Environmental Chemistry for a Sustainable World 61

Lucas Meili
Guilherme Luiz Dotto *Editors*

Advanced Magnetic Adsorbents for Water Treatment

Fundamentals and New Perspectives

Springer

Environmental Chemistry for a Sustainable World

Volume 61

Other Publications by the Editors

Books
Environmental Chemistry
http://www.springer.com/978-3-540-22860-8

Organic Contaminants in Riverine and Groundwater Systems
http://www.springer.com/978-3-540-31169-0

Sustainable Agriculture
Volume 1: http://www.springer.com/978-90-481-2665-1
Volume 2: http://www.springer.com/978-94-007-0393-3

Book series
Environmental Chemistry for a Sustainable World
http://www.springer.com/series/11480

Sustainable Agriculture Reviews
http://www.springer.com/series/8380

Journals
Environmental Chemistry Letters
http://www.springer.com/10311

More information about this series at http://www.springer.com/series/11480

Lucas Meili • Guilherme Luiz Dotto
Editors

Advanced Magnetic Adsorbents for Water Treatment

Fundamentals and New Perspectives

Springer

Editors
Lucas Meili
Center of Technology
Federal University of Alagoas
Maceió, Alagoas, Brazil

Guilherme Luiz Dotto
Department of Chemical Engineering
Universidade Federal de Santa Maria
Santa Maria, Rio Grande do Sul, Brazil

ISSN 2213-7114 ISSN 2213-7122 (electronic)
Environmental Chemistry for a Sustainable World
ISBN 978-3-030-64091-0 ISBN 978-3-030-64092-7 (eBook)
https://doi.org/10.1007/978-3-030-64092-7

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Contents

About the Editors

Lucas Meili is working as Full Professor in the Center of Technology at Federal University of Alagoas (UFAL), Maceió, Alagoas, Brazil. Prof. Meili graduated in Chemical Engineering at Federal University of Rio Grande (Brazil) and obtained his Doctor degree in Chemical Engineering at Federal University of São Carlos (Brazil) in 2009. He is permanent member of Chemical Engineering post-graduation program and also of Materials post-graduation program. His areas of interest are focused in separation processes, water and wastewater treatment, and synthesis of materials. Particularly he has interest in adsorption and advanced oxidation processes. He has several international publications in Chemical Engineering, focusing in adsorption, development of adsorbents and advanced oxidation processes.

Guilherme Luiz Dotto is professor in Chemical Engineering Department at Federal University of Santa Maria (UFSM). Is a permanent member of the Chemical Engineering post-graduation program and also of the Chemistry post-graduation program. Is B.Sc. in Food Engineering, M.Sc. in Food Engineering and Ph.D. in Food Engineering. His research is focused on the following areas: transport phenomena, unit operations, wastewater treatment, physicochemical treatments for wastewater and separation processes. In specific, has specialty in adsorption/biosorption of contaminants from aqueous solutions, preparation and characterization of biomaterials and nanobiomaterials, wastewater treatment, wastes management and reuse, drying of biomaterials, statistical optimization, experimental design, response surface methodology, linear and non-linear regression analysis. In these research areas, has more than 160 published articles and is reviewer of more than 100 international journals. Its H-index is 25.

Chapter 13
Advanced Magnetic Adsorbents Prepared from Emulsion Template for Water Treatment

Yongfeng Zhu, Hui Yu, Bin Mu, and Aiqin Wang

Contents

Abstract Adsorption technology regarded as an ideal method to remove water contaminants has been widely applied in practical applications, as the merit of the wide suitability and low cost. Among various adsorbents, magnetic recyclable adsorbents have gained more and more attention in recent years, which not only decrease the risk of secondary pollution but also realize the cyclic use of the

Y. Zhu · B. Mu · A. Wang (✉)
Key Laboratory of Clay Mineral Applied Research of Gansu Province, Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, People's Republic of China
e-mail: zhuyf@licp.cas.cn; mubin@licp.cas.cn; aqwang@licp.cas.cn

H. Yu
Key Laboratory of Clay Mineral Applied Research of Gansu Province, Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, People's Republic of China

Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, People's Republic of China

L. Meili, G. L. Dotto (eds.), *Advanced Magnetic Adsorbents for Water Treatment*, Environmental Chemistry for a Sustainable World 61,
https://doi.org/10.1007/978-3-030-64092-7_13

adsorbent after being regenerated and even increase significantly the additional value for enriching the scattered metals and precious metals. Recently, more and more studies have concerned the morphological control, homogeneous size, and tuned porous structure of magnetic adsorbents except for the adsorption performance. Hence, the emulsion template technique is applied to construct the magnetic adsorbents based on the advantages of facilely controlling the size distribution, crystallinity, and porous structure of magnetic materials.

Here, recent studies on the preparation of magnetic materials based on the emulsion template are reviewed, including magnetic nanoparticles, magnetic microspheres, and magnetic porous materials, and then the applications of the magnetic adsorbents for water treatment are summarized and discussed. The major points include the following aspects: (1) the emulsion template for preparation of the magnetic materials presents several advantages such as the confined reaction in the "microreactor," controlled shape, particle size and distribution, high polymerization degree, high productivity, low reaction temperature, and sufficient and tuned porous structure. (2) The obtained magnetic adsorbents exhibit excellent adsorption performance to the various pollutants, including heavy metals, dyes, and other organic contaminants, as well as the oil-water separation. It is expected that this review could be regarded as an important reference for the design and fabrication of novel adsorbents.

Keywords Emulsion template · Adsorption · Magnetic · Heavy metals · Organic pollutants · Imprinted polymer · Emulsion polymerization · Spinel ferrites · Porous materials · Nanoparticle

13.1 Introduction

Adsorption technology has been widely studied and used to remove the coexisting water contaminants in practical applications, due to its low cost and wide suitability. Especially, the adsorbents with recyclability always attract much attention in practical, which not only decreases the risk of secondary pollution (Rydin et al. 2000; Yin et al. 2018) but also increases significantly the additional value (Xue et al. 2019; Hashem et al. 2020). Generally, the strategies for designing the recycled adsorbents involve the large volume (Dlamini et al. 2020; Ren et al. 2019) and incorporation of magnetic particles (Yu et al. 2019). Compared with the former, the magnetic adsorbents have got more and more concerns, due to the diversified design, flexible operation, and excellent separating effect (Hua et al. 2012).

Magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are the most popular and widely used magnetic materials and could be directly used as adsorbents to eliminate various pollutants (Patel et al. 2019; Tsedenbal et al. 2020; Liu et al. 2021). However, the unavoidable problems are generally encountered, including magnetism loss and decreased adsorption performance, which might be related to the

oxidization or decomposition of the naked magnetic particles in water (Zhu et al. 2013). Hence, most of the magnetic adsorbents are fabricated by incorporating Fe_3O_4 or γ-Fe_2O_3 into the adsorbent matrix (Ji et al. 2020; Fahimirad et al. 2018; Dehghani et al. 2021; Jung et al. 2019; Nuryono et al. 2020; Maleki et al. 2019; Tang et al. 2019a; Huang et al. 2020). Although magnetic adsorbents prepared by this strategy exhibit better adsorption performance and higher stability against acid or alkaline, their dispersibility and morphologies are ignored, which actually have a significant effect on the adsorption application. For example, nano-adsorbents generally displayed excellent adsorption performance due to the large specific surface area and the amount of active sites. But agglomeration, which could reduce the adsorption capacity, is still an important problem in large-scale applications. In addition, since many adsorbents possess sufficient adsorption sites, the sites located in the adsorbents interior usually fail to play role in the removal of pollutants. What is important is the recycling of the adsorbent is difficult in most of actual situation, and the risk of secondary pollution still exists. Therefore, the research to increase the dispersity of nano-adsorbent and realize the sufficient utilization of the adsorption sites has become the new hotspot.

Among the various strategies, the emulsion template is regarded as one of the classical and effective pathways for the preparation of particles with homogeneous size, controlled shape, or regular pore structure (Weng et al. 2020; Mokadem et al. 2020). With the development of the emulsion technique, novel hybrid materials are designed and prepared using emulsion template, and it indicated three attractive traits compared with other methods. First, the materials could be shaped with various morphologies, including spherical, hollow, and porous (Wang et al. 2020a, b; Stubenrauch et al. 2018; Thompson et al. 2019). Second, the morphologies of novel materials are tuned conveniently by changing the emulsion factors. Last but not least, the obtained materials will be endowed with some new function after incorporation of specific particles, such as photocatalytic or magnetic property derived from TiO_2 or Fe_3O_4 (Li et al. 2014a, b).

In this chapter, we review the studies related to the preparation of magnetic nanoparticle, magnetic microsphere, and magnetic porous material from the emulsion template and the application in water treatment (Fig. 13.1). It is expected that this review will be regarded as an important reference for the design and fabrication of other novel magnetic adsorbents.

13.2 Preparation of Magnetic Materials from Emulsion Template

13.2.1 Magnetic Nanoparticles

Magnetic particles have been widely applied in various fields, such as soil remediation, mineral processing industry, water purification plant, and so on (Anjali et al.

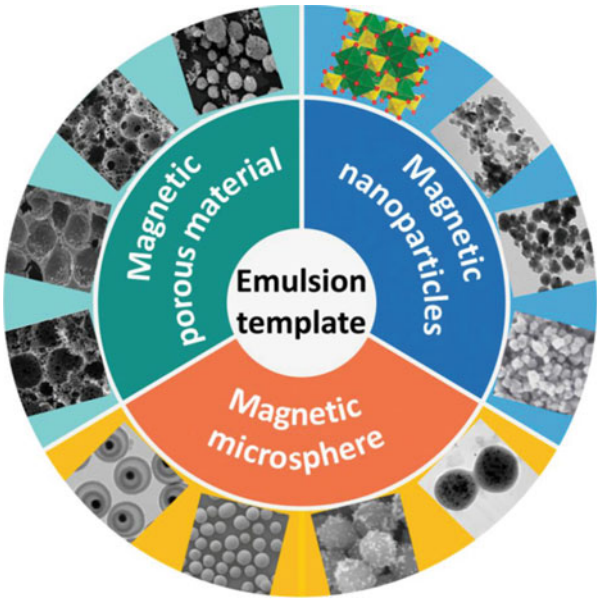

Fig. 13.1 The magnetic adsorbent prepared from the emulsion template

2019; Alhadidi et al. 2021; Li et al. 2021), and can be synthesized from many strategies, including coprecipitation (Aylar et al. 2020; Kavitha and Kurian 2020), thermal decomposition (Jesus et al. 2020), solvothermal (Fotukian et al. 2020), and microemulsion (Yousuf et al. 2019) (Table 13.1). Among these approaches, coprecipitation is most widely used, due to the product exhibited excellent dispersibility in water and convenient production process. And the size, shape, and magnetic property are affected by various parameters, including the type of ferric salts, the ratio of Fe^{2+} to Fe^{3+}, temperature, pH, etc. Even so, coprecipitation has several defects, including the large size and broad size distribution, which derived from the particles nucleation and subsequent growth up (Chen et al. 2016). In comparison, the magnetic nanoparticles prepared from the thermal decomposition at the presence of various stabilizing surfactants have monodisperse nanocrystals (Wu et al. 2008), while this process also has obvious drawbacks, including the complicated preparation process and expensive/toxic raw materials used (Xiao et al. 2016). Moreover, the obtained particles are hydrophobic and present a weak dispersibility in water. Solvothermal and hydrothermal techniques are good at preparing monodisperse magnetic particles with the controllable shape and narrow size distribution, but it is still limited in article due to the long synthetic time and high pressure.

Compared with other methods, the emulsion template, especially the microemulsion, exhibits better superiority in the preparation of magnetic nanoparticle. Because the reaction is limited in the "microreactor," the size, shape, and uniformity of particles could be controlled effectively. The general method is to mix two types of microemulsions, containing a salt or a complex of metal and a

Table 13.1 Comparison of the synthesis methods of iron oxide magnetic particles (Pang et al. 2016)

Methods	Reaction condition	Characteristic of the obtained products
Coprecipitation	Temperature: 20–90 °C	Shape control: Not good
	Duration: Minutes	Size distribution: Broad
	Solvent: Water	Crystallinity: Poor polydispersity
		Magnetization value: 20–80 emu/g
Thermal decomposition	Temperature: 100–320 °C	Shape control: Very good
	Duration: Hours–days	Size distribution: Very narrow
	Solvent: Organic compound	Crystallinity: High monodispersity
		Magnetization value: Up to 91 emu/g
Solvothermal	Temperature: 140–260 °C	Shape control: Good
	Duration: Hours	Size distribution: Narrow broad
	Solvent: Organic solvent or polyglycol	Crystallinity: High monodispersity
		Magnetization value: Up to 93 emu/g
Hydrothermal	Temperature: 150–220 °C	Shape control: Very good
	Solvent: Organic compound	Shape control: Good
		Magnetization value: Up to 113 emu/g

precipitating agent, respectively. Then the droplets take place collision and coalescence, and the magnetic nanoparticles nucleate and grow in the new droplets (Fig. 13.2).

For the fabrication and regulation of the morphology of magnetic nanoparticles, Pileni et al. conducted many pioneering works via emulsion template, including $CoFe_2O_4$ (Moumen et al. 1995a, b; Moumen and Pileni 1996a, b), Fe_3O_4 (Feltin and Pileni 1997), and cobalt-zinc ferrite magnetic nanoparticles (Hochepied and Pileni 2000). The size of the obtained magnetic particle could be adjusted in 2–11.6 nm. Soon afterwards, the magnetic spinel ferrites (SFs) prepared from the microemulsion become one of the hotspots following the relevant research of Pileni et al. SFs are the metal oxides which with the spinel structure, and the chemical constitution can be marked as AB_2O_4, where A and B represented various metal cations situated at tetrahedral (A site) and octahedral (B site), respectively. SFs can be classified as normal, inverse, and mixed based on the distribution of cations in tetrahedral and octahedral sites (Reddy and Yun 2016). The normal spinel includes $ZnFe_2O_4$, while $CdFe_2O_4$, $Fe[MFe]O_4$, $MgFe_2O_4$, $NiFe_2O_4$, $CoFe_2O_4$, and $CuFe_2O_4$ belong to the inverse spinel (Fröhlich et al. 2019; Masunga et al. 2019). The spinel with mixed structures is relatively rare, and $MnFe_2O_4$ is a typical example.

SFs could be synthesized by different methods, like calcination of the precursor (Popkov et al. 2020), sol-gel (Batoo and El-sadek 2013), hydrothermal (Ghahfarokhi and Shobegar 2020), ceramic method (Hilczer et al. 2016), coprecipitation (Ghone et al. 2018), and so on. However, the size of most SFs prepared from these methods is large and uncontrolled. In comparison, emulsion template is in favor of controlling

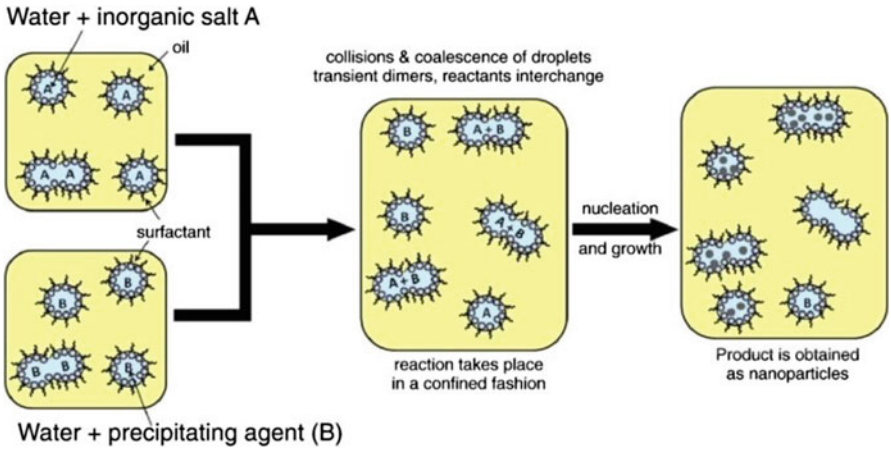

Fig. 13.2 The mechanism for the formation of metal particles by the microemulsion approach. (Reproduced with permission from Sanchez-Dominguez et al. 2012)

the size, morphology, shape and/or geometry, surface area, and homogeneity of magnetic particles (Ghone et al. 2018; Wang et al. 2012; Baig et al. 2019; Yousuf et al. 2019; Rafiq et al. 2020). Therefore, the microemulsion template is developed for the preparation of SFs with the controllable structure. For example, a series of $Mg_{1-x}Ca_xNi_yFe_{2-y}O_4$, $Zn_{1-x}Tb_xFe_2O_4$ were prepared via the microemulsion template, and the crystallite size of the synthesized samples could be facilely adjusted in the range of 15–45 nm.

A critical question is the interrelationship between the size of the obtained particles and the microemulsion characters. Many researches revealed that there is an almost linear correlation between them in few cases, but hardly find any correlation in most studies. So a range of experimental findings can be summarized as follows (Palmqvist 2003): (1) increasing reactant concentration will produce the increased particle size; (2) if the concentration of one of the reactants increases far beyond the other reactants, the particle size decreases; (3) the particle size might increase with the increase in the size of microemulsion droplet. It showed that the particles grown in the microemulsion droplet still have some complicated factors without control.

13.2.2 The Magnetic Microspheres

The introduction of the magnetic particle into the composite is very popular and has been widely reported every year (Fan et al. 2016; Xiao et al. 2016; Duan 2017). The purpose of these works is divided into three types. The first is to protect the magnetic particles from resisting the etching of acid or alkali, especially Fe_3O_4 and γ-Fe_2O_3 (Rott et al. 2018; Zhou et al. 2018). Fe_3O_4 and γ-Fe_2O_3 are the most widely used

magnetic nanoparticles, but their physical properties are susceptible to change under different conditions. They are very unstable and easily transformed to other oxide forms at low pH, which affected their magnetic properties. So the coating or capsulation of magnetic particles is widely used in many studies (Lobato et al. 2019; Lobato et al. 2020). The second is to improve the dispersibility of magnetic particles. The agglomeration and formation the large clusters of magnetic particles in water is very common due to the hydrophobic surface (Lima and Feng 2012). The last reason of coated particles surface is to realize the functionalization of the nanoparticles by incorporation of various organic molecules or polymers (Wu et al. 2008; Ma et al. 2020; Kim et al. 2020).

Actually, the microfluidics technology may be the best method for the preparation of the material with near-perfect spherical shape (Zhang et al. 2018a, b; Kang et al. 2018). But the tedious process and the poor yield limit its large-scale production. In addition, in situ polymerization, pendant drop method, and emulsion template are developed for the preparation of the magnetic microsphere (Wang et al. 2010; Fang et al. 2019), and emulsion template technique is superior due to the high polymerization degree, high yield, and low reaction temperature.

Based on the preparation strategy, magnetic microsphere with four types of morphologies can be obtained by the emulsion template (Gervald et al. 2010) (Fig. 13.3): (a) the core-shell structure (magnetic particles as core and small molecule or polymer as shell), (b) the magnetic particle is embedded into the polymer matrix, (c) polymeric core with a surface layer of magnetic nanoparticles, and (d) the polymer further coats onto the magnetic particle supported polymeric core. Among them, the first three morphologies are very popular, but the reports involved the fourth structure is relatively rare. For example, Wang et al. (Wang et al. 2020a, b) fabricated triethylenetetramine-modified hollow Fe_3O_4/SiO_2/chitosan magnetic nanocomposite (Fe_3O_4/SiO_2/CS-TETA) with high specific surface by the emulsion polymerization. The carboxyl-functionalized polystyrene (PS) nanospheres were formed firstly by copolymerization of styrene and acrylic acid via the emulsion polymerization, and then the Fe_3O_4 nanoparticles were loaded onto. Later, the coating of silica onto the PS/Fe_3O_4 nanospheres and the calcinations at 500°C were carried out, and the hollow Fe_3O_4/SiO_2/CS nanocomposites were obtained finally after the chitosan modification (Fig. 13.4).

