000      | 0.953     | 0.961   | 0.084   | 0.002                       | 0.957       | 0.963   | 0.112   | 0.001       | 0.966       | 0.971   | 0.108   | 0.001       | 0.988       | 0.984   | 0.104   | 0.001       |

Table 4. Drop in the Sorption Efficiency, \( \eta \), after 15 Cycles of γ-Fe₂O₃/ZIF-7 Particle Reuse

| pollutant                  | \( \eta \) for \( C₀ = 200 \text{ mg/L} \) | \( \eta \) for \( C₀ = 3000 \text{ mg/L} \) |
|----------------------------|---------------------------------------------|---------------------------------------------|
| crude oil                  | 3.1                                         | 9                                           |
| acetone                    | 2                                           | 7.5                                         |
| toluene                    | 2.2                                         | 7.5                                         |
| toluene/acetone (50/50)    | 2.5                                         | 7.8                                         |

Figure 18. FE-SEM micrographs of the γ-Fe₂O₃/ZIF-7 composite after 15 cycles of use and reuse during oil sorption.
The results from fitting the $\gamma$-Fe$_2$O$_3$/ZIF-7 particle sorption data to the first-order and pseudo-second-order kinetic models are illustrated in Figure 17. As shown in Table 3, the coefficient of determination, $R^2$, consistently >0.96 for pollutants at all concentrations suggests that a pseudo-second-order model better fits the sorption data. Moreover, the equilibrium sorption capacity for the pseudo-second-order model is slightly closer to the experimental data. It is noted that ultrasonic mixing is essential to attain a sufficiently uniform mixture for accurate and reproducible UV–vis measurements of the oil content. Ultrasonic mixing does not promote pore diffusion and, hence, adsorption kinetics onto the $\gamma$-Fe$_2$O$_3$/ZIF-7 sorbent.

3.2.2. Regeneration Process. Following the sorption step, the regeneration of $\gamma$-Fe$_2$O$_3$/ZIF-7 particles was evaluated. The results of sorption efficiency as calculated from eq 3 are summarized in Table 4. 15 use and reuse cycles corresponded to only 9% reduction in the performance. This observation agrees well with the SEM photographs of recycled $\gamma$-Fe$_2$O$_3$/ZIF-7 particles in Figure 18. Rough particles of the same ranging sizes appeared similar to the freshly prepared particles (Figure 4c–f). It is the evidence that micrographs show only a little loss of ZIF-7 rods due to frequent interactions. The ZIF-7 particles remained intact, indicating good adhesion to the surface of the $\gamma$-Fe$_2$O$_3$ NPs.

4. CONCLUSIONS
This study reported the fabrication of superparamagnetic $\gamma$-Fe$_2$O$_3$/ZIF-7 composite particles with controllable structures. The ZIF-7 nanorods were in situ grown onto dispersed $\gamma$-Fe$_2$O$_3$ NPs by the addition of the precursors and controlling the time and the temperature without physically or chemically modifying the surface. The resultant $\gamma$-Fe$_2$O$_3$/ZIF-7 nanostructures maintained porous and highly crystalline morphology, which effectively accommodated the guest molecules. The combination of ZIF-7 nanorods and the magnetic $\gamma$-Fe$_2$O$_3$ enabled selective sorption of the organic contaminants (vs water) and ease of separation by means of magnetic force, especially for nanorods grown for no more than 1 h. The results showed that the $\gamma$-Fe$_2$O$_3$/ZIF-7 composite is an effective and selective sorbent for different organic pollutants from water, including crude oil, acetone, toluene, and 50/50 acetone/toluene. Rapid sorption at an equilibrium time of 25 min, which could be fit by the pseudo-second-order kinetic model, was reported in the first 5 min for different concentrations of pollutants. 15 cycles of use and reuse without loss of the ZIF-7 coating and with <9% reduction in the sorption efficiency confirmed the successful regeneration of the $\gamma$-Fe$_2$O$_3$/ZIF-7 sorbent.

