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Mini-Review

# RECENT STUDIES ON MAGNETIC MESOPOROUS NANOMATERIALS FOR WATER TREATMENTS

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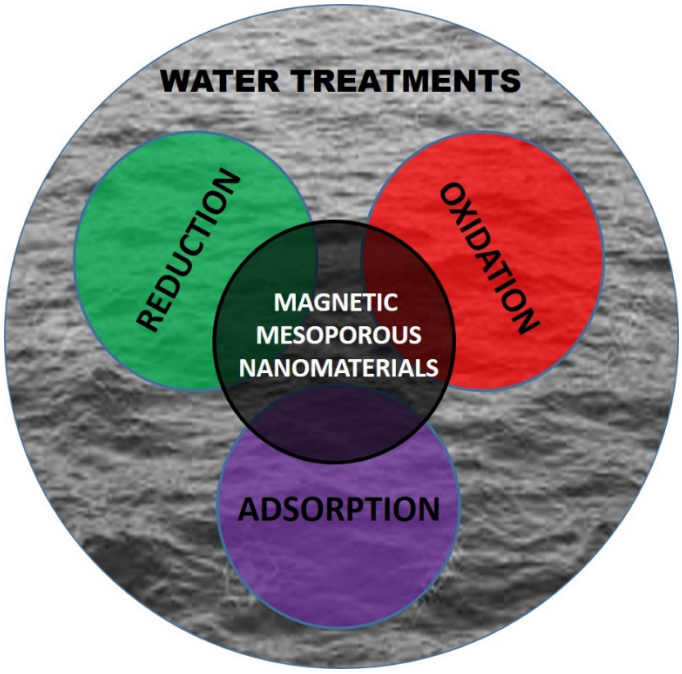
## Graphical abstract




**Resumen**

En el contexto del tratamiento de aguas contaminadas, este trabajo ofrece una visión general y en profundidad de los últimos avances en diseño racional, síntesis y aplicaciones de nanomateriales magnéticos mesoporosos en la adsorción, oxidación química y reacciones de reducción centradas en la eliminación de contaminantes orgánicos. Se presta especial atención a los materiales magnéticos mesoporosos a base de sílice y carbono. Finalmente, se discuten los desafíos que enfrenta la aplicación de estos materiales en sistemas de tratamiento reales.

**Abstract**

Within the context of wastewater treatments, this review offers a general and in-depth overview of the latest advances in rational design, synthesis and applications of mesoporous magnetic nanomaterials in adsorption, chemical oxidation and reduction reactions focused on the removal of organic pollutants. Special attention is paid to magnetic mesoporous silica- and carbon-based materials. Finally, the challenges facing the application of these materials in real treatment systems are discussed.

***Palabras Clave:*** *magnetita, hierro cero valente, sílice mesoporosa, carbón mesoporoso, nanotecnología*

***Keywords:*** *magnetite, zero valent iron, mesoporous silica, mesoporous carbon, nanotechnology.*

## 1. Introduction

The involvement of nanotechnology in environmental applications is an important topic of current research.[1–3] In particular, nanotechnology-mediated processes can provide water treatment solutions and new treatment capabilities, expanding the water supply from unconventional water sources.[4–6] The unique properties of nanomaterials (NMs), including large surface area, catalytic activity, and magnetic properties, are all promising features for water treatment.[7] Among the NMs with potential application in wastewater treatments, mesoporous materials are propitious as adsorbents and catalyst supports due to its regularly ordered mesoscale channels, high specific surface areas and fast mass transfer kinetics.[8] Mesoporous silica- and carbon-based NMs are the most frequently mesoporous NMs studied for removal of organic contaminants by means of adsorption, and oxidation or reduction reactions. One critical point of the application of NMs in a water remediation process is their separation from treated water for further regeneration and reuse. It is important to note that the special properties that make the NMs unique and useful could adversely affect organisms and ecosystems.[9,10] Thus, avoiding its release to the environment by an efficient separation process minimizes risks to public and environmental health. This issue can be overcomed providing magnetic properties to the NMs allowing an efficient separation with an external magnetic field. Magnetic separation has emerged as a highly efficient, simple and cost-effective method compared to conventional