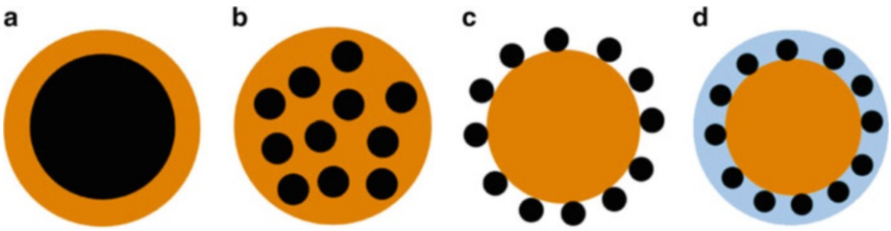

Fig. 13.3 Morphology types of magnetic polymer microspheres. (Reproduced with permission from Gervald et al. 2010)

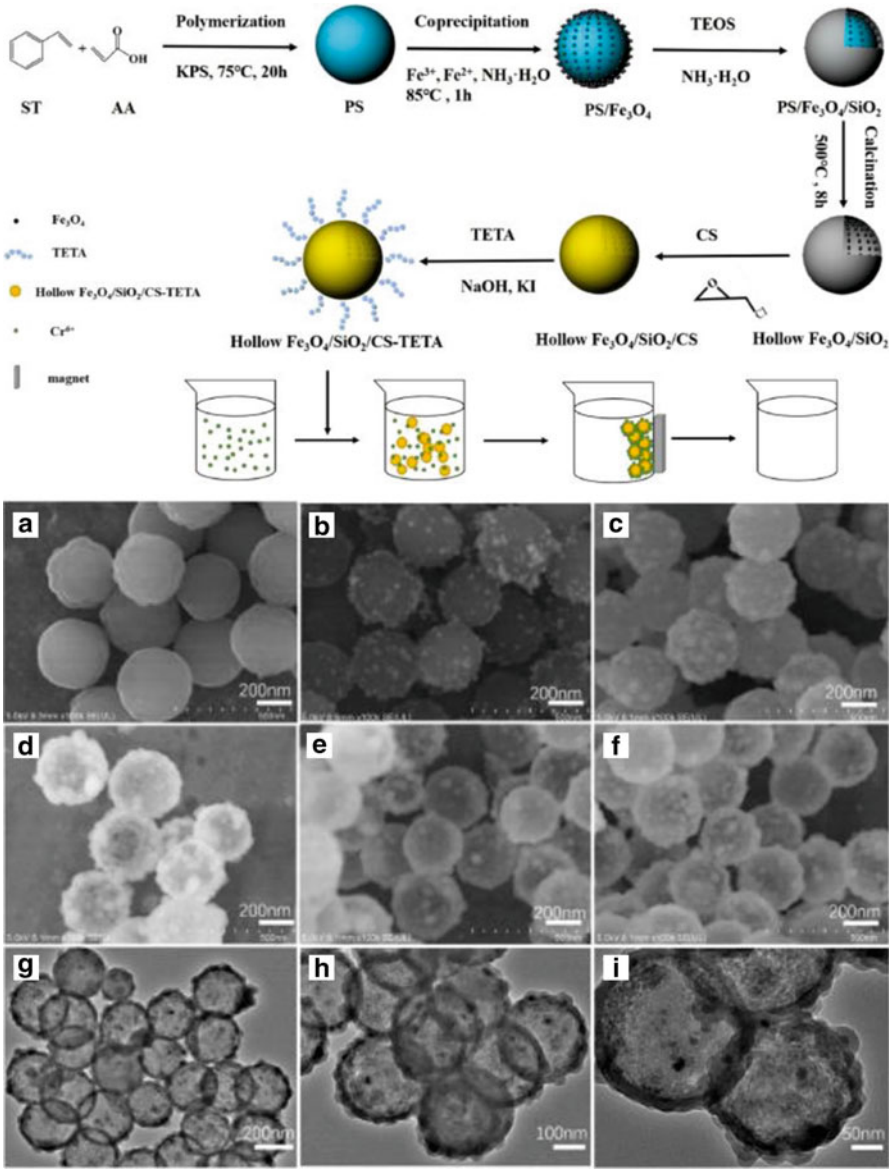

Fig. 13.4 Schematic illustration of the synthesis of hollow Fe_3O_4/SiO_2/CS-TETA nanocomposites and their application in recycle removal of Cr(VI). (Reproduced with permission from Wang et al. 2020a, b)

In order to achieve the coating, embedding, or supporting the magnetic particles, polymerization techniques such as emulsion polymerization, microemulsion polymerization, miniemulsion polymerization, dispersion polymerization, etc. have been used. Among them, emulsion polymerization is the most frequently adopted. However, due to the formation of the polymeric particles and oligomer occurs in the micelles and the aqueous phase simultaneously, the morphology and size of the obtained microspheres are very difficult to control via the emulsion polymerization. Compared with the emulsion polymerization, the structure, morphology, and size of microspheres could be efficiently regulated by microemulsion polymerization, miniemulsion polymerization, and nanoemulsion polymerization (Solans et al. 2005) (Fig. 13.5). But the problem is, if the microemulsion polymerization and miniemulsion polymerization are initiated with the free radical, partial magnetization might be lost due to the oxidizing initiator fragments (Zheng et al. 2005). In fact, the initiator types, concentrations of stabilizer, and the monomers dose also influence the

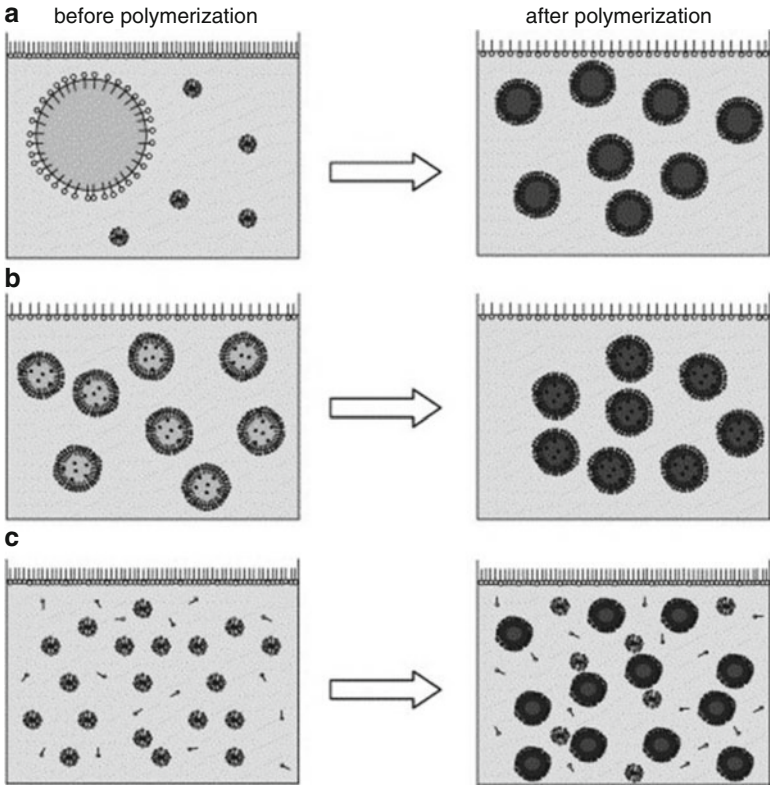

Fig. 13.5 Schematic representation of heterophase polymerization processes: (**a**) emulsion polymerization, (**b**) nanoemulsion polymerization, and (**c**) microemulsion polymerization. (Reproduced with permission from Solans et al. 2005)

morphologies and properties of magnetic nanocomposite (Hu et al. 2011; Feuser et al. 2015).

It is well known that the surfactants play a vital role in the microemulsion polymerization, miniemulsion polymerization, and nanoemulsion polymerization processes, which provide the droplets with colloidal stability against coalescence. But the inevitable migration of surfactants at the interface significantly affects the size and morphology of the obtained magnetic microspheres (Gharieh et al. 2019). In order to avoid this issue, the emulsifier-free miniemulsion polymerization might be a more wise choice (Zhang et al. 2016a, b). However, the stability of miniemulsion would be affected with ionic strength in the aqueous; hence, the hydrophilic monomer copolymerize with the hydrophobic monomer to keep the emulsion stability.

The dispersion of inorganic nanoparticles is another key problem to prepare polymer/inorganic nanocomposites by emulsion polymerization. Due to the nanoparticles have the high surface energy and easy to agglomerate together, the miniemulsion polymerization should be integrated with ultrasonic induction (Qiu et al. 2007). Compared with the conventional miniemulsion polymerization, ultrasound-induced miniemulsion polymerization possesses several advantages, such as no chemical initiators, low reaction temperatures, fast polymerization rate, higher monomer conversion and molecular weight. For instance, Teo et al. (Teo et al. 2009) prepared a novel poly(n-butyl methacrylate) latex bead with strong magnetism via one-pot method (Fig. 13.6). The O/W emulsion was prepared by dispersing the Fe_3O_4 nanoparticles into n-butyl methacrylate first and integrated with the high stirring and sonication under argon atmosphere. The polymerization reaction was preceded via continuous sonication without using any initiator.

13.2.3 The Magnetic Porous Materials

The porous material could be prepared from many approaches, such as hydrothermal synthesis (Kozyatnyk et al. 2019), freeze-drying (Anoshkin et al. 2018), porogenic solvent (Jiang and Kim 2013), or sacrificial hard template (Estevez et al. 2017). The as-prepared materials might have high porosity by these strategies, while the pore

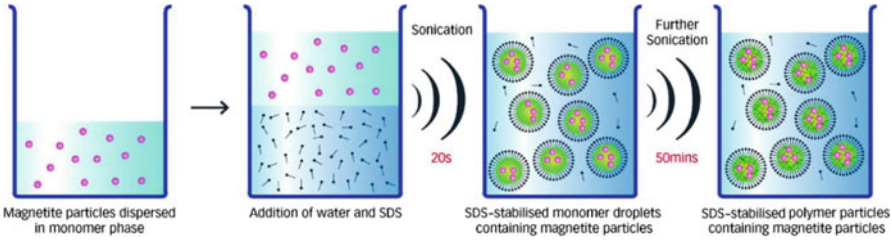

Fig. 13.6 A schematic of the process for magnetite nanocomposite spheres preparation by the sonochemically driven miniemulsion polymerization. (Reproduced with permission from Teo et al. 2009)

structure is not easy to control and tune. In comparison, the soft templates including the block copolymer template and colloidal template have been recognized to be more effective to synthesize ordered and disordered porous matrices (Wright et al. 2017). Especially, the emulsion template method is recognized to be an effective and versatile pathway for the preparation of polymeric materials with a well-defined porous structure, which is known as "polyHIPEs" (Chen et al. 2017, Zhang et al. 2018a, b, Gui et al. 2019). A polyHIPE is usually formed after finishing the polymerization reaction in the continuous phase of high internal phase emulsions (HIPEs), which has the large internal phase volume exceeded 74%, and then removing the dispersed phase. The interconnected pore will be formed as the thin membranes between the adjacent droplets are broke (Fig. 13.7) (Tan et al. 2018).

There are several important differences between the emulsion template used for the formation of the porous materials and the emulsion polymerization described above. First, the internal phase contents of HIPEs are above 74%, but the internal phase volume of emulsion polymerization and microencapsulation is significantly smaller. Second, the polymerization of HIPEs occurs in the continuous phase, while emulsion polymerization takes place in the dispersed phase. Moreover, HIPEs typically generate the monolithic material, but microspheres are obtained through the emulsion polymerization.

Both the surfactants and the amphiphilic solid particles are used to stabilize the HIPEs, but different characters of the surfactants and the amphiphilic particles generate different porous structures (Zhang et al. 2017). Generally speaking, surfactants or surfactant-like molecules are used to stabilize the emulsion in the

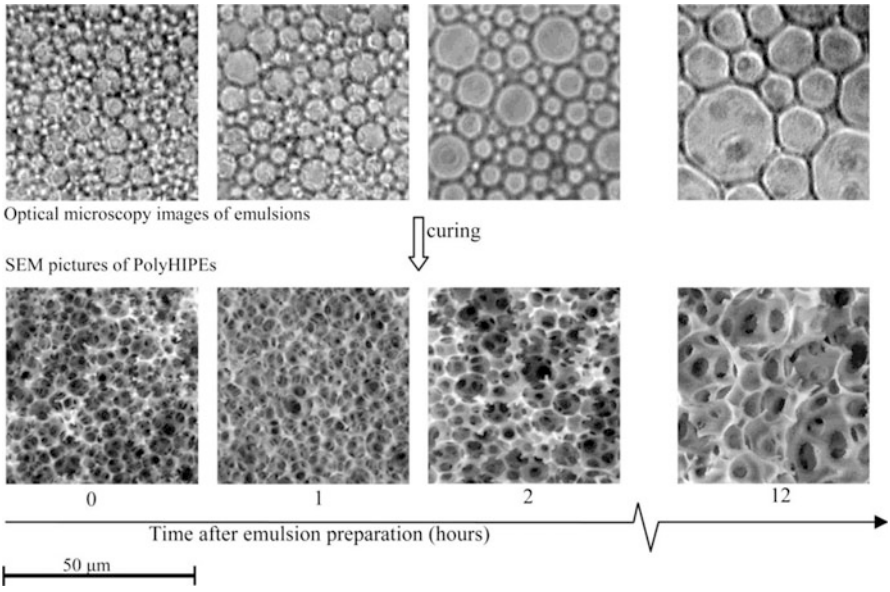

Fig. 13.7 Influence of time-dependent droplet coalescence on the morphology of polyHIPEs. (Reproduced with permission from Kovačič et al. 2007)

micromolecules; the porous materials with interconnected porous structure are obtained. On the contrary, the polymerization of the dispersed phase towards the amphiphilic particle-stabilized HIPEs always results in the closed-cell polymers with poor interconnectivity. Specifically, it has obvious positive effect of the stable particles modified by the surfactants. When the particles and the surfactants are synergistically stabilized in the emulsion, the stability of emulsion would be improved significantly and thus polyHIPEs attain excellent homogeneity. Meanwhile, the surfactants lead to the formation of the interconnected porous structure (Zheng et al. 2013).

At present, there are two approaches to obtain the magnetic porous materials from the emulsion template. The first is to disperse directly the magnetic particles into the emulsion continuous phase and then polymerization (Seeharaj et al. 2019). Due to the aggregation of the magnetic particles in the continuous phase, more researches are focused on the stabilization of the Pickering emulsion template with the magnetic particles. The magnetic particles should be modified with the organic molecules taken into account the inherent hydrophilicity of magnetic particles, such as surfactant, oleic acid, and so on (Zhang et al. 2019a, b, c, d). For example, Zhu et al. applied the amine-functionalized Fe_3O_4 nanoparticles ($Fe_3O_4 - NH_2$) to stabilize the HIPEs and fabricated novel magnetic porous polymers with a surface area of 5.532 m^2/g (Fig. 13.8). Our group also prepared the magnetic porous materials with sufficient interconnected porous structure from the HIPEs, which was stabilized with the amine-functionalized Fe_3O_4 (Zhu et al. 2016b; Lu et al. 2018a). Furthermore, we also developed another new type of magnetic porous adsorbent via the magnetic yeast and chitosan synergistically stabilized Pickering medium internal phase emulsions (Pickering MIPEs). As the droplet size and the stability of Pickering MIPEs could be adjusted by changing the synergistic effect between magnetic yeast

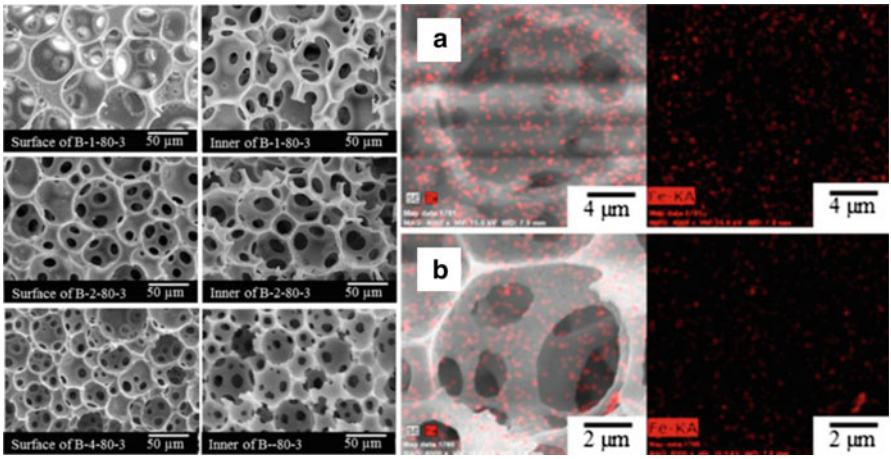

Fig. 13.8 SEM images of the surface and inner morphology of the emulsion-templated beads with different feeding amounts of FeNPs. (Reproduced with permission from Zhang et al. 2019a, b, c, d)

and chitosan, the pore structure of the as-prepared magnetic adsorbent could be flexibly tuned correspondingly (Lu et al. 2019a).

The shapes of the porous materials prepared from the emulsion template could be monolithic, microspherical, and even rod-like (Gokmen et al. 2009). The porous microspheres are formed easily by integrating the emulsion template with precipitation polymerization, but the formation of rod-like porous material still needs the microfluidic setup. We prepared the novel recyclable magnetic porous spheres by dropping the Pickering HIPEs into the hot liquid paraffin. The grafting polymerization reaction occurred between the hydroxypropyl cellulose and acrylic acid in the continuous phase of the Pickering HIPEs when the emulsion droplet fall (Zhu et al. 2017a; Zhu et al. 2017b). The size of as-prepared magnetic porous spheres was about 1.5 mm, and the sufficient porous structure existed in the spheres. The magnetic microsphere also attracts much attention due to the integrated advantages of nanoparticles and porous materials. In general, porous microspheres are formed by using the pore-foaming agent, and the strategy is classified as hard templates or soft templates. The uniform porous structure could be created after removing solid particles via etching in hard template, but the obvious flaws are the complicated removal process of hard templates and the harsh conditions.

In comparison, the post-processing of soft templates is more convenient, as the template removal could be achieved by a simple extraction or evaporation process. The microfluidics technology and the double-emulsion technique are the most representative soft template methods to prepare porous microspheres with interconnected porous structure. But the microfluidics technology possesses the gingerly preparation process, while the double-emulsion technique is simpler. In general, the formation of double emulsions needs a two-step emulsification process and also requires two kinds of surfactants to stabilize the oil-water (O/W) and water-oil (W/O) interfaces, respectively. The preparation process is flexible and suitable for the large-scale production (Fig. 13.9). Our group (Zhu et al. 2016c) prepared a series of magnetic porous microspheres via $(O_1/W)/O_2$ double emulsion. The silane-modified Fe_3O_4 particles and the surfactant of polyglycerol polyricinoleate were used to stabilize the internal O_1/W Pickering emulsion and the $(O_1/W)/O_2$ double emulsion, respectively. The results indicated that the magnetic microspheres presented a mean diameter of about 10 μm and interconnected porous structure.

13.3 The Application of the Magnetic Materials Prepared by Emulsion Template in Water Treatment

13.3.1 Removal of Heavy Metal Ions

Heavy metal ions, such as Pb^{2+}, Cr^{6+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, etc., are extremely noxious water pollutants and imposed serious side effects in living organisms. In addition, the prolonged excessive intake of heavy metal ions could damage the

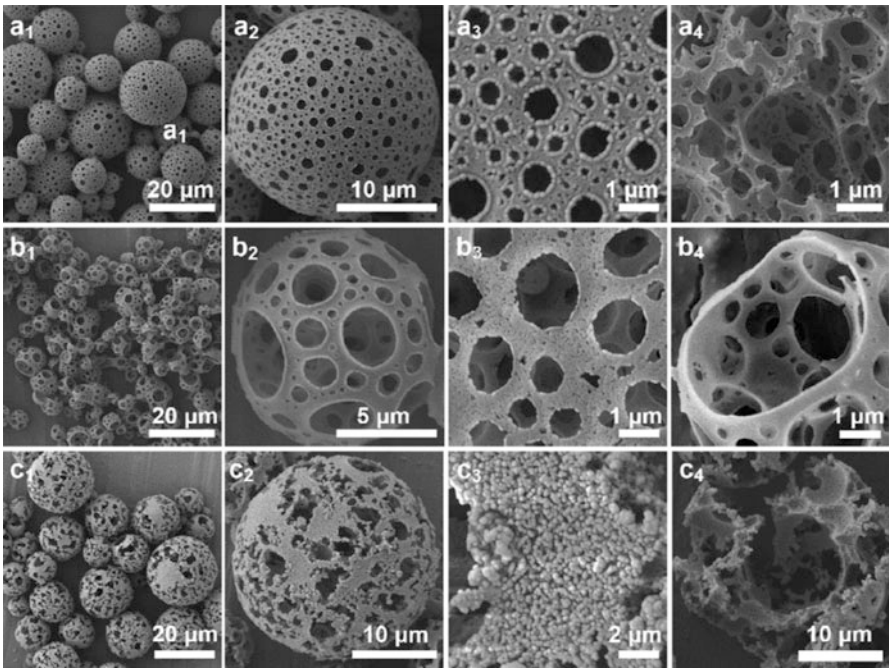

Fig. 13.9 SEM images of microspheres prepared from the double emulsions stabilized by a single anionic surfactant. (Reproduced with permission from Li et al. 2014a, b)

kidney, liver, brain function, and nervous system (Wadhawan et al. 2020). Adsorption is recognized as an efficient method for the removal of heavy metals, and magnetic adsorbents display distinct advantages including magnetic nanoparticles, magnetic composites with the micro−/nanospherical structure, and magnetic porous materials.

Magnetic Nanoparticles

Spinel ferrites (SFs) possess the superior chemical stability, enhanced magnetic properties, large surface area, vast of active sites at the corners, edges, and steps, so SFs applied in water treatment attract much attention and display enormous potential. For example, the adsorption performance of $MnFe_2O_4$ to Cu^{2+} and Pb^{2+} was reported about 197 mg/g and 21.64 mg/g (Ren et al. 2012). The magnetic MFe_2O_4 (M = Co, Ni, Cu, and Zn) nanoparticles had enhanced adsorption capacities of 69.4 and 47.1 mg/g for Cd^{2+} and Pb^{2+}, respectively (Yaqoob et al. 2019). The $MnFe_2O_4$ and $CoFe_2O_4$ prepared by Asadi et al. had the understanding adsorption capacities of 454.5 and 384.6 mg/g for Zn^{2+} (Asadi et al. 2020). The magnetic $Co_{0.6}Fe_{2.4}O_4$ microparticles with a uniform pore size of about 7.432 nm showed a high specific surface area of 97.155 m^2/g, and 80.32 mg/g of adsorption capacities

towards Pb^{2+} (Kaur et al. 2015). The SFs prepared from emulsion template also present good adsorption performance for heavy metals. For instance, magnetic $Ni_{0.6}Fe_{2.4}O_4$ and $Co_{0.6}Fe_{2.4}O_4$ prepared from microemulsion template by Duan et al. had the maximum adsorption capacities of 189.04 mg/g and 80.32 mg/g for U(VI) or Pb(II) (Duan et al. 2015; Duan et al. 2016).