AUTHOR INFORMATION

Corresponding Authors

Mozghan Shahmirzaee — Nanotechnology Group, Department of Materials Engineering and Metallurgy, Shahid Bahonar University of Kerman, Kerman 76169-1411, Iran; 
 orcid.org/0000-0002-2467-5577; 
 Email: shahmirzaeem@yahoo.com

Maen M. Husein — Department of Chemical & Petroleum Engineering, University of Calgary, Calgary T2N 1N4, Canada; Email: mhusein@ucalgary.ca

Authors

Abdolhossein Hemmati-Sarapardeh — Department of Petroleum Engineering, Shahid Bahonar University of Kerman, Kerman 76169-1411, Iran

Mahin Schaffie — Department of Petroleum Engineering, Shahid Bahonar University of Kerman, Kerman 76169-1411, Iran

Mohammad Ranjbar — Mineral Industries Research Center, Shahid Bahonar University of Kerman, Kerman 76169-1411, Iran

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06382

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Jeffery, A. W. A.; Wang, Z.; Stout, S. A. Oil Spill Environmental Forensics: Fingerprinting and Source Identification; Elsevier, 2007; p 207.
(2) Varela, A.; Oliveira, G.; Souza, F. G., Jr.; Rodrigues, C. H. M.; Costa, M. A. S. New petroleum absorbers based on cardanol-furfuraldehyde magnetic nanocomposites. Polym. Eng. Sci. 2013, 53, 44–51.
(3) Yang, S. J.; Kang, J. H.; Jung, H.; Kim, T.; Park, C. R. Preparation of a freestanding, macroporous reduced graphene oxide film as an efficient and recyclable sorbent for oils and organic solvents. J. Mater. Chem. A 2013, 1, 9427–9432.
(4) Zhang, X.; Li, Z.; Liu, K.; Jiang, L. Bioinspired Multifunctional Foam with Self-Cleaning and Oil/Water Separation. Adv. Funct. Mater. 2013, 23, 2881–2886.
(5) Dalton, T.; Jin, D. Extent and frequency of vessel oil spills in US marine protected areas. Mar. Pollut. Bull. 2010, 60, 1939–1945.
(6) Tazikeh, S.; Sayyad Amin, J.; Zendehboudi, S.; Dejam, M.; Chatzis, I. Bi-fractal and bi-Gaussian theories to evaluate impact of polypolyphenoate-coated Fe$_3$O$_4$ nanoparticles on asphaltene precipitation and surface topography. Fuel 2020, 272, 117535.
(7) Tanzadeh, J.; Ghasemi, M. F.; Anvari, M.; Issazadeh, K. Biological removal of crude oil with the use of native bacterial consortia isolated from the shorelines of the Caspian Sea. Biotechnol. Equip. 2020, 34, 361–374.
(8) Rubi, H.; Fall, C.; Ortega, R. E. Pollutant removal from oily wastewater discharged from car washes through sedimentation–coagulation. Water Sci. Technol. 2009, 59, 2359–2369.
(9) Shahmirzaee, M.; Shafiee Afrani, M.; Arabi, A. M.; Iran Nejhad, A. In situ crystallization of ZnAl2O4/ZnO nanocomposite on alumina granule for photocatalytic purification of wastewater. Res. Chem. Intermed. 2017, 43, 321–340.
(10) Kabiri, S.; Tran, D. N. H.; Altalbi, T.; Losic, D. Outstanding adsorption performance of graphene–carbon nanotube aerogels for continuous oil removal. Carbon 2014, 80, 523.
(11) Foschi, M.; Capasso, P.; Maggi, M. A.; Ruggieri, F.; Fioravanti, G. Experimental Design and Response Surface Methodology Applied to Graphene Oxide Reduction for Adsorption of Triazine Herbicides. ACS Omega 2021, 6, 16943–16954.
(12) Dong, X.; Chen, J.; Ma, Y.; Wang, J.; Chan-Park, M. B.; Liu, X.; Wang, L.; Huang, W.; Chen, P. Superhydrophobic and superoleophobic hybrid foam of graphene and carbon nanotube for selective removal of oils or organic solvents from the surface of water. Chem. Commun. 2012, 48, 10660–10662.
(13) He, Y.; Liu, Y.; Wu, T.; Ma, J.; Wang, X.; Gong, Q.; Kong, W.; Xing, F.; Liu, Y.; Gao, J. An environmentally friendly method for the fabrication of reduced graphene oxide foam with a super oil absorption capacity. J. Hazard. Mater. 2013, 260, 795–805.
(14) Sun, H.; Xu, Z.; Gao, C. Multifunctional, Ultra-Flyweight, Synergistically Assembled Carbon Aerogels. Adv. Mater. 2013, 25, 2554–2560.
(15) Peng, J.; Deng, J.; Quan, Y.; Yu, C.; Wang, H.; Gong, Y.; Liu, Y.; Deng, W. Superhydrophobic Melamine Sponge Coated with Striped Polydimethylsiloxane by Thiol–Ene Click Reaction for Efficient Oil/Water Separation. ACS Omega 2018, 3, 5222–5228.
Separation.