separation processes as filtration or centrifugation.[11] Although there are many magnetic materials, the most used in water treatment are NMs based on nanoscale zero-valent iron (nZVI), magnetite ($Fe_3O_4$) and maghemite ($\gamma$-$Fe_2O_3$).[12] They possess diverse physicochemical and magnetic properties originated from the difference in their iron oxidation state and structure. Therefore, NMs with magnetic properties and mesoporous structures are very promising for efficient applications in water treatments. Recently, different strategies have been developed for the synthesis of magnetic mesoporous NMs with different morphologies and several studies related to its applications in water treatments have been performed.[13–15]

This review gives an overview of the application of magnetic mesoporous NMs in adsorption, reduction and oxidation processes for the removal of organic pollutants in water. Special emphasis will be made on mesoporous silica- and carbon-based materials. In particular, the synthesis and features of these NMs will be summarized, and the performance on the organic pollutant removal by these NMs will be addressed.

## 2. Magnetic mesoporous materials.

### 2.1. Silica based materials

Mesoporous silica-based materials are inorganic solids with a three-dimensional structure made of interconnected $SiO_4$ tetrahedra via siloxane bonds. Due to their outstanding properties, these materials have attracted an exceptional attention in water remediation. These properties include large specific surface area (200–1500 $m^2\ g^{-1}$), high pore volume (up to 1 $cm^3\ g^{-1}$), very adjustable structure and surface chemistry (*i.e.* pore size, surface functionalization, etc.), low toxicity, chemical stability and low production cost.

Since the first report of Mobile Composite of Matter family (MCM-41, MCM-48, and MCM-50 with pore sizes between 2–8 nm) in early 1992,[16,17] many other mesoporous silica-based materials were developed. KIT-5 and KIT-6, similar to MCM-41 in high specific surface area and uniform pore size but with enhanced thermal stability, were produced in 1997.[18] In 1998,

researchers of the University of California developed the Santa Barbara Amorphous (SBA) family (SBA-1, SBA-2, SBA-6, SBA-8, SBA-11, SBA-12, SBA-15, and SBA-16) with larger pore diameters (7.5-32.0 nm) and thicker walls.[19,20]

The most common synthesis procedure of mesoporous silica involves a templating agent, typically a surfactant, in aqueous solution that directs the polymerization of a silica precursor, usually a silicon alkoxide like tetraethoxysilane (TEOS) (Figure 1).