It is difficult to correlate the adsorption performance and the preparation method towards SFs, because the adsorption performances of SFs are affected by many factors, e.g., size and shape, metal ion doping, calcination temperature, and so on. Generally, SF nanoparticles with high surface area have superior adsorption performance. For example, Hu et al. (Hu et al. 2007) compared the adsorption capacities of $MnFe_2O_4$, $MgFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$, $NiFe_2O_4$, and $CoFe_2O_4$ to Cr(VI). The adsorption capacities followed the order $MnFe_2O_4$ > $MgFe_2O_4$ > $ZnFe_2O_4$ > $CuFe_2O_4$ > $NiFe_2O_4$ > $CoFe_2O_4$. The $MnFe_2O_4$ nanoparticles with a high surface area of 180 m^2/g showed shorter equilibrium time compared with other SFs. Besides, the chemical doping and calcination temperature also significantly affect the adsorption properties to heavy metals. The chemical doping could tune the adsorption properties of MFe_2O_4 by varying the particle sizes, morphologies, and functionalization, as well as variation of the adsorption characteristics. Especially, the adsorption performance of SFs is enhanced by introducing rare earth metal ions (Jacobo et al. 2004; Kuai et al. 2013). It is attributed to the structural disorders of SFs, caused by the doping of rare earth ions, is beneficial to increase the surface area and active binding sites. In addition, the calcination temperature may change the particle size, morphology, and surface area of SFs, resulting in the changed adsorption capacities (Ahalya et al. 2014).

The Magnetic Microsphere

Although the nano-adsorbents such as Fe_3O_4, $SrFe_2O_4$, and $Ni_{0.6}Fe_{2.4}O_4$ are conveniently prepared and recycled from the water, the adsorption performance still needs to enhance. Because the inherent physical and chemical property and the serious aggregation of nano-magnetic particles in water. Thus, many organic small molecules are used to modify the naked magnetic particles for increasing the adsorption sites, including ascorbic acid, oxalic acid, and so on (Feng et al. 2012). However, the increase in the adsorption performance is still limited. In addition, the organic molecule might diffuse into the water and cause the secondary pollution. Hence, introducing and immobilizing the magnetic particle into the matrix of polymeric adsorbent become the main direction of the current research, and the magnetic polymeric adsorbents with spherical structure are prepared and widely studied.

In this field, incorporation of the natural polymer into the adsorbent via the inverse emulsion is employed to prepare the spherical adsorbents. The natural polymers included carboxymethylcellulose and sodium alginate, especially chitosan and its derivatives have been widely applied, due to low cost, nontoxic, renewable, biodegradable, inherent adsorption performance, and high activity of the amino and hydroxyl. The simplest method for the preparation of the magnetic adsorbent based

on chitosan is to disperse the magnetic particle into chitosan solution via the inverse emulsion and then cross-link with glutaraldehyde and epichlorohydrin or adjust the solution pH from acid to alkaline. The obtained magnetic spherical adsorbent could be used for the removal of many pollutants, including heavy metal, antibiotic, and dyes (Lian et al. 2015). Despite the magnetic adsorbents based on the chitosan and the magnetic particles are easy to prepare in mild condition, the obtained adsorbents usually show the weak adsorption performance for pollutants. For instance, Podzus et al. (Podzus et al. 2009) investigated the adsorption performance of magnetic chitosan composite for Cu^{2+}, the adsorption capacity was only about 19.4 mg/g. Zhang et al. (Zhang et al. 2019a, b, c, d) immobilized the Aspergillus onto the sodium tripolyphosphate crosslinked magnetic chitosan microspheres, the adsorption capacity of Cu^{2+} increased to 119.21 mg/g. It was attributed to the fact that the most of amino group and hydroxyl group, which played a critical role in the adsorption process participated in the cross-link reaction, especially for the chemical cross-link by formaldehyde, glutaraldehyde, epichlorohydrin, tripolyphosphate, ethylene glycol diglycidyl ether, and dimethyloldihydroxy ethylene urea. Hence, two strategies are applied to increase the adsorption performance of this type of adsorbent, that are: using of chitosan derivatives to replace chitosan during preparation of adsorbent, or modification the magnetic chitosan microspheres with others polymer.

For the first strategy, various chitosan derivatives have been used in the preparation of magnetic adsorbents, including quaternized chitosan, carboxylated chitosan, N-acyl chitosan, and so on. For example, Song et al. (Song et al. 2017) replaced the chitosan with derivatives of N-(2-hydroxyl)propyl-3-trimethyl ammonium chitosan chloride (HTCC) to prepare the As(III) imprinted magnetic adsorbent in microemulsions. The magnetic adsorbent showed excellent selectivity and recyclability for As(III) over a wide pH range. Moreover, the adsorption efficiency still maintained above 75% after 10 recycles. Tao et al. (Tao et al. 2016) modified chitosan with glutamine and fabricated a magnetic composite microsphere in the inverse emulsion for adsorbing Hg^{2+} and acid green 25 (AG25). The Hg^{2+} and AG25 all could be efficiently removed in weak acidic conditions, as the effective interactions between Hg^{2+} and the carboxyl, amide groups, as well as the hydrogen bonding between secondary amine of AG25 and carboxyl groups (Fig. 13.10).

Compared with the first strategy, the modification of magnetic chitosan microspheres with other polymers or introducing the other inorganic/organic adsorbents is more widely adopted. It is well known that the magnetic chitosan microspheres could be modified easily based on the high activity of chitosan's amino groups, including grafting polymerization, esterification, and acylation. For instance, the carboxylated chitosan magnetic spherical adsorbents with micro−/submicron size were fabricated by Xu et al. via the microemulsion method for Pb^{2+} removal (Xu et al. 2015). The chitosan magnetic microspheres with different sizes were formed in the microemulsion and then modified with ethylene diamine tetra acetic acid. The favorable recycle of both adsorbents displayed and 94% of elimination capacity could be kept after fifth cycle. Sun et al. (Sun et al. 2016a) grafted the quaternary ammonium groups onto the magnetic chitosan microspheres for removal of the Cr^{6+} under a high acid environment. The adsorption capacity could be reached

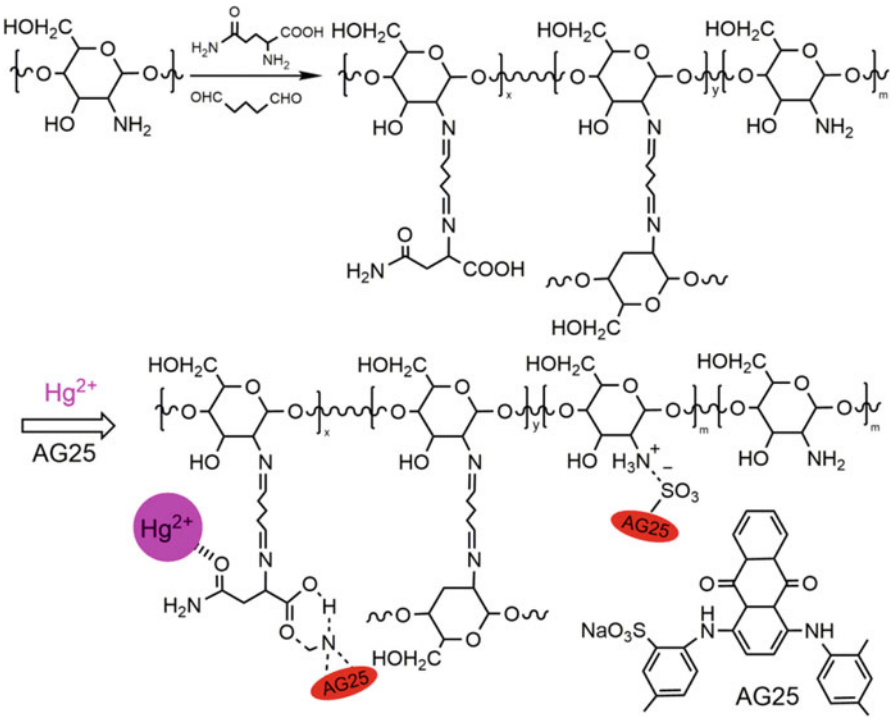

Fig. 13.10 Chemical cross-linking reaction of chitosan modified with glutamine and brief description for available adsorption mechanism of CS-Gln-MCM for removal of AG25 and Hg^{2+}. (Reproduced with permission from Tao et al. 2016)

to 233.1 mg/g for Cr^{6+} at pH 2.5 and 25 °C, depending on the initial Cr^{6+} concentration. Zheng et al. (Zheng et al. 2019) modified the magnetic chitosan microspheres with poly(4-vinyl pyridine) and the poly([2-(methacryloxy)ethyl] trimethylammonium chloride), the maximum adsorption capacities of two adsorbents for Cr^{6+} were 344.83 mg/g and 153.85 mg/g, respectively (Zheng et al. 2018).

Sun et al. (Sun et al. 2016b) adopted a large number of amino groups for modification of magnetic chitosan microspheres to increase the adsorption performance of Cr^{6+}. The adsorbent of polyethylenimine-modified magnetic chitosan microspheres (Fe_3O_4–SiO_2–CTS-PEI) exhibited high acid resistance and magnetic responsiveness, and the maximum adsorption capacity was 236.4 mg/g at 25°C, which was approximately 2.5 times for the unmodified magnetic microspheres. Xiao et al. (Xiao et al. 2017) introduced the amino groups and carboxyl groups into the spherical magnetic chitosan adsorbent for adsorption of Cu^{2+}. The Fe_3O_4 nanoparticles were supported onto the carboxyl-functionalized polystyrene particles (PS) by integrating the emulsifier-free emulsion polymerization and the in situ coprecipitation and then coated with cross-linked chitosan thin film. Finally, branch polyethylenimine (PEI) was grafted on the surface of PS/Fe_3O_4/CS via Michael

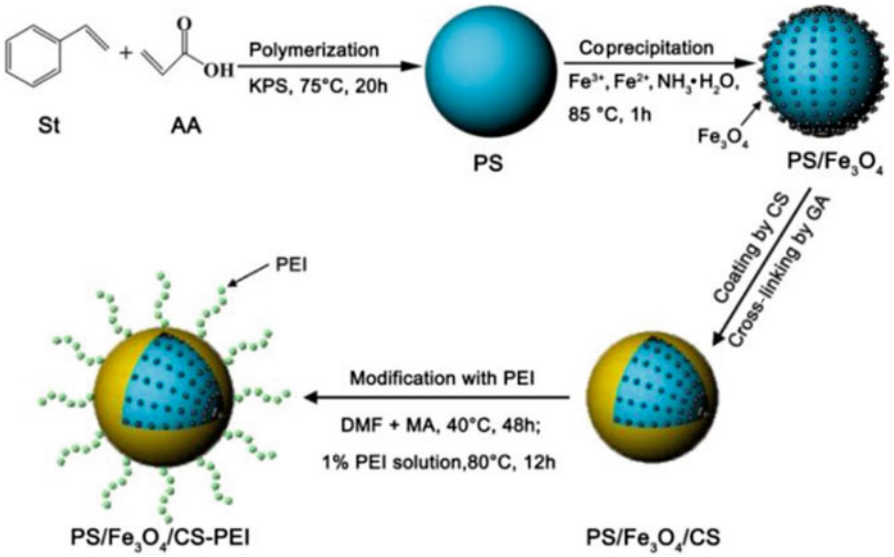

Fig. 13.11 Schematic illustration of the synthesis of PS/Fe_3O_4/CS-PEI composites and the photos of TEM (**a**) and SEM (**b**) of PS, TEM (**c**) and SEM (**d**) of PS/Fe_3O_4, TEM (**e**) of PS/Fe_3O_4/CS, and TEM (**f**) of PS/Fe_3O_4/CS-PEI. (Reproduced with permission from Xiao et al. 2017)

addition reaction and an amidation reaction. The adsorption capacity to Cu^{2+} reached 204.6 mg/g within 15 min (Fig. 13.11). Except for the chemical modification with polymers, some inorganic adsorbents also increased the adsorption capacity of the spherical magnetic chitosan adsorbent. Wang et al. (Wang et al. 2019a, b) introduced zinc oxide into the spherical magnetic chitosan adsorbent to eliminate the arsenic from groundwater, a high As(V) adsorption capacity achieved with 63.69 mg/g.

Due to the high activity of acrylate monomer and the strong affinity of carboxyl and acylamino for heavy metals, the spherical magnetic adsorbents prepared with acrylate monomers of acrylic acid and acrylamide via the emulsion template, especially the inverse emulsion is widely reported. The obtained adsorbents exhibit excellent adsorption performance and favorable reusability. For example, beadlike magnetic nanocomposite microgel adsorbent was prepared by polymerizing and cross-linking the poly(acrylic acid) (PAA) onto the silane-modified Fe_3O_4 particles to remove Pb^{2+} (Jiang et al. 2017) (Fig. 13.12). Due to the plentiful carboxyl groups, high wettability, and high swelling of the Fe_3O_4/PAA microgel adsorbent, the adsorption capacity towards the targeted metal ions of Pb^{2+} can be reached to 123.3 mg/g. Xie et al. (Xie et al. 2017) produced the magnetic microspherical adsorbent by polymerization of acrylic acid and acrylamide onto the cassava residue by an inverse emulsion method. The Cu(II) adsorption capacity of the adsorbents reached 110.5 mg/g when the pH was 6.4. Wanna et al. (Wanna et al. 2016) reported a magnetic adsorbent based on poly(methyl methacrylate) by the emulsion polymerization technique for heavy metal removal. The polyethylene glycol bis(amine)

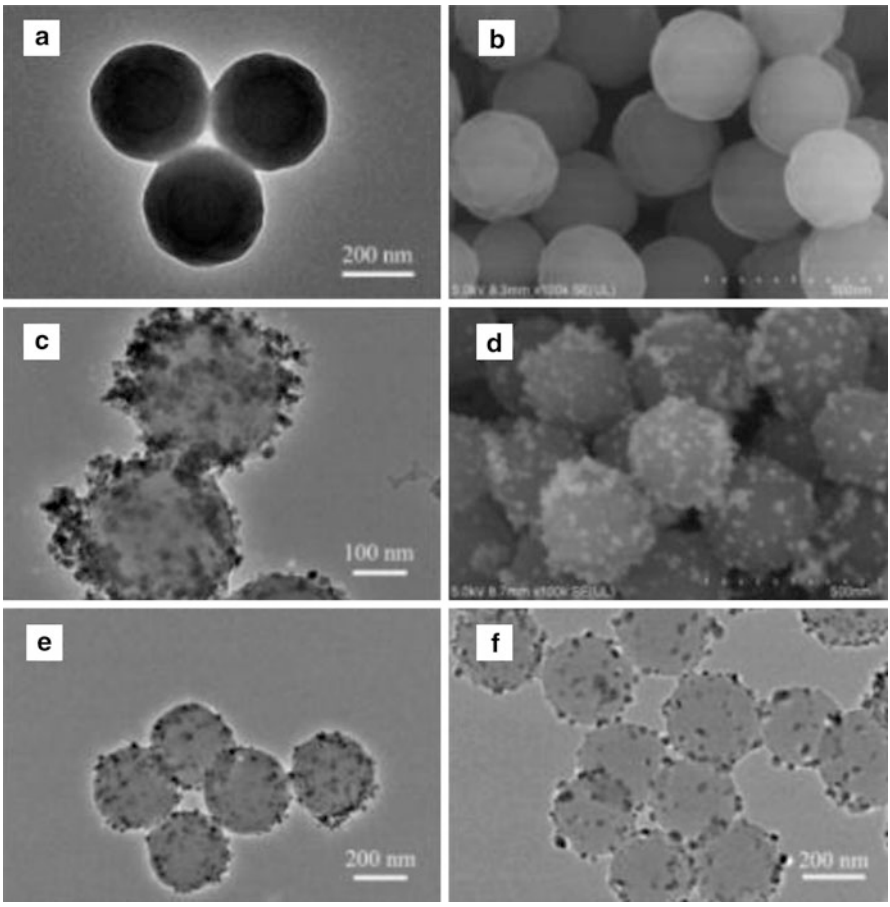

Fig. 13.11 (continued)

(PEG-bis(amine)) was grafted onto the magnetic nanoparticles after being modified with the poly(methyl methacrylate) by the reaction between the carboxyl groups derived from the hydrolysis of PMMA and the amino groups of polyethylene glycol bis(amine). The results indicated that the heavy metal uptake ratios of the adsorbents were 0.08, 0.04, 0.03, and 0.01 mmol/g for Pb^{2+}, Hg^{2+}, Cu^{2+}, and Co^{2+}, respectively. The cation radius of the heavy metal is the main effect factor for affecting the removal efficiency.

The conductive polymers including polypyrrole (PPY), polyaniline (PANI), polyindole (PIn), polythiophene (PTh), etc. have excellent adsorption performance for heavy metals, as the remarkable chelating property derived from the abundant of N-containing heterocyclic group. Due to the weak solubility but high activity of pyrrole, indole, and thiophene, the conductive polymer adsorbent is directly prepared from the O/W emulsion with mild condition. Chavez-Guajardo et al. coated

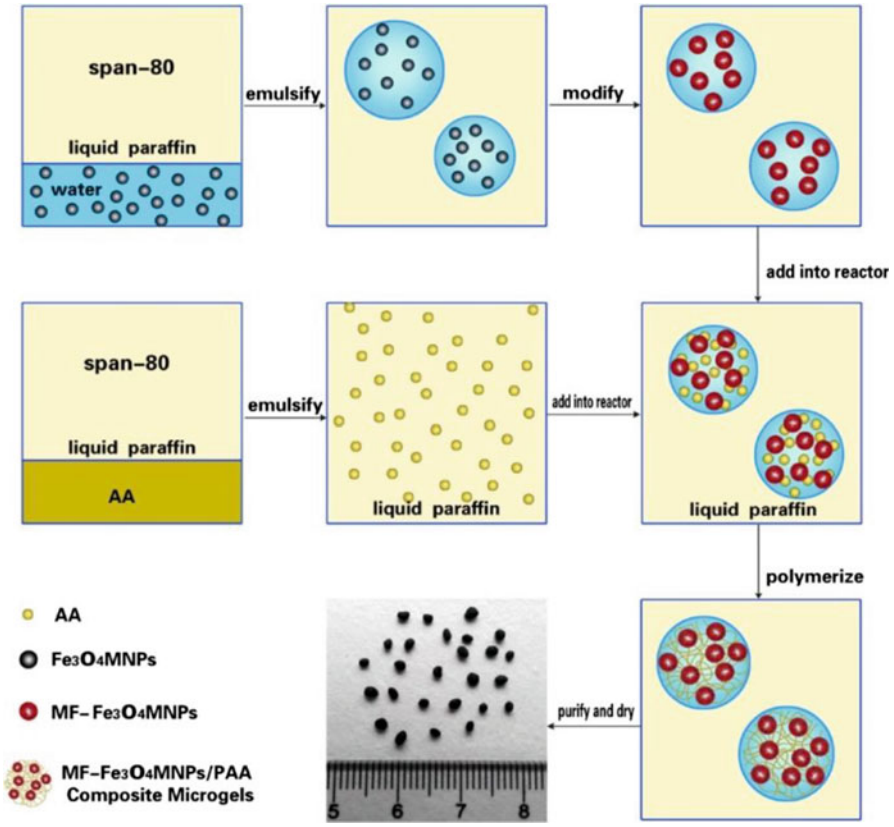

Fig. 13.12 Synthesis procedures of multi-functionalized Fe_3O_4 magnetite nanoparticles/polyacrylic acid (MF-Fe_3O_4MNPs/PAA) composite microgels. (Reproduced with permission from Jiang et al. 2017)

the PPY and PANI onto the γ-Fe_2O_3 (PPY/γ-Fe_2O_3 and PANI/γ-Fe_2O_3) through the emulsion polymerization at room temperature. The maximum adsorption capacities of PPY/γ-Fe_2O_3 and PANI/γ-Fe_2O_3 were 209 and 196 mg/g and 171 and 107 mg/g for Cr^{6+} and Cu^{2+} (Chávez-Guajardo et al. 2015). Ebrahimpour et al. (Ebrahimpour et al. 2017) prepared three magnetic conductive polymers of PIn@Fe_3O_4, PTh@Fe_3O_4, and PIn-co-PTh@Fe_3O_4 by modification of Fe_3O_4 nanoparticles with polyindole (PIn), polythiophene (PTh), and poly(indole-co-thiophene) via in situ emulsion polymerization. The magnetic conductive polymers were used to pre-concentrate and determinate the aromatic amines in different real samples, and the PIn-co-PTh@Fe_3O_4 nanocomposite sorbent displayed higher extraction efficiency.

The Magnetic Porous Material

The powder adsorbent presents excellent adsorption performance in the treatment of wastewater, but the adsorption performance easily reduced as the inevitably aggravation in water. Although the millimeter-sized spherical adsorbent overcomes this shortcoming, most of the microspherical adsorbents have dense surface, and thus ions and organic molecules are difficult to diffuse into the matrix of the adsorbent, which limited the adsorption performance. Interestingly, the porous adsorbent could be good at resolving this problem. It possesses stable physical-chemical property, large specific surface area, and substantial exposed adsorption sites inside the adsorbent and high porosity, which could reduce mass transfer resistance. Hence, more and more studies are focused on the porous adsorbents for removal of pollutants. Among various methods, emulsion template technology might be the more effective approach for successful synthesis of porous materials with ordered porous structure, especially HIPEs. Up to now, the porous materials prepared from the HIPEs have been widely acted as the adsorbent for removal of various pollutants, including metal ions, dyes, antibiotic, and so on (Han et al. 2015; Pan et al. 2016; Zhang et al. 2019a, b, c, d). Due to the high porosity, the adsorbent prepared from HIPEs presents excellent removal efficiency for heavy metal ions. For example, Mert et al. used the humic acid-modified Fe_3O_4 (Fe_3O_4@HA) to stabilize HIPEs and formed magnetic polyHIPEs using styrene/divinylbenzene as monomer. Magnetic polyHIPEs were tested to remove Hg^{2+}, and the maximum adsorption capacity of 20.44 mmol/g was achieved (Mert et al. 2013). Zhu et al. prepared magnetic porous adsorbent of Pb^{2+} and Cd^{2+} from HIPEs, which was stabilized with amine-functionalized Fe_3O_4. The surface of the magnetic porous adsorbent possessed abundant benzene rings and was peculiarly prone to attach with the cation by π-bond, and the removal capacities of Pb^{2+} and Cd^{2+} were 257 and 129 mg/g at pH 5.5 (Zhu et al. 2018).