Eichhornia crassipes for Highly Efficient Oil Adsorption and

H.; Sun, S.; Li, C. Hydrophobic Magnetic Porous Material of

between Underwater Superoleophobicity and Superhydrophobicity of

Pollutant Removal.

Wood Filter for Simultaneous Oil/Water Separation and Organic

Cellulose Aerogels for Efficient Oil/Water Separation.

ACS Omega 2020, 5, 52596–52603.

(19) Shu, D.; Xi, P.; Li, S.; Li, C.; Wang, X.; Cheng, B. Morphologies and Properties of PET Nano Porous Luminescence Fiber: Oil Absorption and Fluorescence-Indicating Functions. ACS Appl. Mater. Interfaces 2018, 10, 2828–2836.

(34) Rojas, S.; Colinet, I.; Cunha, D.; Hidalgo, T.; Salles, F.; Serre, C.; Guillou, N.; Horcajada, P. Toward Understanding Drug Incorporation and Delivery from Biocompatible Metal–Organic Frameworks in View of Cutaneous Administration. ACS Omega 2018, 3, 2994–3003.

(35) Zheng, F.; Zhang, Z.; Zhang, C.; Chen, W. Advanced Electrocatlysts Based on Metal–Organic Frameworks. ACS Omega 2020, 5, 2495–2502.

(36) Xue, B.; Li, K.; Gu, S.; Lu, J. Zeolitic imidazolate frameworks (ZIFs)-derived NiCo3O4@CNTs nanocomposites with enhanced electrochemical performance for supercapacitor. J. Colloid Interface Sci. 2018, 530, 233–242.

(37) Hassanpouryouzband, A.; Yang, J.; Tohidi, B.; Chuvilin, E.; Istomin, V.; Bukhanov, B.; Chemerisn, A. Insights into CO2 Capture by Fluor Gas Hydrate Formation: Gas Composition Evolution in Systems Containing Gas Hydrates and Gas Mixtures at Stable Pressures. ACS Sustainable Chem. Eng. 2018, 6, 5732–5736.

(38) Cui, K.; Zhong, W.; Li, L.; Zhong, Z.; Li, L.; Bi, J.; Yu, Y. Well-Defined Metal Nanoparticles@Covalent Organic Framework Yolk–Shell Nanocages by ZIF-8 Template as Catalytic Nanoreactors. Small 2019, 15, No. e1804419.

(39) Abdi, J. Synthesis of Ag-doped ZIF-8 photocatalyst with excellent performance for dye degradation and antibacterial activity. Colloids Surf, A 2020, 604, 125330.

(40) Abdi, J.; Abedini, H. MOF-based polymeric nanocomposite beads as an efficient adsorbent for wastewater treatment in batch and continuous systems: Modelling and experiment. Chem. Eng. J. 2020, 400, 125862.

(41) Panakajaskhan, A.; Sinha, M.; Ojha, A. A.; Mandal, S. Water-Stable Nanoscale Zirconium-Based Metal–Organic Frameworks for the Effective Removal of Glyphosate from Aquiferous Water. ACS Omega 2018, 3, 7832–7839.

(42) Shahmirzae, M.; Hemmati-Sarapardeh, A.; Husein, M. M.; Schaffie, M.; Ranjbar, M. Development of a powerful zeolitic imidazolate framework (ZIF-8)/carbon fiber nanocomposite for separation of hydrocarbons and crude oil from wastewater. Microporous Mesoporous Mater. 2020, 307, 110463.

(43) Shahmirzae, M.; Hemmati-Sarapardeh, A.; Husein, M. M.; Schaffie, M.; Ranjbar, M. A review on zeolitic imidazolate frameworks use for crude oil spills cleanup. Adv. Geo-Energy Res. 2019, 3, 320–342.

(44) Thomas, A.; Majivelvanagan, K. R.; Kamalakannan, S.; Prakash, M. Density Functional Theory Studies on Zeolitic Imidazolate Framework-8 and Ionic Liquid-Based Composite Materials. ACS Omega 2019, 4, 22655–22666.