Our group devotes to study the porous adsorbent prepared from emulsion template for elimination of heavy metal (Zhu et al. 2016a; Zhu et al. 2016d; Zhu et al. 2017b). And the macroporous magnetic adsorbent of chitosan-g-poly(acrylic acid) was produced using the Fe_3O_4 nanoparticle-stabilized Pickering HIPE template. The porous adsorbent showed the high adsorption capacities of 308.84 mg/g and 695.22 mg/g, as well as a fast adsorption rate of 40 min for Cd^{2+} and Pb^{2+}, respectively (Zhu et al. 2016b; Lu et al. 2018a). Moreover, the favorable adsorption capacity of 88.95 mg/g for Sr^{2+} was reached by coating the magnetic porous materials with polyaniline (PANI), which was better than most of the other adsorbents (Lu et al. 2018b).

However, high consumption of organic phase and the addition of large amounts of surfactants restrict the application of conventional HIPE templates in the construction of porous adsorbents. To address these problems, we replaced the synthetic surfactant with the magnetic yeast (P-Yeast) to stabilize the HIPEs and developed a series of magnetic porous adsorbents from the HIPE template (Lu et al. 2019a). The stability of Pickering HIPEs and the corresponding porous structure could be controlled with the interaction between P-Yeast and acrylic acid. The open-cell

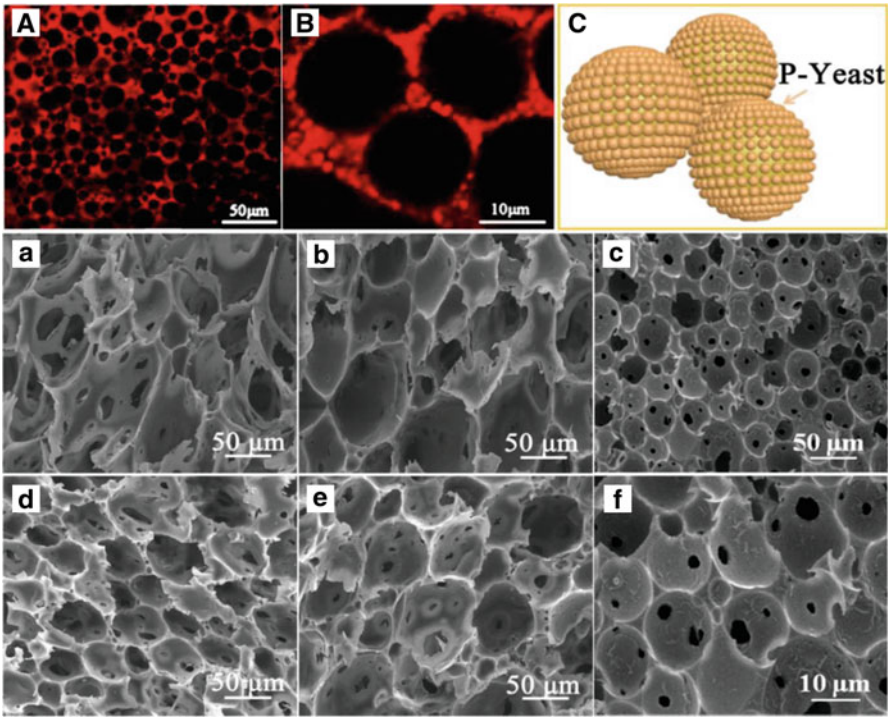

Fig. 13.13 CLSM images and the schematic diagram of P-Yeast-stabilized Pickering emulsions at 75% oil fraction. SEM images of the superporous adsorbent P-Yeast-PAA prepared with different amounts of AA. (Reproduced with permission from Lu et al. 2019a)

superporous adsorbent showed the fast and strong adsorption performance of 179.69 mg/g, 229.52 mg/g, and 166.81 mg/g for scattered metals of Rb^+, Cs^+, and Sr^{2+} (Fig. 13.13). Furthermore, another novel magnetic porous adsorbent was fabricated from the surfactant-free Pickering emulsion template stabilized with magnetic yeast (MY) and chitosan (Lu et al. 2019b). The Pickering emulsion had high stability at the middle phase emulsion (MIPEs) level, and the droplet size could be adjusted easily by controlling the interaction between yeast and chitosan via the pH varying. The microporous magnetic adsorbents with sufficient porous structure also exhibited excellent adsorption performance for Rb^+ and Sr^{2+}, and the saturation adsorption capacities of 168.98 and 151.91 mg/g for Rb^+ and Sr^{2+} were achieved within 25 or 10 min, respectively.

Despite the porous adsorbents with order porous structure are prepared from the emulsion template, but the monolithic adsorbent is needed to smash before using in some case, and the drastic process might destroy thoroughly the porous structure. So how to integrate the advantages of the spherical adsorbent and the porous structure is the research hotspot (Pan et al. 2015). The exciting finding is the porous spherical adsorbent could be directly formed in the multiphase emulsion, including the water-in-oil-in-water (W/O/W) emulsion or the oil-in-water-in-oil (O/W/O) emulsion. It

should be pointed out the emulsion integrated with the microfluidic technique could obtain the porous spheres with perfect structure (Cao et al. 2016). For example, Cao constructed a kind of three-dimensional magnetic porous multi-walled carbon nanotube bead via the multiphase emulsion using a modified microfluidic device. The magnetic porous multi-walled carbon nanotube beads had good adsorption capability to oils and organic solvents with six times recyclability. However, it is difficult to realize the practical application of the porous microspherical adsorbent prepared by the microfluidic technique due to the complicated preparation process, the high production cost, and the toxic organic solvents.

Mudassir et al. (Mudassir et al. 2019) reported a magnetic microporous adsorbent by loading the Fe_3O_4 nanoparticles onto the macroporous polymeric beads, which prepared via the O/W/O emulsion, and finally modified with the poly(acrylic acid) for removal of Pb(II) and crystal violet. The adsorption capacities of 290.69 and 80.20 mg/g for Pb(II) and crystal violet were derived from the sufficient porous structure and abundant acrylic acid. The introduced Fe_3O_4 NPs not only endowed the magnetic property to the microsphere but also improved the BET surface area. Furthermore, the introduced Fe_3O_4 nanoparticles provided the auxiliary cross-linking point to enhance the mechanical strength of the adsorbent (Fig. 13.14).

A magnetic spherical porous adsorbent was synthesized through the integrated process of Pickering emulsion and precipitation polymerization (Zhu et al. 2016e; Zhu et al. 2017a; Zhu et al. 2017b). The Rb^+ and Cs^+ could be effectively removed within 15 and 30 min with the remarkable adsorption capacities of 310 and 448 mg/g, respectively (Fig. 13.15). In addition, the diameter of the spherical adsorbent was reduced from millimeter-level to micron order by adopting the O/W/O double emulsion. The microspherical adsorbent displayed the significant adsorption performance boost, and the removal for Cu^{2+} and Pb^{2+} could be achieved only within 3 min or 5 min, respectively, regardless of high (400 mg/L) or low (100 mg/L) initial concentrations (Zhu et al. 2016d).

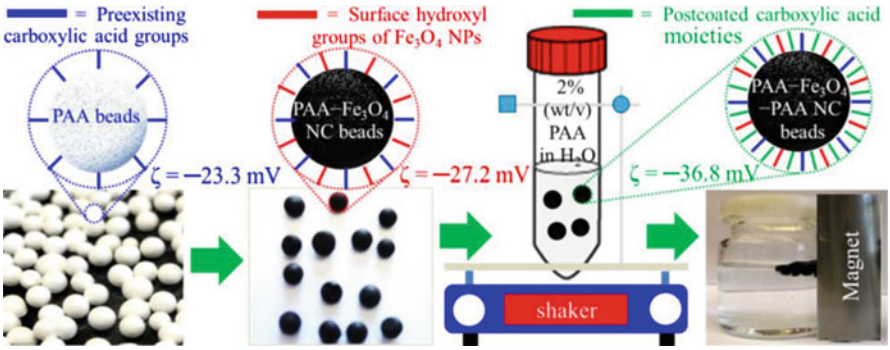

Fig. 13.14 Schematic view of the preparation of PAA (2.28–2.22 mm), PAA-Fe_3O_4 NC (2.26–2.20 mm), and PAA-Fe_3O_4-PAA NC (2.26–2.21 mm) beads. (Reproduced with permission from Mudassir et al. 2019)

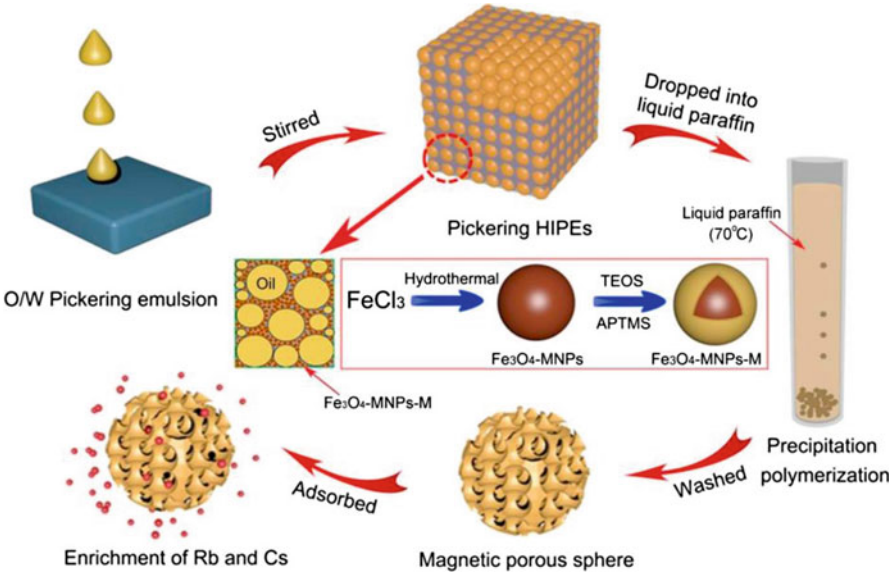

Fig. 13.15 Synthetic route of the interconnected magnetic porous spheres for enrichment of Rb^+ and Cs^+. (Reproduced with permission from Zhu et al. 2017a)

13.3.2 Removal of Organic Pollutant

Organic pollutants have become one of the most critical environmental issues besides heavy metals in water, as their durability and toxicity in the environment. The scope of organic pollutants is very broad, including endocrine-disrupting chemicals, pharmaceuticals, detergents, organic dyes, personal care products, pesticides, and common industrial organic chemicals (Lu and Astruc 2020; Routoula and Patwardhan 2020). And the adsorption technique plays an important role in the elimination of organic contaminants.

Magnetic Nanoparticles

The SFs used to adsorb organic pollutants are more common than in the removal of heavy metals, because SFs not only adsorb heavy metals and cationic dyes, other negatively charged organic pollutants also could be eliminated from aqueous solution (Konicki et al. 2013; Ding et al. 2015). For instance, the magnetic nanocomposite of $CaFe_2O_4$ and $MnFe_2O_4$ was synthesized for the removal of methyl orange, and the maximum capacity reached 344.83 mg/g. The $Ni_{0.6}Fe_{2.4}O_4$ nanoparticles fabricated by emulsion template for adsorption of Congo red, and 92.04% of Congo red could be removed within 9 min (Zeng et al. 2014). The adsorption mechanism of SFs to various cationic or anionic species included

ion-exchange, electrostatic interactions, hydrogen bonding, and π-π interactions surface complexation (Zhang et al. 2010; Wang et al. 2012; Zhou et al. 2014). Particularly, the hydroxyl groups derived from M-OH and Fe-OH play an important role. More importantly, the charge of the hydroxyl groups would change with the variation of solution pH. Generally, SFs possess positive charge at low pH but will convert to the negative charge in the alkaline environment, due to the deprotonation of hydroxyl groups (Zafar et al. 2018) (Fig. 13.16). Except the surface charge, the recent reports revealed that the microstructure, particle size, and surface morphologies of SFs also affect the adsorption performance (Ding et al. 2015).

Except for the adsorption mechanism, the role of SFs for the removal of the organic pollutants also includes the catalytic degradation. SFs generate oxygen free radicals in the presence of strong oxidizing agents. For example, the peroxymonosulfate could be activated with the $CoFe_2O_4$ and then generated the sulfate radicals for the degradation of organic pollutants, such as diclofenac (Deng et al. 2013), methylene blue (Salami et al. 2019), and so on. In fact, many SFs possess the photocatalytic performance under visible light, such as $NiFe_2O_4$, $CuFe_2O_4$, and $ZnFe_2O_4$ (Mahmoodi 2013). Therefore, the integrated performances of the adsorption and the catalysis contribute to enhancing the adsorption properties of SFs to many pollutants.

The Magnetic Microsphere

The magnetic chitosan microspheres exhibit excellent adsorption performance for many organic pollutants. The adsorption capacities of chitosan-coated Fe_3O_4 for patulin and methylene blue (MB) were determined about 6.67 mg/g and 122 mg/g (Luo et al. 2017; Liu et al. 2018). And the performance was affected by the amount of the chitosan, magnetic particles, and cross-linking density. It was crucial to

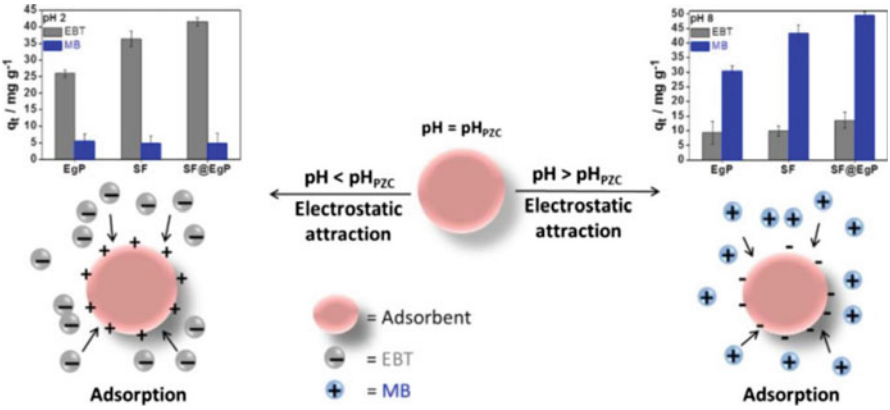

Fig. 13.16 Role of pH on $SrFe_2O_4$ (SF) for tunable adsorption of anionic dye Eriochrome Black T (EBT) and cationic dye methylene blue (MB). (Reproduced with permission from Zafar et al. 2018)

prevent from the inevitable agglomeration of magnetic particles in chitosan solution for the preparation of the magnetic chitosan adsorbent, which caused the heterogeneous magnetism to magnetic adsorbents. It confirms that this problem could be solved completely by supporting the magnetic particles onto inorganic materials, e.g., clay minerals and carbon nanotube. For example, the magnetic particles of chitosan/organic rectorite-Fe_3O_4 were prepared for removal of methylene blue (MB) and methyl orange (MO), and the maximum adsorption capacities for MB and MO were 24.69 mg/g and 5.56 mg/g, respectively (Fig. 13.17). The Fe_3O_4 was supported onto the rectorite first and then obtained the magnetic adsorbent of chitosan/organic rectorite-Fe_3O_4 microspheres (CS/Mt-OREC microspheres) by dispersing the rectorite-Fe_3O_4 into chitosan solution and cross-linked with the formaldehyde and epichlorohydrin in reversed-phase microemulsion (Zeng et al. 2015). Ma et al. prepared a chitosan/kaolin/Fe_3O_4 magnetic microsphere by supporting the Fe_3O_4 onto kaolin and emulsion cross-linking (Ma et al. 2014). The obtained microspheres showed stable adsorption performance for ciprofloxacin removal at least four adsorption-desorption cycles. Except the increased dispersity after incorporation of inorganic materials, it is also in favor of enhancing the mechanical strength of magnetic adsorbent, due to the additional cross-linking point of inorganic materials in the polymeric structure.

Above studies are focused on preparation with the magnetic spherical adsorbent based on the chitosan solution via the common inverse emulsion, which is stabilized

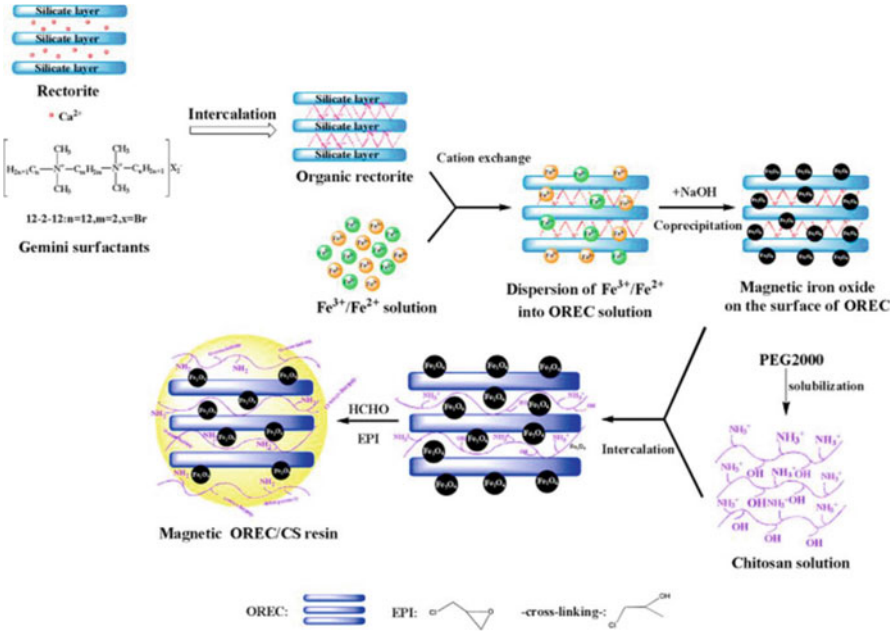

Fig. 13.17 The formation process of chitosan/organic rectorite-Fe_3O_4 microspheres. (Reproduced with permission from Zeng et al. 2015)

with surfactant. However, the residual surfactant might lead to the risk of secondary pollution for water. Recently, Pickering emulsion has been studied widely, due to the low usage levels and the high stability of the obtained emulsion, in which the surfactant is replaced with particles for stabilizing emulsion (Murray 2019). In addition, natural particles as the stabilized particle of Pickering emulsion become the study trend in recent years. In fact, chitosan also could be served as the stabilized particles for the formation of Pickering emulsion as its pH sensitivity (Li et al. 2019). Ou et al. prepared an imprint polymeric adsorbent by using the Pickering emulsion stabilized with chitosan nanoparticles (Fig. 13.18). Fe_3O_4 embedded into the matrix of adsorbent by directly dispersing the hydrophobic Fe_3O_4 into the dispersed phase. The erythromycin (ERY) adsorption capacity of magnetic adsorbent was about 52.32 μmol/g at 15 °C (Ou et al. 2015).

The functional groups of carboxyl, acylamino, amino, etc. have been widely incorporated into the adsorbent for removal of organic pollutants. For instance, Dai et al. (Dai et al. 2012) fabricated the Fe_3O_4/PAA microgel adsorbent by similar method for selective adsorption of tetracycline. The Fe_3O_4/PAA microgels possessed the molecular recognition ability by adopting the molecular imprinting technique, and the estimated adsorption capacity towards tetracycline was about 6.33 times higher than that of magnetic adsorbent without imprinting. Mao et al. (Mao et al. 2016) synthesized a pH-sensitive magnetic molecularly imprinted polymer via Pickering emulsion polymerization of methacrylic acid for selective adsorption of bifenthrin. The magnetic adsorbent displayed the outstanding adsorptive selectivity for bifenthrin, and the adsorption-desorption cycle could be easily operated by changing the pH of the solution.

Resin is also applied to remove pollutants due to favorable mechanical strength and abundant adsorption groups (Ming et al. 2015). The emulsion template is often adopted during the synthesis process at the aim of obtaining monodisperse resin microspheres. For example, iron-oxide nanoparticles were first coated with γ-methacryloxypropyl-trimethoxysilane and then polymerized with styrene and divinylbenzene in an O/W emulsion (Sehlleier et al. 2016). The MB adsorption capacity of the obtained adsorbents was about 298 mg/g. Lu et al. (Lu et al. 2017) fabricated magnetic hollow carbon microspheres (MHCMs) to remove rhodamine B by alternation of surfactant-free emulsion polymerization and microwave-assistant polycondensation (Fig. 13.19). The magnetic adsorbent with the multilayer core-shell structure was obtained through the emulsion polymerization and microwave-assistant hydrothermal method. The magnetic hollow carbon microspheres had uniform morphologies and high surface area. And the removal efficiency of rhodamine B (RB) reached to 99.5% and the adsorption capacity was 300 mg/g.

Wang et al. (Wang et al. 2019a, b) prepared a novel core-shell microspherical resin adsorbent of Fe_3O_4@lignosulfonate/phenolic through the emulsion polymerization to adsorb dyes. The maximum capacity was 283.6 mg/g in 40 min, which was much higher than those of most lignins and lignin-rich biomass. Zhu et al. (Zhu et al. 2016) synthesized magnetic resin polymer adsorbent with molecularly imprinted structure by Pickering emulsion, stabilized with magnetic eggshells. The

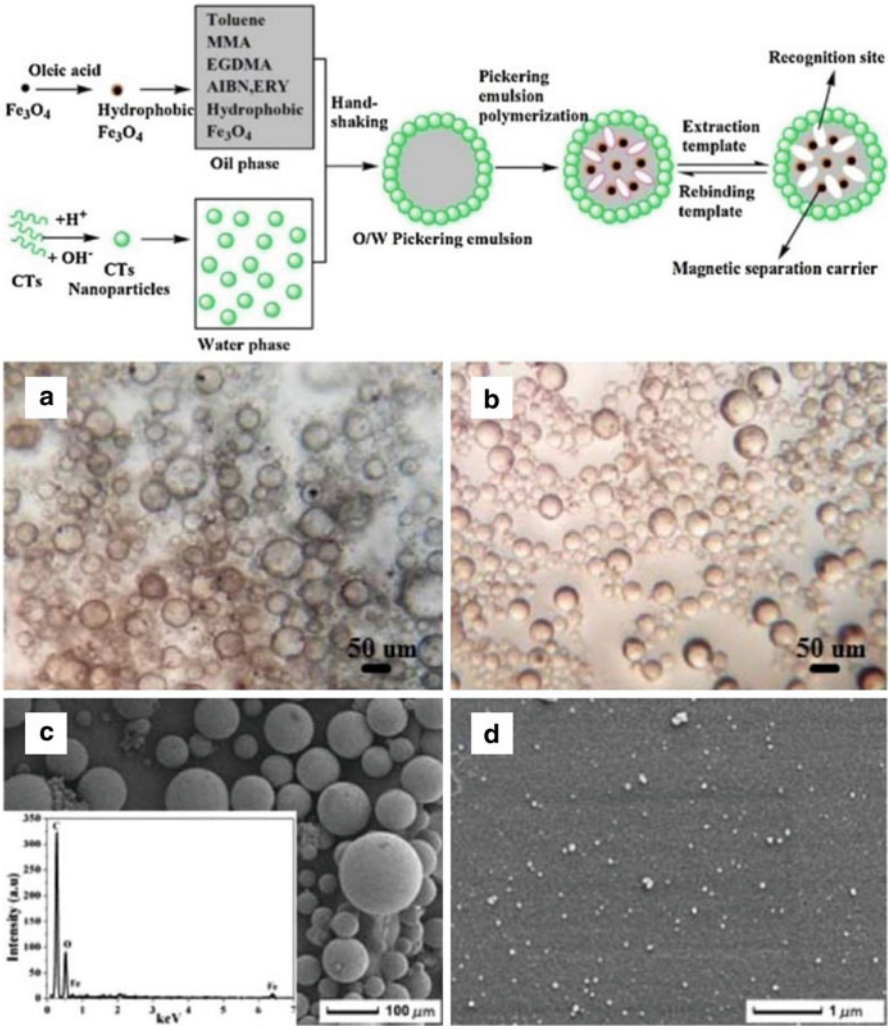

Fig. 13.18 Formation of magnetic imprinted polymers (MIPs) from O/W Pickering emulsion polymerization and the optical micrographs and SEM images of the Pickering emulsion and imprint polymeric adsorbent. (Reproduced with permission from Ou et al. 2015)

molecularly imprinted adsorbent with spherical and wrinkled morphology was obtained in the dispersed phase by polymerization of the monomer of methyl methacrylate. Adsorption experiments showed that the as-prepared molecularly imprinted adsorbent could selectively adsorb erythromycin, but it presented a low adsorption capacity of 47.393 mg/g, which might be due to the dense coating of the magnetic eggshell.

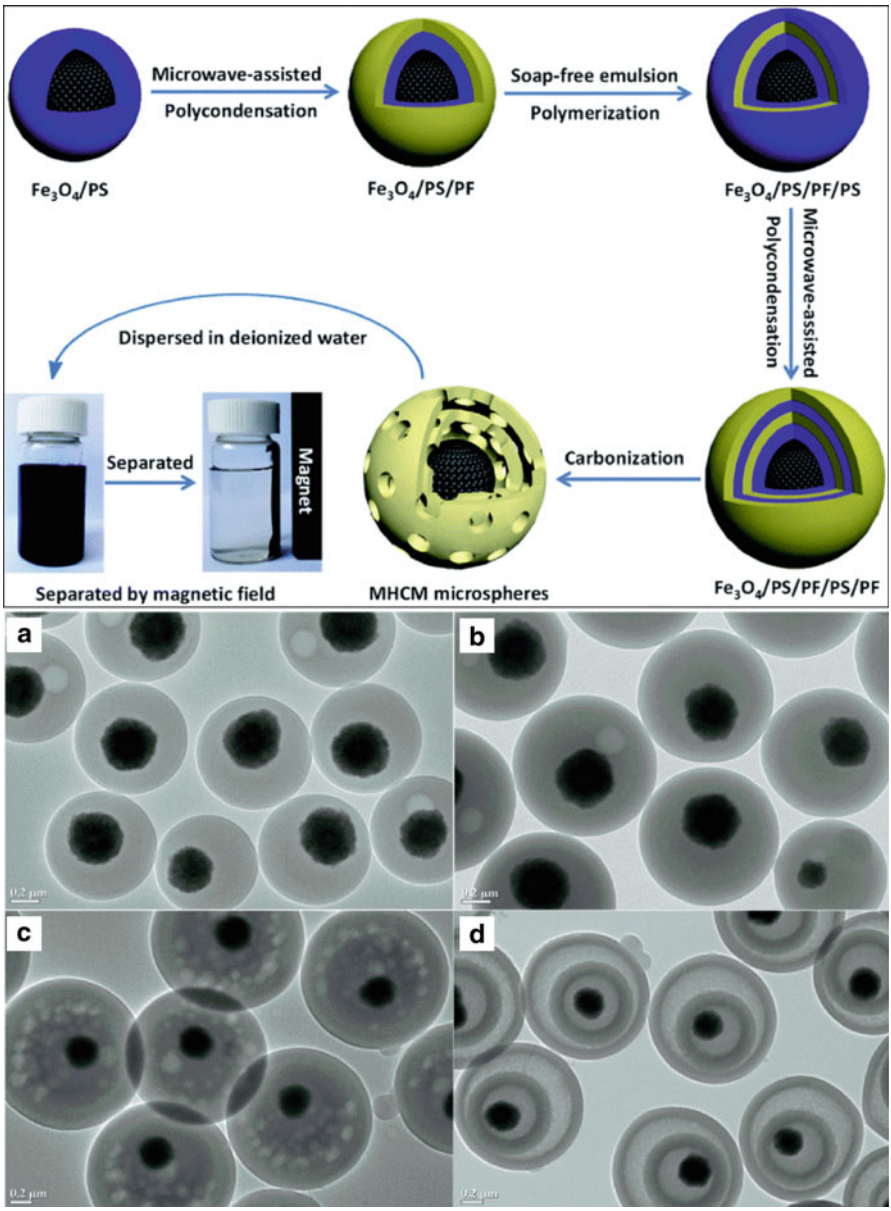

Fig. 13.19 Synthetic procedure of the MHCMs and the TEM images of the multilayer core-shell structure. (Reproduced with permission from Lu et al. 2017)

Magnetic Porous Material

More and more researches on the use of porous adsorbents for removal of organic pollutants are published in recent years (Wright et al. 2017; Kovačič et al. 2018). The sufficient porous structure of magnetic porous materials is conductive to fast the mass diffusion of organic pollutants in the matrix of adsorbent. In addition, the functional groups sited in the interior of adsorbent could be adequately exposed, resulting in the increased adsorption performance. For example, Du et al. (Du et al. 2019) fabricated Fe_3O_4@$Cu_3(btc)_2$ (Fe_3O_4@HKUST-1) magnetic particles and embedded into polyHIPEs, which were synthesized by ethylamine, divinylbenzene, and methyl methacrylate to form a polyHIPE composite by in situ polymerization. The adsorption experiment revealed that polyHIPEs introduced the Fe_3O_4@HKUST-1 displayed the higher removal efficiency for antibiotics of oxytetracycline (OTC), tetracycline, duomycin, and chlortetracycline than the unmodified polyHIPEs. Multiple actions including π-π interactions, hydrogen bonding, and electrostatic interactions resulted in the high extraction ability of magnetic polyHIPEs cake for antibiotics. Wu et al. (Wu et al. 2017) prepared a series of magnetic porous adsorbents through Pickering HIPEs for the removal of λ-cyhalothrin; the Fe_3O_4 nanoparticles coated with oleic acid (Fe_3O_4-OA) were applied to stabilize the emulsion. Because the irreversible adsorption of Fe_3O_4-OA at the oil-water interfaces, the throats decreased with the variation of Fe_3O_4-OA content. The maximum λ-cyhalothrin adsorption capacity at 298 K was 404.4 μmol/g (Fig. 13.20).

Azhar et al. (Azhar et al. 2019) obtained novel porous materials from the HIPE template stabilized with humic acid-modified Fe_3O_4 (HA-Fe_3O_4) and cationic fluorosurfactant (CFS). The HIPEs had increased stability than the emulsion only stabilized with CFS. The porous structure of as-prepared polyHIPEs was easily controlled by altering the concentrations of HA-Fe_3O_4 and/or CFS. The porous materials showed the high capacity for the raised oil absorption and methylene blue. More importantly, the foams adsorbent could be recycled by a simple centrifugation at least 10 cycles without obvious decrease in adsorption capacity. Zhu et al. (Zhu et al. 2015) fabricated multihollow magnetic imprinted microspheres by polymerization of Pickering double emulsion. The hydrophobic Fe_3O_4 nanoparticles

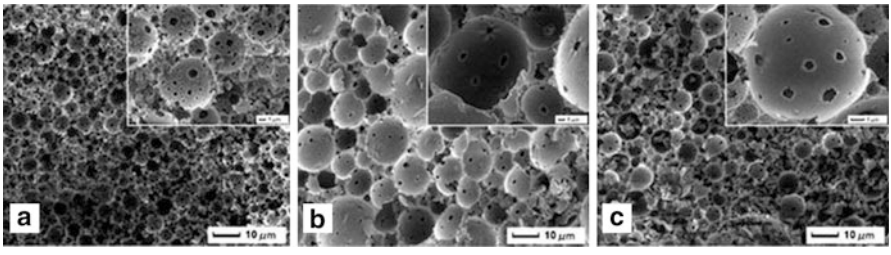

Fig. 13.20 SEM images of magnetic porous adsorbent with different amounts of Fe_3O_4 particles. (Reproduced with permission from Wu et al. 2017)

and hydrophilic cellulose nanocrystals were used to stabilize the W/O interface and the O/W interface, respectively. The selective recognition capability of the as-prepared microspheres for bifenthrin was proved to be more effective. Wang et al. (Wang et al. 2018a, b) also reported a molecularly imprinted multicore rattle-type microsphere for selective adsorption of bisphenol A through a facile Pickering emulsion polymerization, using silica nanoparticles as the stabilizer. Our group (Lu et al. 2018a) also prepared a novel magnetic porous adsorbent of chitosan-g-poly(2-acrylamide-2-methylpropanesulfonic acid) (CTS-g-AMPS) by grafting AMPS onto CTS in the Fe_3O_4-stabilized Pickering HIPEs; the as-prepared porous adsorbents could be employed to eliminate tetracycline and chlortetracycline. The adsorption capacities for tetracycline and chlortetracycline were 806.60 and 876.60 mg/g in a wide pH range of 3.0–11.0, respectively.

13.3.3 The Oil-Water Separation

Besides the soluble pollutants such as heavy metal ions, dyes, and antibiotics, many insoluble or weakly soluble pollutants are also contained in the wastewater. These pollutants may be originated from industrial oily wastewater or oil spill accidents. These types of insoluble or weakly soluble pollutants are also one of the most serious problems for the water environment (Zhang et al. 2019a, b, c, d). Generally, the separation of oil/water mixture can be classified into three main categories: oil removal, water removal, and controllable separation of oil and water. Among them, oil removal is the most attractive as compared to the other two, because of its simplicity and easiness.

Magnetic Nanoparticles

The magnetic nanoparticles could be served as the oil adsorbent, but the premise is the magnetic nanoparticles should be coated with the organic compounds. The functionalized magnetic nanoparticles have strong affinity for oil and thus could be to adsorb oil effectively. Oleic acid is widely used, as oleic acid has a high affinity to the Fe atoms of magnetic nanoparticles. Osama et al. (Osama et al. 2015) functionalized the Fe_3O_4 with oleic acid in the miniemulsion and then to remove oil. The result indicated that 95 wt. % of crude oil could be removed from the water surface. Zhu et al. also modified the Fe_3O_4 with sodium oleate; the obtained Fe_3O_4/sodium oleate showed excellent performance for the elimination of engine oil from the water surface (Zhu et al. 2012).

Magnetic Microsphere

Although the magnetic nanoparticles have the adsorption performance for oil after the coated with the organic small molecules, the adsorption capacity is relatively low, and thus the magnetic nanoparticles are incorporated into natural or synthetic polymers, including starch, alginic acid, chitosan, and so on. Among of them, the relevant studies of application chitosan to modify magnetic nanoparticles take the most part. Lü et al. (Lü et al. 2017) fabricated a class of chitosan-grafted magnetic nanoparticles by grafting the chitosan onto the silica-functionalized Fe_3O_4 via the Schiff base reaction. The chitosan-grafted magnetic nanoparticles could efficiently flocculate oil droplets at different pH conditions. The electrostatic attraction is dominant in acidic and neutral condition, but hydrophobic interaction plays a vital role in the alkaline condition.

The materials with superhydrophobic and superoleophilic properties could selectively collect oils or organic chemicals from water, which provide a novel strategy for the water-oil separation techniques (Chen et al. 2013). So many oil-adsorbed adsorbents are prepared with the hydrophobic monomer. For instance, Fe_3O_4/PS microspheres prepared through emulsion polymerization exhibited the fast rate for adsorption oil and the best oil absorbency, which was up to 2.492 times of their weight (Yu et al. 2015a, b). Chen also used the Fe_3O_4/PS microsphere to adsorb lubricating oil, and the adsorption amount was three times as the particles' weight (Chen et al. 2013). Another example involved the microspheres for adsorption of oil was prepared by coating the methyl methacrylate onto the Fe_3O_4/PS nanoparticles through secondary polymerization. The high hydrophobicity of the microspheres maintained in the wide pH range of 1–13. After 10 cycles, the nanoparticles still had a high oil absorption capacity of 3.22 g/g (Gu et al. 2014).

Magnetic Porous Material

The limited oil storage capacity of traditional oil/water separation materials (e.g., active carbon, zeolites, and other adsorbents) might restrict their practical applications. In comparison, the monolithic porous materials such as aerogels, sponges, and foams possessed sufficient and interconnected porous structure, which have the great potential in oil absorption, as their features of high oil adsorption capacities and easily recycling and reusing. The porous materials prepared from the HIPE template could be served as excellent oil adsorbents (Zheng et al. 2013; Yu et al. 2015a, b; Wang et al. 2018a, b; Zhang et al. 2019a, b, c, d).

Zhang et al. (Zhang et al. 2016a, b) prepared a poly(styrene-divinylbenzene) foam by the Pickering HIPEs through a one-step reaction process. The materials with different hierarchical pore structures were obtained by various Pickering emulsion stabilized with different types of Fe_3O_4. The adsorption capacity of the monolithic foam for chloroform was as high as 57.00 g/g. Zhou et al. prepared a hierarchical porous resin for removal of oily substance through the HIPE template stabilized with

phenolic resin precursor and Tween 80. And then the dopamine hydrochloride, 1-dodecanethiol, and Fe_3O_4 particles grafted onto the interface of porous resin via adhesion of dopamine and Markel addition reaction. The as-synthesized hierarchical porous resin possessed a typical hierarchical porous structure, and the porous structure could be adjusted by varying the emulsion factors. The oil adsorption rate and the oil retention rate for toluene were 11.765 g/g and 86.43%, respectively (Zhou et al. 2019).

Zhang et al. employed the Span 20 together with Fe_3O_4 to synergistically stabilize styrene-based HIPEs and produced magnetic solid foam for removal of oil. The interconnected porous structure was constructed by varying the surfactant content, the amount of Fe_3O_4 particles, and other emulsion factors. The resulting magnetic solid foam exhibited excellent thermal stability. The oil adsorption capacity of the solid foam was 16 times its own mass even after 10 cycles of oil/water separation (Fig. 13.21) (Zhang et al. 2017).

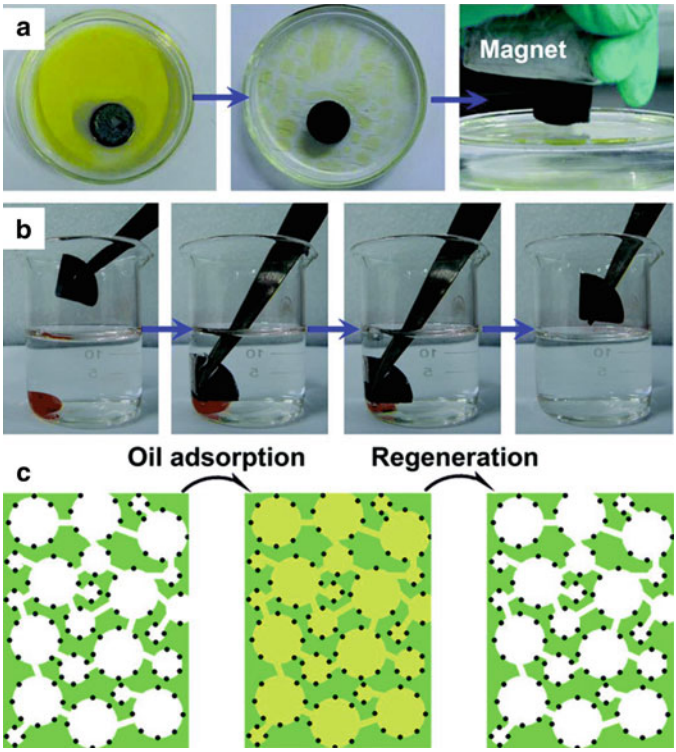

Fig. 13.21 Removal of diesel from the water by the magnetic polystyrene foam. (Reproduced with permission from Zhang et al. 2017)

13.4 Conclusions and Future Prospects

Magnetic adsorbents prepared from emulsion template have been attracting much attention in recent years. The magnetic materials prepared by emulsion template for water treatment are reviewed, including the magnetic nano-adsorbent, the spherical adsorbent, and the magnetic porous adsorbent. Magnetic nano-adsorbents of spinel ferrite exhibit high stability towards acid and excellent removal performance for various pollutants containing heavy metal and organic pollutant. Magnetic spherical adsorbent might be the most wide studies due to the flexible preparation method, various functionalization ways, and sufficient functional groups. Moreover, the molecular imprinting technique could be conveniently integrated with the preparation process to realize the adsorption selectivity. By contrast, the porous magnetic materials prepared from the HIPEs as adsorbent have increasingly been recognized as one of the research hotspots, which exhibit high porosity and excellent adsorption performance, tunable pore structure, pore size distribution, and mechanical strength. Although magnetic adsorbents prepared from the emulsion template present many advantages, some drawbacks still need to be solved.

First, the preparation process of magnetic adsorbent needs a large of organic phase. Although magnetic nanoparticles, magnetic microspheres, or magnetic porous materials prepared from the emulsion template display excellent adsorption performance in water treatment, it is unavoidable to consume highly the organic solvent and surfactant. Because the organic solvent contained much metal salt, residual monomer, cross-link, surfactant, and oligomer after being used, the attempt to cyclic utilization of organic solvent is not found in the relative studies. However, it might be the most important issue for realizing the practical application of magnetic adsorbent prepared from the emulsion template. In order to resolve this problem, the emulsion template is developed for the preparation of porous material by decreasing progressively the organic phase from 75% to 50%, even to 25% (Fresco-Cala and Cárdenas 2019; Kavousi and Nikfarjam 2019). Furthermore, the environmental harm of the toxic organic solvents could be alleviated by replacing with the edible oils, such as canola oil, sunflower oil, and so on (Zhu et al. 2020). More importantly, many researchers have focused on the preparation of porous materials from the water-based foam (Fig. 13.22) (Cervin et al. 2013; Huang et al. 2018). The water-based foam without any organic solvent, and the stability could be significantly increased when stabilization the interface between air and liquid with amphiphilic particles. Due to the green and easy preparation process, it must be the research hotspot in future beyond all doubt. For magnetic nanoparticles and magnetic microspheres, the ratio of water to oil has a significant effect on the size, crystallinity, and morphology of the product, and thus the green synthesis still takes a lot of efforts.

The second issue is the adsorption selectivity to different pollutants. Although many works involved the selective adsorption of organic pollutants by molecular imprinting technique (Cyganowski, 2020; Liu et al. 2020), the recycled and refined of valuable metal from the wastewater might be more meaningful. At present, a few works report the selective adsorption of metal ions based on the magnetic spherical

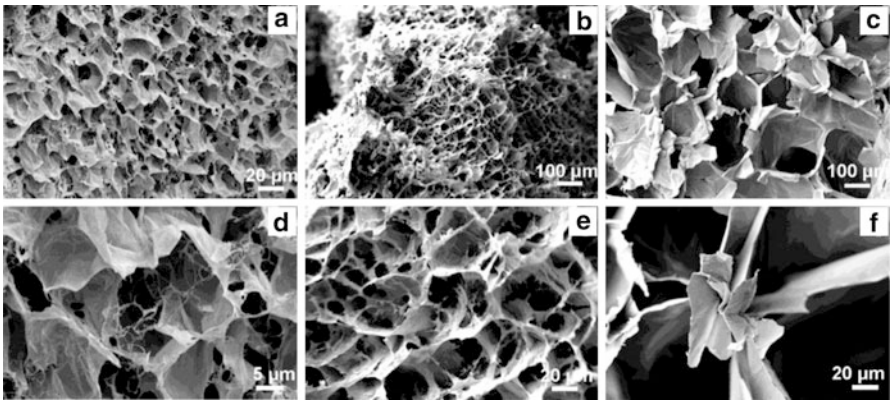

Fig. 13.22 SEM images of the porous structure template from water-based foam. (Reproduced with permission from Huang et al. 2018)

adsorbents, but the low adsorption efficiency limits the potential applications in practice. Therefore, many efforts should be paid to design and construct the functional magnetic adsorbents with excellent adsorption selectivity for rare and precious metals.