(45) Shahmirzae, M.; Hemmati-Sarapardeh, A.; Husein, M. M.; Schaffie, M.; Ranjbar, M. ZIF-8/carbon fiber for continuous adsorption of sodium dodecyl sulfate (SDS) from aqueous solutions: Kinetics and equilibrium studies. J. Water Proc. Eng. 2021, 44, 102437.

(46) Wu, L.; Li, B.; Wang, X.; Yu, S.; Pang, H.; Liu, Y.; Xie, W.; Zhang, X. Magnetic metal-organic frameworks (Fe3O4@ZIF-8) composites for the separation of uranium and americium: simultaneous achievement of optimal adsorption and desorption performance. J. Radioanal. Nucl. Chem. 2021, 318, 105–111.

(47) Zhang, G.; Zhang, J.; Su, P.; Xu, Z.; Li, W.; Shen, C.; Meng, Q. Non-activation MOF arrays as a coating layer to fabricate a stable superhydrophobic micro/nano flower-like architecture. Chem. Commun. 2017, 53, 8340–8343.

(48) Eom, S. B.; Cardona, D. S.; da Silva, H. D. T.; Nassar, N. N.; Carriilo, E. N. V. M.; Haddad, P. S.; Labuto, G. Oil spill cleanup employing magnetite nanoparticles and yeast-based magnetic bionanocomposite. J. Environ. Manag. 2019, 230, 405–412.

(49) Wang, J.; Xu, J.; Chen, G.; Lian, Z.; Tu, H. Reversible Wettability between Underwater Superoleophobicity and Superhydrophobicity of Stainless Steel Mesh for Efficient Oil–Water Separation. ACS Omega 2020, 5, 77–84.

(50) Sun, R.; He, L.; Shang, Q.; Jiang, S.; Zhou, C.; Hong, P.; Zhao, H.; Sun, S.; Li, C. Hydrophobic Magnetic Porous Material of Eichhornia crassipes for Highly Efficient Oil Adsorption and Separation. ACS Omega 2020, 5, 9920–9928.

(51) Yu, L.; Hao, G.; Gu, J.; Zhou, S.; Zhang, N.; Jiang, W. Fe3O4/PS magnetic nanoparticles: Synthesis, characterization and their application as sorbents of oil from water waste. J. Magn. Magn. Mater. 2015, 394, 14–21.

(52) Lesin, V. I.; Kolokshov, Y. A.; Khomutov, G. B. Magnetic nanoparticles in petroleum. Pet. Chem. 2010, 50, 102–105.

(53) Nejati, P. B.; Cardona, D. S.; da Silva, H. D.; Nassar, N. N.; Carrillo, E. N. V. M.; Haddad, P. S.; Labuto, G. Oil spill cleanup employing magnetite nanoparticles and yeast-based magnetic bionanocomposite. J. Environ. Manag. 2019, 230, 405–412.

(54) Feng, M.; Li, B.; Wu, H. Large-scale blow spinning of carbon microfiber sponge as efficient and recyclable oil sorbent. ACS Appl. Mater. Interfaces 2020, 12, 2502–2509.

(55) Li, Q.; Zhang, X.; Guo, Y.; Xu, J.; Li, M.; Wang, Y.; Yu, S.; Zhang, W.; Hu, Y. A simple, effective and low-cost filtration material for oil/water separation. J. Water Proc. Eng. 2021, 44, 102437.
(53) Hima, H. L.; Xiang, X.; Zhang, L.; Li, F. Novel carbon nanostructures of catenular-like fibers and interwoven spheres with excellent surface super-hydrophobicity produced by chemical vapor deposition. J. Mater. Chem. 2008, 18, 1245–1252.

(54) Wang, C.; Yao, T.; Wu, J.; Ma, C.; Fan, Z.; Wang, Z.; Cheng, Y.; Lin, Q.; Yang, B. Facile Approach in Fabricating Superhydrophobic and Superoleophobic Surface for Water and Oil Mixture Separation. ACS Appl. Mater. Interfaces 2009, 1, 2631–2617.

(55) Wu, C.; Liu, Q.; Chen, R.; Liu, J.; Zhang, H.; Li, R.; Takashi, K.; Liu, P.; Wang, J. Fabrication of ZIF-8@SiO2 Micro/Nano Hierarchical Superhydrophobic Surface on AZ31 Magnesium Alloy with Impressive Corrosion Resistance and Abrasion Resistance. ACS Appl. Mater. Interfaces 2017, 9, 11106–11115.