Last but not least, the weak reusability of most of the reported magnetic adsorbents should be resolved. The separation and reuse are the most important advantages of magnetic adsorbents, and there are many approaches to realize their cyclic utilization. The most common regeneration of the spent adsorbents is using the organic solvent (methyl alcohol, ethyl alcohol, etc.), acid (hydrochloric acid, sulfuric acid, etc.), or alkaline (sodium hydroxide, potassium hydroxide, etc.) (Ye et al. 2020; Zhao et al. 2020). Despite the adsorbents display excellent desorption and reusability under the evaluation condition, but it is urgent to explore the feasible and green approach to prevent from the secondary pollution, which derived from the desorbing agents, regenerating agents, and the desorbed pollutants from the spent adsorbents. This problem might be not important for the recycle and enrichment of the value metal ions, but it is crucial for adsorption of organic pollutants. In order to actually realize the recycle of the spent magnetic adsorbents, the carbonization technique might be a promising strategy for the regeneration of the spent adsorbent after adsorption organic pollutants.

Recently, the carbonaceous adsorbents have been applied in water treatment (Xiao et al. 2018; Dai et al. 2020). Because it exhibits excellent adsorption performance to organic or inorganic pollutants based on various adsorption mechanisms, including H-bond, π-π stacking, polar interaction to organic pollutant and coprecipitation, and electrostatic interaction to inorganic pollutants (Fig. 13.23). Moreover, the carbonization strategy as the potential approach to realize the recycle of adsorbent has been verified with our group's work (Tang et al. 2016). The cost-effective carbon/attapulgite composites were developed using waste hot-pot oil as a carbon precursor through a facile one-step calcination process (Tang et al. 2017;

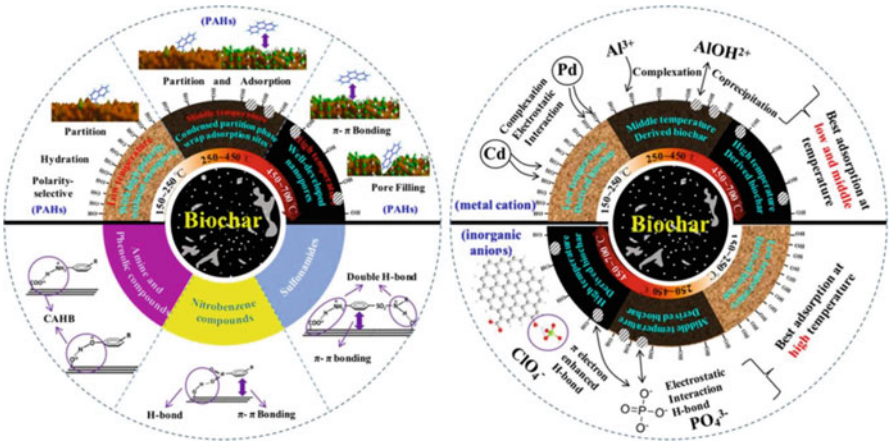

Fig. 13.23 Sorption mechanisms of organic (left) and inorganic pollutants (right) to biochars prepared under different pyrolytic temperatures. PAHs: polycyclic aromatic hydrocarbons. CAHB: charge-assisted H-bond, including negative charge-assisted H-bond (−) CAHB and positive charge-assisted H-bond (+) CAHB. (Reproduced with permission from Xiao et al. 2018)

Tang et al. 2018a; Tang et al. 2018b). The removal ratios to methyl violet and tetracycline still remained 77.6% and 60.2%, after ten times cycles of adsorption-regeneration via a facile thermal regeneration strategy, respectively (Tang et al. 2019b). Furthermore, a series of carbon/attapulgite composite adsorbents were successfully fabricated by a one-step in situ carbonization process using natural starch as the carbon source to decolorate the crude palm oil (Tian et al. 2018). And then the spent bleaching earth was further continuously transformed into carbon/attapulgite composite adsorbents after cyclic adsorption-thermal regeneration for the removal of dyes from wastewater. Therefore, the spent magnetic adsorbent after adsorption organic pollutants could be repeatedly regenerated and finally to be applied into soil for the remediation of heavy metal-polluted soil.

Acknowledgments The authors thank the funds by the National Natural Science Foundation of China (21706267), the Major Projects of the Natural Science Foundation of Gansu, China (No. 18JR4RA001), and the Youth Innovation Promotion Association CAS (2016370).

References

Ahalya K, Suriyanarayanan N, Sangeetha S (2014) Effect of pH and annealing temperatures on structural, magnetic, electrical, dielectric and adsorption properties of manganese ferrite nano particles. Mat Sci Semicon Proc 27:672–681. https://doi.org/10.1016/j.mssp.2014.08.009

Alhadidi QA, Zhou Z, Quiñones Deliz KY, Greenslet HY, Bonzongo JCJ (2021) Removal of type-A, type-B, and borderline metals from contaminated soils using zero valent iron and magnetic separation technology: a predictive approach for metal resources recovery. Chemosphere 274:129980. https://doi.org/10.1016/j.chemosphere.2021.129980

Ali R, Khan MA, Mahmood A, Chughtai AH, Sultan A, Shahid M, Ishaq M, Warsi MF (2014a) Structural, magnetic and dielectric behavior of $Mg_{1-x}Ca_xNiyFe_{2-y}O_4$ nano-ferrites synthesized by the micro-emulsion method. Ceram Int 40:3841–3846. https://doi.org/10.1016/j.ceramint.2013.08.024

Ali R, Mahmood A, Khan MA, Chughtai AH, Shahid M, Shakir I, Warsi MF (2014b) Impacts of Ni–Co substitution on the structural, magnetic and dielectric properties of magnesium nano-ferrites fabricated by micro-emulsion method. J Alloy Compd 584:363–368. https://doi.org/10.1016/j.jallcom.2013.08.114

Anjali C, Devendra S, Shekhar A (2019) Removal of pharmaceutical contaminants in wastewater using nanomaterials: a comprehensive review. Curr Drug Metab 20:483–505. https://doi.org/10.2174/1389200220666181127104812

Anoshkin VI, Campion J, Lioubtchenko DV, Oberhammer J (2018) Freeze-dried carbon nanotube aerogels for high-frequency absorber applications. ACS Appl Mater Int 10:19806–19811. https://doi.org/10.1021/acsami.8b03983

Asadi R, Abdollahi H, Gharabaghi M, Boroumand Z (2020) Effective removal of Zn (II) ions from aqueous solution by the magnetic $MnFe_2O_4$ and $CoFe_2O_4$ spinel ferrite nanoparticles with focuses on synthesis, characterization, adsorption, and desorption. Adv Powder Technol. https://doi.org/10.1016/j.apt.2020.01.028

Aylar N, Ali Reza M, Afshin F (2020) Alternating magnetic field and ultrasound waves as size controlling parameters in preparation of superparamagnetic Fe_3O_4 nanoparticles. J Nanosci Nanotechnol 20:871–877. https://doi.org/10.1166/jnn.2020.16904

Azhar U, Huyan C, Wan X, Zong C, Xu A, Liu J, Ma J, Zhang S, Geng B (2019) Porous multifunctional fluoropolymer composite foams prepared via humic acid modified Fe_3O_4 nanoparticles stabilized Pickering high internal phase emulsion using cationic fluorosurfactant as co-stabilizer. Arab J Chem 12:559–572. https://doi.org/10.1016/j.arabjc.2018.04.003

Baig MM, Yousuf MA, Agboola PO, Khan MA, Shakir I, Warsi MF (2019) Optimization of different wet chemical routes and phase evolution studies of $MnFe_2O_4$ nanoparticles. Ceram Int 45:12682–12690. https://doi.org/10.1016/j.ceramint.2019.03.114

Batoo KM, El-sadek MSA (2013) Electrical and magnetic transport properties of Ni–Cu–Mg ferrite nanoparticles prepared by sol–gel method. J Alloy Comp 566:112–119. https://doi.org/10.1016/j.jallcom.2013.02.129

Cao X, Zang L, Bu Z, Sun L, Guo D, Wang C (2016) Microfluidic fabrication of magnetic porous multi-walled carbon nanotube beads for oil and organic solvent adsorption. J Mater Chem A 4:10479–10485. https://doi.org/10.1039/C6TA01179A

Cervin NT, Andersson L, Sing Ng JB, Olin P, Bergström L, Wågberg L (2013) Lightweight and strong cellulose materials made from aqueous foams stabilized by nanofibrillated cellulose. Biomacromolecules 14:503–511. https://doi.org/10.1021/bm301755u

Chávez-Guajardo AE, Medina-Llamas JC, Maqueira L, Andrade CAS, Alves KGB, Melo CP (2015) Efficient removal of Cr (VI) and Cu (II) ions from aqueous media by use of polypyrrole/maghemite and polyaniline/maghemite magnetic nanocomposites. Chem Eng J 281:826–836. https://doi.org/10.1016/j.cej.2015.07.008

Chen M, Jiang W, Wang F, Shen P, Ma P, Gu J, Mao J, Li F (2013) Synthesis of highly hydrophobic floating magnetic polymer nanocomposites for the removal of oils from water surface. Appl Surf Sci 286:249–256. https://doi.org/10.1016/j.apsusc.2013.09.059

Chen L, Zhou C, Fiore S, Tong D, Zhang H, Li C, Ji S, Yu W (2016) Functional magnetic nanoparticle/clay mineral nanocomposites: preparation, magnetism and versatile applications. Appl Clay Sci 127–128:143–163. https://doi.org/10.1016/j.clay.2016.04.009

Chen X, Song X, Huang J, Wu C, Ma D, Tian M, Jiang H, Huang P (2017) Phase behavior of Pickering emulsions stabilized by graphene oxide sheets and resins. Energ Fuel 31:13439–13447. https://doi.org/10.1021/acs.energyfuels.7b02672

Cyganowski P (2020) Synthesis of adsorbents with anion exchange and chelating properties for separation and recovery of precious metals-a review. Sol Extr Ion Exc 38:143–165. https://doi.org/10.1080/07366299.2020.1720117

Dai J, Pan J, Xu L, Li X, Zhou Z, Zhang R, Yan Y (2012) Preparation of molecularly imprinted nanoparticles with superparamagnetic susceptibility through atom transfer radical emulsion polymerization for the selective recognition of tetracycline from aqueous medium. J Hazard Mater 205–206:179–188. https://doi.org/10.1016/j.jhazmat.2011.12.056

Dai Y, Zhang N, Xing C, Cui Q, Sun Q (2020) The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: a review. Chemosphere 223:12–27. https://doi.org/10.1016/j.chemosphere.2019.01.161

Dehghani MH, Gholami S, Karri RR, Lima EC, Mahvi AH, Nazmara S, Fazlzadeh M (2021) Process modeling, characterization, optimization, and mechanisms of fluoride adsorption using magnetic agro-based adsorbent. J Environ Manag 286:112173. https://doi.org/10.1016/j.jenvman.2021.112173

Deng J, Shao Y, Gao N, Tan C, Zhou S, Hu X (2013) $CoFe_2O_4$ magnetic nanoparticles as a highly active heterogeneous catalyst of oxone for the degradation of diclofenac in water. J Hazard Mater 262:836–844. https://doi.org/10.1016/j.jhazmat.2013.09.049

Ding Z, Wang W, Zhang Y, Li F, Liu JP (2015) Synthesis, characterization and adsorption capability for Congo red of $CoFe_2O_4$ ferrite nanoparticles. J Alloy Comp 640:362–370. https://doi.org/10.1016/j.jallcom.2015.04.020

Dlamini DS, Tesha JM, Vilakati GD, Mamba BB, Mishra AK, Thwala JM, Li J (2020) A critical review of selected membrane- and powder-based adsorbents for water treatment: sustainability and effectiveness. J Clean Prod 277:123497. https://doi.org/10.1016/j.jclepro.2020.123497

Du F, Sun L, Tan W, Wei Z, Nie H, Huang Z, Ruan G, Li J (2019) Magnetic stir cake sorptive extraction of trace tetracycline antibiotics in food samples: preparation of metal–organic framework-embedded polyHIPE monolithic composites, validation and application. Anal Bioanal Chem 411:2239–2248. https://doi.org/10.1007/s00216-019-01660-1

Duan Y (2017) Novel preparation of Fe_3O_4/styrene-co-butyl acrylate composite microspheres via a phase inversion emulsion process. Colloid Polym Sci 295:1757–1763. https://doi.org/10.1007/s00396-017-4154-1

Duan S, Tang R, Xue Z, Zhang X, Zhao Y, Zhang W, Zhang J, Wang B, Zeng S, Sun D (2015) Effective removal of Pb(II) using magnetic $Co_{0.6}Fe_{2.4}O_4$ micro-particles as the adsorbent: synthesis and study on the kinetic and thermodynamic behaviors for its adsorption. Colloid Surf A-Physicochem Eng Asp 469:211–223. https://doi.org/10.1016/j.colsurfa.2015.01.029

Duan S, Liu X, Wang Y, Shao D, Alharbi NS, Alsaedi A (2016) Li J highly efficient entrapment of U(VI) by using porous magnetic $Ni_{0.6}Fe_{2.4}O_4$ micro-particles as the adsorbent. J Taiwan Inst Chem Eng 65:367–377. https://doi.org/10.1016/j.jtice.2016.05.041

Ebrahimpour E, Amiri A, Baghayeri M, Rouhi M, MansourLakouraj M (2017) Poly (indole-co-thiophene)@Fe_3O_4 as novel adsorbents for the extraction of aniline derivatives from water samples. Microchem J 131:174–181. https://doi.org/10.1016/j.microc.2016.12.022

Estevez L, Prabhakaran V, Garcia LA, Shin Y, Tao J, Schwarz MA, Darsell J, Bhattacharya P, Shutthanandan V, Zhang J (2017) Hierarchically porous graphitic carbon with simultaneously high surface area and colossal pore volume engineered via ice templating. ACS Nano 11:11047–11055. https://doi.org/10.1021/acsnano.7b05085

Fahimirad B, Rajabi M, Elhampour A (2018) A rapid and simple extraction of anti-depressant drugs by effervescent salt-assisted dispersive magnetic micro solid-phase extraction method using new adsorbent Fe_3O_4@SiO_2@N_3. Anal Chim Acta 1047:275–284. https://doi.org/10.1016/j.aca.2018.10.028

Fan L, Zhang B, Zhang H, Jia X, Chen X, Zhang Q (2016) Preparation of light core/shell magnetic composite microspheres and their application for lipase immobilization. RSC Adv 6:65911–65920. https://doi.org/10.1039/C6RA12764A

Fang Q, Zhang J, Bai L, Duan J, Xu H, Leung KCF, Xuan S (2019) In situ redox-oxidation polymerization for magnetic core-shell nanostructure with polydopamine-encapsulated-Au hybrid shell. J Hazard Mater 367:15–25. https://doi.org/10.1016/j.colsurfa.2010.04.016

Feltin N, Pileni MP (1997) New technique for synthesizing iron ferrite magnetic nanosized particles. Langmuir 13:3927–3933. https://doi.org/10.1021/la960854q

Feng L, Cao M, Ma X, Zhu Y, Hu C (2012) Superparamagnetic high-surface-area Fe_3O_4 nanoparticles as adsorbents for arsenic removal. J Hazard Mater 217–218:439–446. https://doi.org/10.1016/j.jhazmat.2012.03.073

Feuser PE, BubniakL S, Silva MCS, Viegas AC, Fernandes AC, Ricci-Junior E, Nele M, Tedesco AC, Sayer C, Araújo PHH (2015) Encapsulation of magnetic nanoparticles in poly(methyl methacrylate) by miniemulsion and evaluation of hyperthermia in U87MG cells. Eur Polym J 68:355–365. https://doi.org/10.1016/j.eurpolymj.2015.04.029

Fotukian SM, Barati A, Soleymani M, Alizadeh AM (2020) Solvothermal synthesis of $CuFe_2O_4$ and Fe_3O_4 nanoparticles with high heating efficiency for magnetic hyperthermia application. J Alloy Compd 816:152548. https://doi.org/10.1016/j.jallcom.2019.152548

Fresco-Cala B, Cárdenas S (2019) Preparation of macroscopic carbon nanohorn-based monoliths in polypropylene tips by medium internal phase emulsion for the determination of parabens in urine samples. Talanta 1981:295–301. https://doi.org/10.1016/j.talanta.2019.02.029

Fröhlich AC, Foletto EL, Dotto GL (2019) Preparation and characterization of $NiFe_2O_4$/activated carbon composite as potential magnetic adsorbent for removal of ibuprofen and ketoprofen pharmaceuticals from aqueous solutions. J Clean Prod 229:828–837. https://doi.org/10.1016/j.jclepro.2019.05.037

Gervald AY, Gritskova IA, Prokopov NI (2010) Synthesis of magnetic polymeric microspheres. Russ Chem Rev 79:219–229. https://doi.org/10.1070/RC2010v079n03ABEH004068

Ghahfarokhi SEM, Shobegar EM (2020) An investigation of the ethylene glycol surfactant on the structural, microstructure, magnetic and optical properties of $SrFe_2O_4$ nanoparticles. J Magn Magn Mater 495:165866. https://doi.org/10.1016/j.jmmm.2019.165866

Gharieh A, Khoee S, Mahdavian RA (2019) Emulsion and miniemulsion techniques in preparation of polymer nanoparticles with versatile characteristics. Adv Colloid Int Sci 269:152–186. https://doi.org/10.1016/j.cis.2019.04.010

Ghone DM, Mathe VL, Patankar KK, Kaushik SD (2018) Microstructure, lattice strain, magnetic and magnetostriction properties of holmium substituted cobalt ferrites obtained by co-precipitation method. J Alloy Comp 739:52–61. https://doi.org/10.1016/j.jallcom.2017.12.219

Gilani ZA, Warsi MF, Khan MA, Shakir I, Shahid M, Anjum MN (2015) Impacts of neodymium on structural, spectral and dielectric properties of $LiNi_{0.5}Fe_2O_4$ nanocrystalline ferrites fabricated via micro-emulsion technique. Phys E 73:169–174. https://doi.org/10.1016/j.physe.2015.06.001

Gokmen MT, Van Camp W, Colver PJ, Bon SAF, Du Prez FE (2009) Fabrication of porous, "clickable", polymer beads and rods through generation of high internal phase emulsion (HIPE) droplets in a simple microfluidic device. Macromolecules 42:9289–9294. https://doi.org/10.1021/ma9018679

Gu J, Jiang W, Wang F, Chen M, Mao J, Xie T (2014) Facile removal of oils from water surfaces through highly hydrophobic and magnetic polymer nanocomposites. Appl Surf Sci 301:492–499. https://doi.org/10.1016/j.apsusc.2014.02.112

Gui HG, Guan GW, Zhang T, Guo QP (2019) Crophase-separated, hierarchical macroporous polyurethane from a nonaqueous emulsion-templated reactive block copolymer. Chem Eng J 365:369–377. https://doi.org/10.1016/j.cej.2019.02.015

Han J, Du Z, Zou W, Li H, Zhang C (2015) In-situ improved phenol adsorption at ions-enrichment interface of porous adsorbent for simultaneous removal of copper ions and phenol. Chem Eng J 262:571–578. https://doi.org/10.1016/j.cej.2014.10.018

Hashem MA, Elnagar MM, Kenawy IM, Ismail MA, Qu W (2020) Synthesis and application of hydrazono-imidazoline modified cellulose for selective separation of precious metals from geological samples. Carbohydr Polym 237:116177. https://doi.org/10.1016/j.carbpol.2020.116177

Hilczer A, Kowalska K, Markiewicz E, Pietraszko A, Andrzejewski B (2016) Dielectric and magnetic response of $SrFe_{12}O_{19}$–$CoFe_2O_4$ composites obtained by solid state reaction. Mater Sci Eng B 207:47–55. https://doi.org/10.1016/j.mseb.2016.02.003

Hochepied JF, Pileni MP (2000) Magnetic properties of mixed cobalt–zinc ferrite nanoparticles. J Appl Phys 87:2472–2478. https://doi.org/10.1063/1.372205

Hu J, Lo IMC, Chen G (2007) Comparative study of various magnetic nanoparticles for Cr (VI) removal. Sep Purif Technol 56:249–256. https://doi.org/10.1016/j.seppur.2007.02.009

Hu J, Chen M, Wu L (2011) Organic-inorganic nanocomposites synthesized via miniemulsion polymerization. Polym Chem 2:760–772. https://doi.org/10.1039/C0PY00284D

Hua M, Zhang S, Pan B, Zhang W, Lv L, Zhang Q (2012) Heavy metal removal from water/wastewater by nanosized metal oxides: a review. J Hazard Mater 211–212:317–331. https://doi.org/10.1016/j.jhazmat.2011.10.016

Huang Y, Yang J, Chen L, Zhang L (2018) Chitin nanofibrils to stabilize long-life pickering foams and their application for lightweight porous materials. ACS Sustain Chem Eng 6:10552–10561. https://doi.org/10.1021/acssuschemeng.8b01883

Huang Y, Zhang W, Bai M, Huang X (2020) One-pot fabrication of magnetic fluorinated carbon nanotubes adsorbent for efficient extraction of perfluoroalkyl carboxylic acids and perfluoroalkyl sulfonic acids in environmental water samples. Chem Eng J 380:122392. https://doi.org/10.1016/j.cej.2019.122392

Jacobo SE, Duhalde S, Bertorello HR (2004) Rare earth influence on the structural and magnetic properties of NiZn ferrites. J Magn Magn Mater 272–276:2253–2254. https://doi.org/10.1016/j.jmmm.2003.12.564

Jesus ABC, Jesus JR, Lima RJS, Moura KO, Almeida JMA, Duque JGS, Meneses CT (2020) Synthesis and magnetic interaction on concentrated Fe_3O_4 nanoparticles obtained by the co-precipitation and hydrothermal chemical methods. Ceram Int in press. https://doi.org/10.1016/j.ceramint.2020.01.135

Ji J, Chen G, Zhao J, Wei Y (2020) Efficient removal of Pb (II) by inexpensive magnetic adsorbents prepared from one-pot pyrolysis of waste tyres involved magnetic nanoparticles. Fuel 282:118715. https://doi.org/10.1016/j.fuel.2020.118715

Jiang Y, Kim D (2013) Synthesis and selective adsorption behavior of Pd (II)-imprinted porous polymer particles. Chem Eng J 232:503–509. https://doi.org/10.1016/j.cej.2013.08.008

Jiang L, Chai F, Chen Q (2017) Soft magnetic nanocomposite microgels by in-situ crosslinking of poly acrylic acid onto superparamagnetic magnetite nanoparticles and their applications for the removal of Pb(II) ion. Eur Polym J 89:468–481. https://doi.org/10.1016/j.eurpolymj.2017.02.045

Jung Y, Ko YG, Do T, Chu Y, Choi US, C. Kim CH (2019) Core/shell hybrid fiber with aminated PAN and Fe_2O_3 as a high-capacity adsorbent for phosphate ions. J Hazard Mater 378:120726. doi:https://doi.org/10.1016/j.jhazmat.2019.06.003

Kang S, Rethinasabapathy M, Hwang SK, Lee GW, Jang SC, Kwak CH, Choe SR, Huh YS (2018) Microfluidic generation of Prussian blue-laden magnetic micro-adsorbents for cesium removal. Chem Eng J 341:218–226. https://doi.org/10.1016/j.cej.2018.02.025

Kaur M, Kaur N, Jeet K, Kaur P (2015) Effective removal of Pb(II) using magnetic $Co_{0.6}Fe_{2.4}O_4$ micro-particles as the adsorbent: synthesis and study on the kinetic and thermodynamic behaviors for its adsorption. Colloid Surf A 469:211–223. https://doi.org/10.1016/j.colsurfa.2015.01.029

Kavitha S, Kurian M (2020) Role of doped nitrogen and Sulphur in cobalt/cobalt-zirconium nanoferrites synthesized by facile methods. Ceram Int 46:4423–4434. https://doi.org/10.1016/j.ceramint.2019.10.168

Kavousi F, Nikfarjam N (2019) Highly interconnected macroporous structures made from starch nanoparticle-stabilized medium internal phase emulsion polymerization for use in cell culture. Polymer 18010:121744. https://doi.org/10.1016/j.polymer.2019.121744

Khan MA, Sabir M, Mahmood A, Asghar M, Mahmood K, Afzal Khan M, Ahmad I, Sher M, Warsi MF (2014) High frequency dielectric response and magnetic studies of $Zn_{1-x}Tb_xFe_2O_4$ nanocrystalline ferrites synthesized via micro-emulsion technique. J Magn Magn Mater 360:188–192. https://doi.org/10.1016/j.jmmm.2014.02.059

Kim JH, Kim SM, Yoon IH, Choi SJ, Kim I (2020) Selective separation of Cs-contaminated clay from soil using polyethylenimine-coated magnetic nanoparticles. Sci Total Environ 706:130020. https://doi.org/10.1016/j.scitotenv.2019.136020

Konicki W, Sibera D, Mijowska E, Lendzion-Bieluń Z, Narkiewicz U (2013) Equilibrium and kinetic studies on acid dye acid red 88 adsorption by magnetic $ZnFe_2O_4$ spinel ferrite nanoparticles. J Colloid Interf Sci 398:152–160. https://doi.org/10.1016/j.jcis.2013.02.021

Kovačič S, Štefanec D, Krajnc P (2007) Highly porous open-cellular monoliths from 2-hydroxyethyl methacrylate based high internal phase emulsions (HIPEs): preparation and void size tuning. Macromolecules 2007:8056–8060. https://doi.org/10.1021/ma071380c

Kovačič S, Drašinac N, Pintar A, Žagar E (2018) Highly porous cationic polyelectrolytes via oil-in-water concentrated emulsions: synthesis and adsorption kinetic study. Langmuir 34:10353–10362

Kozyatnyk I, Latham GK, Jansson S (2019) Valorization of humic acids by hydrothermal conversion into carbonaceous materials: physical and functional properties. ACS Sustain Chem Eng 7:2585–2592. https://doi.org/10.1021/acssuschemeng.8b05614

Kuai S, Zhang Z, Nan Z (2013) Synthesis of Ce^{3+} doped $ZnFe_2O_4$ self-assembled clusters and adsorption of chromium (VI). J Hazard Mater 250–251:229–237. https://doi.org/10.1016/j.jhazmat.2013.01.074

Li X, Sun G, Li Y, Yu JC, Wu J, Ma GH, Ngai T (2014a) Porous TiO_2 materials through Pickering high-internal phase emulsion templating. Langmuir 30:2676–2683. https://doi.org/10.1021/la404930h

Li Z, Liu H, Zeng L, Liu H, Yang S, Wang Y (2014b) Preparation of high internal water-phase double emulsions stabilized by a single anionic surfactant for fabricating interconnecting porous polymer microspheres. Langmuir 2014:12154–12163. https://doi.org/10.1021/la502564r

Li Q, Mao Q, Yang C, Zhang SJ, He GH, Zhang XJ, Zhang WJ (2019) Hydrophobic-modified montmorillonite coating onto crosslinked chitosan as the core-shell micro-sorbent for iodide adsorptive removal via Pickering emulsion polymerization. Inter J Biol Macromol 141:987–996. https://doi.org/10.1016/j.ijbiomac.2019.09.065

Li Y, Zhang Q, Yuan S, Yin H (2021) High-efficiency extraction of iron from early iron tailings via the suspension roasting-magnetic separation. Powder Technol 379:466–477. https://doi.org/10.1016/j.powtec.2020.10.005

Lian Q, Cui Y, Zheng X, Wu H (2015) Preparation and adsorption of magnetic $Co_{0.5}Ni_{0.5}Fe_2O_4$-chitosan nanoparticles. Russ J Appl Chem 88:1877−1883. https://doi.org/10.1134/S10704272150110208

Lima EWC, Feng R (2012) Agglomeration of magnetic nanoparticles. J Chem Phys 136:124109. https://doi.org/10.1063/1.3697865

Liu S, Ge H, Cheng S, Zou Y (2018) Green synthesis of magnetic 3D bio-adsorbent by corn straw core and chitosan for methylene blue removal. Environ Technol. https://doi.org/10.1080/09593330.2018.1556345

Liu Q, ZhouY LJ, Zho YB (2020) Novel cyclodextrin-based adsorbents for removing pollutants from wastewater: a critical review. Chemosphere 241:125043. https://doi.org/10.1016/j.chemosphere.2019.125043

Liu J, Zhang J, Xing L, Wang D, Wang L, Xiao H, Ke J (2021) Magnetic Fe_3O_4/attapulgite hybrids for cd(II) adsorption: performance, mechanism and recovery. J Hazard Mater 412:125237. https://doi.org/10.1016/j.jhazmat.2021.125237

Lobato NCC, Ferreira AD, Weidler PG, Franzreb M, Silva GC, Mansur MB (2019) Improvement of magnetic solvent extraction using functionalized silica coated Fe_3O_4 nanoparticles. Sep Purif Technol 229:115839. https://doi.org/10.1016/j.seppur.2019.115839

Lobato NCC, Ferreira AD, Weidler PG, Franzreb M, Silva GC, Mansur MB (2020) Microstructure and chemical stability analysis of magnetic core coated with SILICA and functionalized with silane OTS. Appl Surf Sci 505:144565–144571. https://doi.org/10.1016/j.apsusc.2019.144565

Lu F, Astruc D (2020) Nanocatalysts and other nanomaterials for water remediation from organic pollutants. Coordin Chem Rev 408:213180. https://doi.org/10.1016/j.ccr.2020.213180

Lu F, Huang C, You L, Wang J, Zhang Q (2017) Magnetic hollow carbon microspheres as a reusable adsorbent for rhodamine B removal. RSC Adv 7:23255–23264. https://doi.org/10.1039/C7RA03045B

Lü T, Chen Y, Qi DM, Cao ZH, Zhang D, Zhao HT (2017) Treatment of emulsified oil wastewaters by using chitosan grafted magnetic nanoparticles. J Alloy Compd 696:1205–1212. https://doi.org/10.1016/j.jallcom.2016.12.118

Lu T, Zhu Y, Qi Y, Wang W, Wang A (2018a) Magnetic chitosan-based adsorbent prepared via Pickering high internal phase emulsion for high-efficient removal of antibiotics. Int J Biol Macromol 106:870–877. https://doi.org/10.1016/j.ijbiomac.2017.08.092

Lu T, Zhu Y, Wang W, Qi Y, Wang A (2018b) Polyaniline-functionalized porous adsorbent for Sr^{2+} adsorption. J Radioanal Nucl Chem 317:907–917. https://doi.org/10.1007/s10967-018-5935-9

Lu T, Zhu Y, Qi Y, Kang Y, Wang A (2019a) Tunable superporous magnetic adsorbent prepared via eco-friendly Pickering MIPEs for high-efficiency adsorption of Rb^{+} and Sr^{2+}. Chem Eng J 368:988–998. https://doi.org/10.1016/j.cej.2019.03.040

Lu T, Zhu Y, Wang W, Qi Y, Wang A (2019b) Interconnected superporous adsorbent prepared via yeast-based Pickering HIPEs for high-efficiency adsorption of Rb^{+}, Cs^{+} and Sr^{2+}. Chem Eng J 361:1411–1422. https://doi.org/10.1016/j.cej.2018.11.006

Luo Y, Zhou Z, Yue T (2017) Synthesis and characterization of nontoxic chitosan-coated Fe_3O_4 particles for patulin adsorption in a juice-pH simulation aqueous. Food Chem 221:317–323. https://doi.org/10.1016/j.foodchem.2016.09.008

Ma W, Dai J, Dai X, Yan Y (2014) Preparation and characterization of chitosan/kaolin/Fe_3O_4 magnetic microspheres and their application for the removal of ciprofloxacin. Adsorpt Sci Technol 32:775–790. https://doi.org/10.1260/0263-6174.32.10.775

Ma J, Xia W, Fu X, Ding L, Kong Y, Zhang H, Fu K (2020) Magnetic flocculation of algae-laden raw water and removal of extracellular organic matter by using composite flocculant of Fe_3O_4/cationic polyacrylamide. J Clean Prod 248:119276. https://doi.org/10.1016/j.jclepro.2019.119276

Mahmoodi NM (2013) Zinc ferrite nanoparticle as a magnetic catalyst: synthesis and dye degradation. Mater Res Bull 48:4255–4260. https://doi.org/10.1016/j.materresbull.2013.06.070

Maleki A, Hajizadeh Z, Sharifi V, Emdadi Z (2019) A green, porous and eco-friendly magnetic geopolymer adsorbent for heavy metals removal from aqueous solutions. J Clean Prod 215:1233–1245. https://doi.org/10.1016/j.jclepro.2019.01.084

Mao Y, Cui J, Zhao J, Wu Y, Wang C, Lu J, Lin X, Yan Y (2016) Selective separation of bifenthrin by pH-sensitive/magnetic molecularly imprinted polymers prepared by Pickering emulsion polymerization. Fiber Polym 17:1531–1539. https://doi.org/10.1007/s12221-016-6570-0

Masunga N, Mmelesi OK, Kefeni KK, Mamba BB (2019) Recent advances in copper ferrite nanoparticles and nanocomposites synthesis, magnetic properties and application in water treatment: review. J Environ Chem Eng 7:103179. https://doi.org/10.1016/j.jece.2019.103179

Mert EH, Yıldırım H, Üzümcü AT, Kavas H (2013) Synthesis and characterization of magnetic polyHIPEs with humic acid surface modified magnetic iron oxide nanoparticles. React Funct Polym 73:175–181. https://doi.org/10.1016/j.reactfunctpolym.2012.09.005

Ming G, Duan H, Meng X, Sun G, Sun W, Liu Y, Lucia L (2015) A novel fabrication of monodisperse melamine-formaldehyde resin microspheres to adsorb lead (II). Chem Eng J 288:745–757. https://doi.org/10.1016/j.cej.2015.12.007

Mokadem Z, Saidi-Besbes S, Lebaz N, Elaissari A (2020) Magnetic monolithic polymers prepared from high internal phase emulsions and Fe_3O_4 triazole-functionalized nanoparticles for Pb^{2+}, Cu^{2+} and Zn^{2+} removal. React Funct Polym 155:104693. https://doi.org/10.1016/j.reactfunctpolym.2020.104693

Moumen N, Pileni MP (1996a) Control of the size of cobalt ferrite magnetic fluid. J Phys Chem 100:1867–1873. https://doi.org/10.1021/jp9524136

Moumen N, Pileni MP (1996b) New syntheses of cobalt ferrite particles in the range 2–5 nm: comparison of the magnetic properties of the nanosized particles in dispersed fluid or in powder form. Chem Mater 8:1128–1134. https://doi.org/10.1021/cm950556z

Moumen N, Lisiecki I, Briois V, Pileni MP (1995a) Micellar factors which play a role in the control of the nanosize particles of cobalt ferrite. Supramol Sci 2:161–168. https://doi.org/10.1016/0968-5677(96)89671-4

Moumen N, Veillet P, Pileni MP (1995b) Controlled preparation of nanosize cobalt ferrite magnetic particles. J Magn Magn Mater 149:67–71. https://doi.org/10.1016/0304-8853(95)00340-1

Mudassir MA, Hussain SZ, Jilani A, Zhang H, Ansari TM, Hussain I (2019) Magnetic hierarchically macroporous emulsion-templated poly(acrylic acid)–iron oxide nanocomposite beads for water remediation. Langmuir 35:8996–9003. https://doi.org/10.1021/acs.langmuir.9b01121

Murray BS (2019) Pickering emulsions for food and drinks. Curr Opin Food Sci 27:57–63. https://doi.org/10.1016/j.cofs.2019.05.004

Nuryono N, Miswanda D, Sakti SCW, Rusdiarso B, Krisbiantoro PA, Utami N, Otomo R, Kamiya Y (2020) Chitosan-functionalized natural magnetic particle@silica modified with (3-chloropropyl)trimethoxysilane as a highly stable magnetic adsorbent for gold(III) ion. Mater Chem Phys. https://doi.org/10.1016/j.matchemphys.2020.123507

Osama S, Nermen MH, Abdullah A (2015) Synthesis of magnetic nanoparticles and nanosheets for oil spill removal. Bentham Sci Pub 1:32–43. https://doi.org/10.2174/2210681205666150601215445

Ou H, Chen Q, Pan J, Zhang Y, Huang Y, Qi X (2015) Selective removal of erythromycin by magnetic imprinted polymers synthesized from chitosan-stabilized Pickering emulsion. J Hazard Mater 289:28–37. https://doi.org/10.1016/j.jhazmat.2015.02.030

Palmqvist AEC (2003) Synthesis of ordered mesoporous materials using surfactant liquid crystals or micellar solutions. Curr Opin Colloid Inter Face Sci 8:145–155. https://doi.org/10.1016/S1359-0294(03)00020-7

Pan J, Yin Y, Gan M, Meng M, Dai X, Wu R, Shi W, Yan Y (2015) Fabrication and evaluation of molecularly imprinted multi-hollow microspheres adsorbents with tunable inner pore structures derived from templating Pickering double emulsions. Chem Eng J 266:299–308. https://doi.org/10.1016/j.cej.2014.11.126

Pan J, Zeng J, Cao Q, Gao H, Gen Y, Peng Y, Dai X, Yan Y (2016) Hierarchical macro and mesoporous foams synthesized by HIPEs template and interface grafted route for simultaneous removal of λ-cyhalothrin and copper ions. Chem Eng J 284:1361–1372. https://doi.org/10.1016/j.cej.2015.09.023

Pang YL, Lim S, Ong HC, Chong WT (2016) Research progress on iron oxide-based magnetic materials: synthesis techniques and photocatalytic applications. Ceram Int 42:9–34. https://doi.org/10.1016/j.ceramint.2015.08.144

Patel RK, Chawla AK, Loulergue P, Teychene B, Pandey JK (2019) 3D printed microchannel loaded with hematite nanoadsorbent for fluoride removal from water. Mater Lett 254:190–193. https://doi.org/10.1016/j.matlet.2019.07.061

Podzus PE, Daraio ME, Jacobo SE (2009) Chitosan magnetic microspheres for technological applications: preparation and characterization. Physica B 404:2710–2712. https://doi.org/10.1016/j.physb.2009.06.093

Popkov V, Tolstoy VP, Semenov VG (2020) Synthesis of phase-pure superparamagnetic nanoparticles of $ZnFe_2O_4$ via thermal decomposition of zinc-iron layered double hydroxysulphate. J Alloy Comp 813:152179. https://doi.org/10.1016/j.jallcom.2019.152179

Qiu G, Wang Q, Wang C, Lau W, Guo Y (2007) Polystyrene/Fe_3O_4 magnetic emulsion and nanocomposite prepared by ultrasonically initiated miniemulsion polymerization. Ultrason Sonochem 14:55–61. https://doi.org/10.1016/j.ultsonch.2006.03.001

Rafiq MA, Javed A, Rasul MN, Khan MA, Hussain A (2020) Understanding the structural, electronic, magnetic and optical properties of spinel MFe_2O_4 (M = Mn, Co, Ni) ferrites. Ceram Int 46:4976–4983. https://doi.org/10.1016/j.ceramint.2019.10.237

Reddy DHK, Yun YS (2016) Spinel ferrite magnetic adsorbents: alternative future materials for water purification? Coordin Chem Rev 315:90–111. https://doi.org/10.1016/j.ccr.2016.01.012

Ren Y, Li N, Feng J, Luan T, Wen Q, Li Z, Zhang M (2012) Adsorption of Pb(II) and Cu(II) from aqueous solution on magnetic porous ferrospinel $MnFe_2O_4$. J Colloid Interface Sci 367:415–421. https://doi.org/10.1016/j.jcis.2011.10.022

Ren H, Hao J, Kang W, Wang G, Ju J, Li L, Cheng B (2019) Waste spunlaced facial puff derived monolithic flexible carbon framework (WCF): an ultralow-cost, recyclable and eco-friendly sorbent for oils and organic solvents. RSC Adv 9:31255–31263. https://doi.org/10.1039/C9RA05681E

Rott E, Nouri M, Meyer C, Minke R, Schneider M, Mandel K, Drenkova-Tuhtan A (2018) Removal of phosphonates from synthetic and industrial wastewater with reusable magnetic adsorbent particles. Water Res 145:608–617. https://doi.org/10.1016/j.watres.2018.08.067

Routoula E, Patwardhan SV (2020) Degradation of anthraquinone dyes from effluents: a review focusing on enzymatic dye degradation with industrial potential. Environ Sci Technol 54:647–664. https://doi.org/10.1021/acs.est.9b03737

Rydin E, Huser B, Welch EB (2000) Amount of phosphorus inactivated by alum treatments in Washington lakes. Limnol Oceanogr 45:226–230. https://doi.org/10.4319/lo.2000.45.1.0226

Salami R, Amini M, Bagherzadeh M, Hosseini H (2019) Vanadium supported on spinel cobalt ferrite nanoparticles as an efficient and magnetically recoverable catalyst for oxidative degradation of methylene blue. Appl Organomet Chem 33:e5127. https://doi.org/10.1002/aoc.5127

Sanchez-Dominguez M, Pemartin K, Boutonnet M (2012) Preparation of inorganic nanoparticles in oil-in-water microemulsions: a soft and versatile approach. Curr Opin Collid Int Sci 17:297–305. https://doi.org/10.1016/j.cocis.2012.06.007

Seeharaj P, Thasirisap E, Tridech C, Jindasuwan S (2019) Magnetic PolyHIPE composites with activated carbon and Iron oxide nanoparticles. IEEE T Magn 55:1–4. https://doi.org/10.1109/TMAG.2018.2862429

Sehlleier YH, Hardt S, Schulz C, Wiggers H (2016) A novel magnetically-separable porous iron-oxide nanocomposite as an adsorbent for methylene blue (MB) dye. J Environ Chem Eng 4:3779–3787. https://doi.org/10.1016/j.jece.2016.08.018

Solans C, Izquierdo P, Nolla N, Azemar MJ, Garcia-Celma (2005) Nano-emulsions. Curr Opin Colloid Interface Sci 10(3–4):102–110

Song X, Li L, Geng Z, Zhou L, Ji L (2017) Effective and selective adsorption of As(III) *via* imprinted magnetic Fe_3O_4/HTCC composite nanoparticles. J Environ Chem Eng 5:16–25. https://doi.org/10.1016/j.jece.2016.11.016

Stubenrauch C, Menner A, Bismarck A, Drenckhan W (2018) Emulsion and foam templating-promising routes to tailor-made porous polymers. Angew Chem Int Edit 57:10024–10032. https://doi.org/10.1002/anie.201801466

Sun X, Li Q, Yang L, Liu H (2016a) Chemically modified magnetic chitosan microspheres for Cr (VI) removal from acidic aqueous solution. Particuology 26:79–86. https://doi.org/10.1016/j.partic.2015.11.003

Sun X, Yang L, Dong T, Liu Z, Liu H (2016b) Removal of Cr(VI) from aqueous solution using amino-modified Fe_3O_4–SiO_2–chitosan magnetic microspheres with high acid resistance and adsorption capacity. J Appl Polym Sci 133:1–11. https://doi.org/10.1002/app.43078