(56) Chen, Y.; Li, H.; Ma, Q.; Che, Q.; Wang, J.; Wang, G.; Yang, P. ZIF-8 derived hexagonal-like α-Fe2O3/ZnO/Au nanoplates with tunable surface heterostructures for superior ethanol gas-sensing performance. Appl. Surf. Sci. 2018, 439, 649–659.

(57) Abdi, J.; Mahmoodi, N. M.; Vossoughi, M.; Alemzadeh, I. Synthesis of magnetic metal-organic framework nanocomposite (ZIF-8@SiO2@MnFe2O4) as a novel adsorbent for selective dye removal from multicomponent systems. Microporous Mesoporous Mater. 2019, 273, 177–188.

(58) Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Vander Elst, L.; Muller, R. N. Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications. Chem. Rev. 2008, 108, 2064–2110.

(59) Liu, H.; Chen, L.; Ding, J. A core-shell magnetic organic framework of type Fe3O4@ZIF-8 for the extraction of tetracycline antibiotics from water samples followed by ultra-HPLC-MS analysis. Microchim. Acta 2017, 184, 4091–4098.

(60) Darezershki, E. Synthesis of maghemite (γ-Fe2O3) nanoparticles by wet chemical method at room temperature. Mater. Lett. 2010, 64, 1471–1472.

(61) Huo, J.-B.; Xu, L.; Wang, J.-C.; Cui, H.-J.; Yuan, B.; Fu, M.-L. Magnetic responsive Fe3O4-ZIF-8 core-shell composites for efficient removal of As(III) from water. Colloids Surf. A 2018, 539, 59–68.

(62) Zheng, J.; Cheng, C.; Fang, W.-J.; Chen, C.; Yan, R.-W.; Huai, H.-X.; Wang, C.-C. Surfactant-free synthesis of a Fe3O4@ZIF-8 core–shell heterostructure for adsorption of methylene blue. CrystEngComm 2014, 16, 3960–3964.

(63) Azizian, S. Kinetic models of sorption: a theoretical analysis. J. Colloid Interface Sci. 2004, 276, 47–52.

(64) Wu, X.; Niknam Shahrak, M.; Yuan, B.; Deng, S. Synthesis and characterization of zeolitic imidazolate framework ZIF-7 for CO2 and CH4 separation. Microporous Mesoporous Mater. 2014, 190, 189–196.

(65) Xiao, T.; Liu, D. Progress in the synthesis, properties and applications of ZIF-7 and its derivatives. Mater. Today Energy 2019, 14, 100357.

(66) Wu, Y.-n.; Zhou, M.; Li, S.; Li, Z.; Li, J.; Wu, B.; Li, G.; Li, F.; Guan, X. Magnetic Metal–Organic Frameworks: γ-Fe2O3@MOFs via Confined In Situ Pyrolysis Method for Drug Delivery. Small 2014, 10, 2927–2936.

(67) Thommes, M. Physical Adsorption Characterization of Nanoporous Materials. Chem. Eng. Tech. 2010, 82, 1059–1073.

(68) Kaminski, T.; Husein, M. M. Thermal cracking of atmospheric residue versus vacuum residue. Fuel Process. Technol. 2018, 181, 331–339.

(69) Azadmanjiri, J.; Simon, G. P.; Suzuki, K.; Selomulya, C.; Cashion, J. D. Phase reduction of coated maghemite (γ-Fe2O3) nanoparticles under microwave-induced plasma heating for rapid heat treatment. J. Mater. Chem. 2012, 22, 617–625.

(70) Zhu, H.-Y.; Jiang, R.; Xiao, L.; Li, W. A novel magnetically separable γ-Fe2O3/crosslinked chitosan adsorbent: Preparation, characterization and adsorption application for removal of hazardous azo dye. J. Hazard. Mater. 2010, 179, 251–257.

(71) Zhang, P.; Sun, F.; Xiang, Z.; Shen, Z.; Yun, J.; Cao, D. ZIF-derived in situ nitrogen-doped porous carbons as efficient metal-free electrocatalysts for oxygen reduction reaction. Energy Environ. Sci. 2014, 7, 442–450.