Tan H, Tu Z, Jia H, Gou X, Ngai T (2018) Hierarchical porous protein scaffold templated from high internal phase emulsion costabilized by gelatin and gelatin nanoparticles. Langmuir 34:4820–4829. https://doi.org/10.1021/acs.langmuir.7b04047

Tang J, Mu B, Wang W, Zheng M, Wang A (2016) Fabrication of manganese dioxide/carbon/attapulgite composites derived from spent bleaching earth for adsorption of Pb(II) and brilliant green. RSC Adv 6:36534–36543. https://doi.org/10.1039/C5RA26362J

Tang J, Mu B, Zong L, Zheng M, Wang A (2017) Facile and green fabrication of magnetically recyclable carboxyl-functionalized attapulgite/carbon nanocomposites derived from spent bleaching earth for wastewater treatment. Chem Eng J 322:102–114. https://doi.org/10.1016/j.cej.2017.03.116

Tang J, Zong L, Mu B, Kang Y, Wang A (2018a) Attapulgite/carbon composites as a recyclable adsorbent for antibiotics removal. Korean J Chem Eng 35:1650–1661. https://doi.org/10.1007/s11814-018-0066-0

Tang J, Zong L, Mu B, Zhu Y, Wang A (2018b) Preparation and cyclic utilization assessment of palygorskite/carbon composites for sustainable efficient removal of methyl violet. Appl Clay Sci 161:317–325. https://doi.org/10.1016/j.clay.2018.04.039

Tang J, Wu I, Yu L, Fan X, Liu G, Yu Y (2019a) Study on adsorption properties and mechanism of thallium onto titanium-iron magnetic adsorbent. Sci Total Environ 694:133625. https://doi.org/10.1016/j.scitotenv.2019.133625

Tang J, Mu B, Zong L, Wang A (2019b) From waste hot-pot oil as carbon precursor to development of recyclable attapulgite/carbon composites for wastewater treatment. J Environ Sci 75:346–358. https://doi.org/10.1016/j.jes.2018.05.014

Tao X, Li K, Yan H, Yang H, Li A (2016) Simultaneous removal of acid green 25 and mercury ions from aqueous solutions using glutamine modified chitosan magnetic composite microspheres. Environ Pollut 209:21–29. https://doi.org/10.1016/j.envpol.2015.11.020

Teo BM, Chen F, Hatton TA, Grieser F, Ashokkumar M (2009) Novel one-pot synthesis of magnetite latex nanoparticles by ultrasound irradiation. Langmuir 25:2593–2595. https://doi.org/10.1021/la804278w

Thompson BR, Horozov TS, Stoyanov SD, Paunov VN (2019) Hierarchically structured composites and porous materials from soft templates: fabrication and applications. J Mater Chem A 14:8030–8049. https://xs.scihub.ltd/10.1039/C8TA09750J

Tian G, Wang W, Zhu Y, Zong L, Kang Y, Wang A (2018) Carbon/Attapulgite composites as recycled palm oil-Decoloring and dye adsorbents. Materials 11:86. https://doi.org/10.3390/ma11010086

Tsedenbal B, Hussain I, Lee JE, Koo BH (2020) Removal of Lead contaminants with gamma-Fe_2O_3 nanocrystals. Sci Adv Mater 12:422–426. https://doi.org/10.1166/sam.2020.3654

Wadhawan S, Jain A, Nayyar J, Mehta SK (2020) Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: a review. J Water Pro Eng 33:101038. https://doi.org/10.1016/j.jwpe.2019.101038

Wang C, Yan J, Cui X, Cong D, Wang H (2010) Preparation and characterization of magnetic hollow PMMA nanospheres via in situ emulsion polymerization. Colloid Surf A: Physicochem Eng Asp 363:71–77. https://doi.org/10.1016/j.colsurfa.2010.04.016

Wang L, Li J, Wang Y, Zhao L, Jiang Q (2012) Adsorption capability for Congo red on nanocrystalline MFe_2O_4 (M = Mn, Fe, Co, Ni) spinel ferrites. Chem Eng J 181–182:72–79. https://doi.org/10.1016/j.cej.2011.10.088

Wang F, Yu X, Yang Z, Duan H, Zhang Z, Liu H (2018a) Dual pH- and light-responsive amphiphilic random copolymer nanomicelles as particulate emulsifiers to stabilize the oil/water interface. J Phys Chem C 122:18995–19003. https://doi.org/10.1021/acs.jpcc.8b05065

Wang X, Azhar U, Wang Y, Chen J, Xu A, Zhang S, Geng B (2018b) Highly porous and chemical resistive P(TFEMA-DVB) monolith with tunable morphology for rapid oil/water separation. RSC Adv 8:8355–8364. https://doi.org/10.1039/C8RA00501J

Wang G, Liu Q, Chang M, Jang J, Sui W, Si C, Ni Y (2019a) Novel Fe_3O_4@lignosulfonate/phenolic core-shell microspheres for highly efficient removal of cationic dyes from aqueous solution. Ind Crop Prod 127:110–118. https://doi.org/10.1016/j.indcrop.2018.10.056

Wang S, Lu Y, Ouyang X, Liang X, Yu D, Yang L, Huang F (2019b) Fabrication of chitosan-based MCS/ZnO@Alg gel microspheres for efficient adsorption of As(V). Inter J Biol Macromol 139:886–895. https://doi.org/10.1016/j.ijbiomac.2019.08.070

Wang R, Li W, Lu R, Peng J, Liu X, Liu K, Peng H (2020a) A facile synthesis of cationic and superhydrophobic polyHIPEs as precursors to carbon foam and adsorbents for removal of non-aqueous-phase dye. Colloid Surf A 605:125334. https://doi.org/10.1016/j.colsurfa.2020.125334

Wang X, Liu X, Xiao C, Zhao H, Zhang M, Zheng N, Kong W, Zhang L, Yuan H, Zhang L, Lu J (2020b) Triethylenetetramine-modified hollow Fe_3O_4/SiO_2/chitosan magnetic nanocomposites

for removal of Cr(VI) ions with high adsorption capacity and rapid rate. Micropor Mesopor Mater 297:110041. https://doi.org/10.1016/j.micromeso.2020.110041

Wanna Y, Chindaduang A, Tumcharern G, Phromyothin D, Porntheerapat S, Nukeaw J, Hofmann H, Pratontep S (2016) Efficiency of SPIONs functionalized with polyethylene glycol bis(amine) for heavy metal removal. J Magn Magn Mater 414:32–37. https://doi.org/10.1016/j.jmmm.2016.04.064

Weng S, Jin M, Wan D (2020) An emulsion-templated and amino diol-dictated porous material as an efficient and well recyclable boric acid scavenger. Colloid Surf A 611:125873. https://doi.org/10.1016/j.colsurfa.2020.125873

Wright AJ, Main MJ, Cooper NJ, Blight BA, Holder SJ (2017) Poly high internal phase emulsion for the immobilization of chemical warfare agents. ACS Appl Mater Int 9:31335–31339. https://doi.org/10.1021/acsami.7b09188

Wu W, He Q, Jiang C (2008) Magnetic Iron oxide nanoparticles: synthesis and surface functionalization strategies. Nanos Res Lett 3:397–415. https://doi.org/10.1007/s11671-008-9174-9

Wu Y, Ma Y, Pan J, Gu R, Luo J (2017) Porous and magnetic molecularly imprinted polymers via Pickering high internal phase emulsions polymerization for selective adsorption of λ-cyhalothrin. Front Chem 5:1–10. https://doi.org/10.3389/fchem.2017.00018

Xiao D, Lu T, Zeng R, Bi Y (2016) Preparation and highlighted applications of magnetic microparticles and nanoparticles: a review on recent advances. Microchim Acta 183:2655–2675. https://doi.org/10.1007/s00604-016-1928-y

Xiao C, Liu X, Mao S, Zhang L, Lu J (2017) Sub-micron-sized polyethylenimine-modified polystyrene/Fe_3O_4/chitosan magnetic composites for the efficient and recyclable adsorption of Cu(II) ions. Appl Surf Sci 394:378–385. https://doi.org/10.1016/j.apsusc.2016.10.116

Xiao X, Chen B, Chen Z, Zhu L, Schnoor JL (2018) Insight into multiple and multilevel structures of biochars and their potential environmental applications: a critical review. Environ Sci Technol 52:5027–5047. https://doi.org/10.1021/acs.est.7b06487

Xie X, Xiong H, Zhang Y, Tong Z, Liao A, Qin Z (2017) Preparation magnetic cassava residue microspheres and its application for Cu(II) adsorption. J Environ Chem Eng 5:2800–2806. https://doi.org/10.1016/j.jece.2017.05.024

Xu Y, Dang Q, Liu C, Yan J, Fan B, Cai J, Li J (2015) Preparation and characterization of carboxyl-functionalized chitosan magnetic microspheres and submicrospheres for Pb2+ removal. Colloid Surf A Physicochem Eng Asp 482:353–364. https://doi.org/10.1016/j.colsurfa.2015.06.028

Xue D, Li T, Liu Y, Yang Y, Zhang Y, Cui J, Guo D (2019) Selective adsorption and recovery of precious metal ions from water and metallurgical slag by polymer brush graphene–polyurethane composite. React Funct Polym 136:138–152. https://doi.org/10.1016/j.reactfunctpolym.2018.12.026

Yaqoob KA, Bououdina M, Najar BA AMS, Vijaya JJ (2019) Selectivity and efficient Pb and Cd ions removal by magnetic MFe_2O_4 (M=Co, Ni, Cu and Zn) nanoparticles. Mater Chem Phys 232:254–264. https://doi.org/10.1016/j.matchemphys.2019.04.077

Ye J, Nyobe D, Tang B, Bin L, Pi L, Huang S, Fu F, Cai Y, Guan G, Hao X (2020) Facilely synthesized recyclable mesoporous magnetic silica composite for highly efficient and fast adsorption of methylene blue from wastewater: thermodynamic mechanism and kinetics study. J Mol Liq 303:112656. https://doi.org/10.1016/j.molliq.2020.112656

Yin H, Ren C, Li W (2018) Introducing hydrate aluminum into porous thermally-treated calcium-rich attapulgite to enhance its phosphorus sorption capacity for sediment internal loading management. Chem Eng J 348:704–712. https://doi.org/10.1016/j.cej.2018.05.065

Yousuf MA, Baig MM, Waseem M, Haider S, Shakir I, Khand SUD, Warsi MF (2019) Low cost micro-emulsion route synthesis of Cr-substituted $MnFe_2O_4$ nanoparticles. Ceram Int 45:22316–22323. https://doi.org/10.1016/j.ceramint.2019.07.259

Yu L, Hao G, Gu J, Zhou S, Zhang N, Jiang W (2015a) Fe_3O_4/PS magnetic nanoparticles: synthesis, characterization and their application as sorbents of oil from waste water. J Magn Magn Mater 394:4–21. https://doi.org/10.1016/j.jmmm.2015.06.045

Yu S, Tan H, Wang J, Liu X, Zhou K (2015b) High porosity supermacroporous polystyrene materials with excellent oil–water separation and gas permeability properties. ACS Appl Mater Interfaces 7:6745–6753. https://doi.org/10.1021/acsami.5b00196

Yu M, Wang L, Hu L, Li Y, Luo D, Mei S (2019) Recent applications of magnetic composites as extraction adsorbents for determination of environmental pollutants. TrAC Trends Anal Chem 11:115611. https://doi.org/10.1016/j.trac.2019.07.022

Zafar MN, Amjad M, Tabassum M, Ahmad I, Zubair M (2018) $SrFe_2O_4$ nanoferrites and $SrFe_2O_4$/ground eggshell nanocomposites: fast and efficient adsorbents for dyes removal. J Clean Prod 199:983–994. https://doi.org/10.1016/j.jclepro.2018.07.204

Zeng S, Duan S, Tang R, Li L, Liu C, D. Sun (2014) Magnetically separable $Ni_{0.6}Fe_{2.4}O_4$ nanoparticles as an effective adsorbent for dye removal: synthesis and study on the kinetic and thermodynamic behaviors for dye adsorption. Chem Eng J 258:218–228. doi:https://doi.org/10.1016/j.cej.2014.07.093

Zeng L, Xie M, Zhang Q, Kang Y, Guo X, Xiao H, Peng Y, Luo J (2015) Chitosan/organic rectorite composite for the magnetic uptake of methylene blue and methyl orange. Carbohydr Polym 123:89–98. https://doi.org/10.1016/j.carbpol.2015.01.021

Zhang S, Niu H, Cai Y, Zhao X, Shi Y (2010) Arsenite and arsenate adsorption on coprecipitated bimetal oxide magnetic nanomaterials: $MnFe_2O_4$ and $CoFe_2O_4$. Chem Eng J 158:599–607. https://doi.org/10.1016/j.cej.2010.02.013

Zhang L, Liang S, Liu R, Yuan T, Zhang S, Xu Z, Xu H (2016a) Facile preparation of multifunctional uniform magnetic microspheres for T1-T2 dual modal magnetic resonance and optical imaging. Colloid Surf B: Physicochem Eng Asp 144:344–354. https://doi.org/10.1016/j.colsurfb.2016.04.014

Zhang N, Zhong S, Zhou X, Jiang W, Wang T, Fu J (2016b) Superhydrophobic P (St-DVB) foam prepared by the high internal phase emulsion technique for oil spill recovery. Chem Eng J 298:117–124. https://doi.org/10.1016/j.cej.2016.03.151

Zhang N, Zhong S, Chen T, Zhou Y, Jiang W (2017) Emulsion-derived hierarchically porous polystyrene solid foam for oil removal from aqueous environment. RSC Adv 7:22946–22953. https://doi.org/10.1039/C7RA02953E

Zhang B, Huyan Y, Wang J, Chen X, Zhang H, Zhang Q (2018a) Fe_3O_4@SiO_2@CCS porous magnetic microspheres as adsorbent for removal of organic dyes in aqueous phase. J Alloy Compd 735:1986–1996. https://doi.org/10.1016/j.jallcom.2017.11.349

Zhang S, Fan X, Zhang F, Zhu Y, Chen J (2018b) Synthesis of emulsion-templated magnetic porous hydrogel bead and their application for catalyst of fenton reaction. Langmuir 34:3669–3677. https://doi.org/10.1021/acs.langmuir.8b00009

Zhang C, Liu S, Li S, Tao Y, Wang P, Ma X, Chen L (2019a) Enahanced biosorption of Cu(II) by magnetic chitosan microspheres immobilized Aspergillus sydowii (MCMAs) from aqueous solution. Colloid Surface A 581:123813. https://doi.org/10.1016/j.colsurfa.2019.123813

Zhang H, Zhao R, Pan M, Deng J, Wu Y (2019b) Biobased, porous poly(high internal phase emulsions): prepared from biomass-derived vanillin and laurinol and applied as an oil adsorbent. Ind Eng Chem Res 58:5533–5542. https://doi.org/10.1021/acs.iecr.9b00515

Zhang T, Sanguramath AR, Israel S, Silverstein SM (2019c) Emulsion templating: porous polymers and beyond. Macromolecules 52:5445–5479. https://doi.org/10.1021/acs.macromol.8b02576

Zhang W, Ruan G, Li X, Jiang X, Huang Y, Du F, Li J (2019d) Novel porous carbon composites derived from a graphene-modified high-internal-phase emulsion for highly efficient separation and enrichment of triazine herbicides. Anal Chim Acta 1071:17–24. https://doi.org/10.1016/j.aca.2019.04.041

Zhao L, Lv W, Hou J, Li Y, Duan J, Ai S (2020) Synthesis of magnetically recyclable g-C_3N_4/Fe_3O_4/ZIF-8 nanocomposites for excellent adsorption of malachite green. Microchem J 152:104425. https://doi.org/10.1016/j.microc.2019.104425

Zheng W, Gao F, Gu H (2005) Magnetic polymer nanospheres with high and uniform magnetite content. J Magn Magn Mater 288:403–410. https://doi.org/10.1016/j.jmmm.2004.09.125

Zheng Z, Zheng X, Wang H, Du Q (2013) Macroporous graphene oxide-polymer composite prepared through Pickering high internal phase emulsions. ACS Appl Mater Interf 5:7974–7982. https://doi.org/10.1021/am4020549

Zheng C, Zheng H, Wang Y, Wang Y, Qu W, An Q (2018) Synthesis of novel modified magnetic chitosan particles and their adsorption performance toward Cr (VI). Bioresour Technol 267:1–8. https://doi.org/10.1016/j.biortech.2018.06.113C

Zheng C, Zheng H, Sun Y, Xu B, Wang Y, Zheng X, Wang Y (2019) Simultaneous adsorption and reduction of hexavalent chromium on the poly(4-vinyl pyridine) decorated magnetic chitosan biopolymer in aqueous solution. Bioresour Technol 293:122038. https://doi.org/10.1016/j.biortech.2019.122038

Zhou L, Ji L, Ma P, Shao Y, Zhang H, Gao W, Li Y (2014) Development of carbon nanotubes/$CoFe_2O_4$ magnetic hybrid material for removal of tetrabromobisphenol A and Pb(II). J Hazard Mater 265:104–114. https://doi.org/10.1016/j.jhazmat.2013.11.058

Zhou J, Liu Y, Zhou X, Ren J, Zhong C (2018) Magnetic multi-porous bio-adsorbent modified with amino siloxane for fast removal of Pb(II) from aqueous solution. Appl Surf Sci 427:976–985. https://doi.org/10.1016/j.apsusc.2017.08.110

Zhou X, Zhou W, Ju D, Peng Y, Zhou L, Tang S, Wang J (2019) A research on the preparation of oil-adsorbing hydrophobic porous resins by high internal phase emulsions (HIPEs) template. Sci Eng Compos Mater 26:261–269. https://doi.org/10.1515/secm-2019-0015

Zhu L, Li C, Wang J, Zhang H, Zhang J, Shen Y, Li C, Wang C, Xie A (2012) A simple method to synthesize modified Fe_3O_4 for the removal of organic pollutants on water surface. Appl Surf Sci 258:6326–6330. https://doi.org/10.1016/j.apsusc.2012.03.031

Zhu J, Wei J, Chen M, Gu H, Rapole SB, Pallavkar S, Ho TC, Hopper J, Guo Z (2013) Magnetic nanocomposites for environmental remediation. Adv Powder Technol 24:459–467. https://doi.org/10.1016/j.apt.2012.10.012

Zhu W, Ma W, Li C, Pan J, Dai X (2015) Well-designed multihollow magnetic imprinted microspheres based on cellulose nanocrystals (CNCs) stabilized Pickering double emulsion polymerization for selective adsorption of bifenthrin. Chem Eng J 276:249–260. https://doi.org/10.1016/j.cej.2015.04.084

Zhu Y, Jiang D, Sun D, Yan Y, Li C (2016) Fabrication of magnetic imprinted sorbents prepared by Pickering emulsion polymerization for adsorption of erythromycin from aqueous solution. J Environ Chem Eng 4:3570–3579. https://doi.org/10.1016/j.jece.2016.07.036

Zhu Y, Wang F, Zheng Y, Wang F, Wang A (2016a) Rapid enrichment of rare-earth metals by carboxymethyl cellulose-based open-cellular hydrogel adsorbent from HIPEs template. Carbohydr Polym 140:51–58. https://doi.org/10.1016/j.carbpol.2015.12.003

Zhu Y, Zheng Y, Wang F, Wang A (2016b) Fabrication of magnetic macroporous chitosan-*g*-poly (acrylic acid) hydrogel for removal of Cd^{2+} and Pb^{2+}. Inter J Biol Macromol 93:483–492. https://doi.org/10.1016/j.ijbiomac.2016.09.005

Zhu Y, Zheng Y, Wang F, Wang A (2016c) Fabrication of magnetic porous microspheres via (O_1/W)/O_2 double emulsion for fast removal of Cu^{2+} and Pb^{2+}. J Taiwan Inst Chem E 67:505–510. https://doi.org/10.1016/j.jtice.2016.08.006

Zhu Y, Zheng Y, Wang F, Wang A (2016d) Monolithic supermacroporous hydrogel prepared from high internal phase emulsions (HIPEs) for fast removal of Cu^{2+} and Pb^{2+}. Chem Eng J 284:422–430. https://doi.org/10.1016/j.cej.2015.08.157

Zhu Y, Zheng Y, Zong L, Wang F, Wang A (2016e) Fabrication of magnetic hydroxypropyl cellulose-g-poly(acrylic acid) porous spheres via Pickering high internal phase emulsion for removal of Cu^{2+} and Cd^{2+}. Carbohydr Polym 149:242–250. https://doi.org/10.1016/j.carbpol.2016.04.107

Zhu Y, Wang W, Zhang H, Ye X, Wu Z, Wang A (2017a) Fast and high-capacity adsorption of Rb^+ and Cs^+ onto recyclable magnetic porous spheres. Chem Eng J 327:982–991. https://doi.org/10.1016/j.cej.2017.06.169

Zhu Y, Zhang H, Wang W, Ye X, Wu Z, Wang A (2017b) Fabrication of a magnetic porous hydrogel sphere for efficient enrichment of Rb^+ and Cs^+ from aqueous solution. Chem Eng Res Des 125:214–225. https://doi.org/10.1016/j.cherd.2017.07.021

Zhu H, Tan X, Tan L, Zhang H, Liu H, Fang M, Hayat T, Wang X (2018) Magnetic porous polymers prepared via high internal phase emulsions for efficient removal of Pb^{2+} and Cd^{2+}. ACS Sustainable Chem Eng 6:5206–5213. https://doi.org/10.1021/acssuschemeng.7b04868

Zhu Y, Wang W, Yu H, Wang A (2020) Preparation of porous adsorbent via Pickering emulsion template for water treatment: a review. J Environ Sci 88:217–236. https://doi.org/10.1016/j.jes.2019.09.001