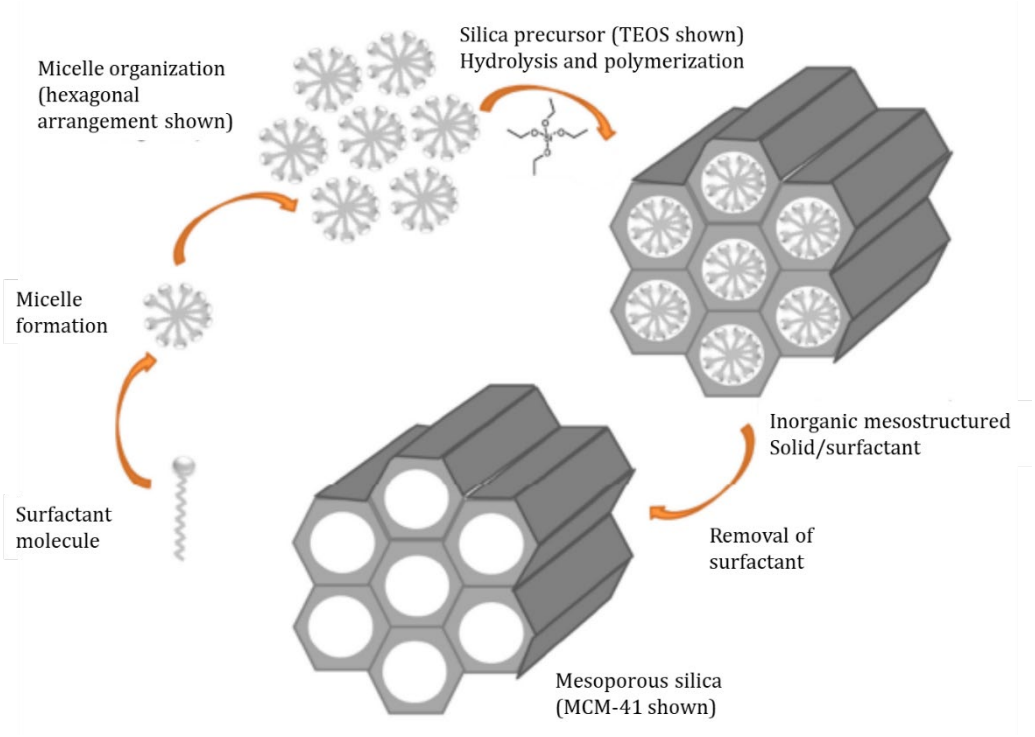



**Figure 1.** Synthesis procedure of mesoporous silica. Adapted from reference 21.

The pore size, particle size and morphology of mesoporous silica can be adjusted by selecting different surfactants, by controlling pH and by using additives.[22] For instance, the synthesis of MCM-41 typically involves the cationic surfactant cetyltrimethylammonium bromide (CTAB) obtaining a pore size between 2-3 nm; meanwhile the neutral co-polymer with larger molecular weight Pluronic P123, leads to around 9 nm pore width in the preparation of SBA-15.[3] Adding a co-solvent, like trimethylbenzene, to expand the micelle formed by the templating agent is another way to obtain wider pores.[23] It is also possible to increase the pore size by post-synthesis hydrothermal treatment.[24–26] The pore structure mainly depends on the relative amounts of

template and silica precursor and the packing ability of the surfactant.[27] For silica with pore sizes among 2-5 nm the most usual structures are the hexagonal (MCM-41), 3D cubic (MCM-48) and lamellar (MCM-50), while for larger pore sizes, between 6 and 20 nm, the most common structure is 2D hexagonal (SBA-15).[28] On the other hand, mesoporous silica-based materials can be prepared in neutral, basic or acid media. Highly basic conditions (pH > 12) generate fast condensations inducing lamellar mesophases (MCM-50), while moderate alkaline ones (10 < pH < 12) preferentially produce hexagonal structures (MCM-48). SBA-15, KIT-5 and KIT-6 are prepared in acid media[29] whereas HMS (hexagonal mesoporous silica)[30] and MSU mesoporous materials[31] are synthetized at neutral pH.

Bare mesoporous silica is rarely reported as a candidate material for water remediation. Usually, a surface functionalization is needed to obtain a material with specific properties regarding of the water remediation method. For instance, functional groups (*i.e.* amino, thiol, aromatic, etc.) that can interact with pollutants (*i.e.* heavy metals, organic molecules) are usually bonded to the silica for adsorption process. Organo-substituted trialkoxysilanes are the most typical molecules applied to functionalize the silica surface.[28] This procedure can be done both post-synthesis or during the synthesis. In post-synthesis methods the alkoxysilane is added to bare silica, their alkoxy groups are hydrolysed and a covalent bond with the silanol groups of the silica surface is formed by condensation.[32] Moreover, it is possible to perform a further reaction of a previously grafted functional group, for example a polymerization of a vinyl alkoxysilane bonded to a mesoporous silica resulting in a polymer functionality.[33,34] Functionalization in the synthesis can be achieved by a co-condensation reaction adding an alkoxysilane, like (3-aminopropyl)triethoxysilane, along with the primary silica precursor in the presence of a surfactant.[35–37]

In order to provide magnetic properties to mesoporous silica-based materials, the integration of iron and iron oxides, such as magnetite or maghemite, to the mesopores structure is commonly carried out. To this end, two approaches are commonly used to prepare materials for

environmental applications: **1)** nano- and micro-spheres encapsulating magnetic cores into perpendicularly aligned mesoporous shells. This approach consists in covering a core of iron oxide nanoparticles with a shell of mesoporous silica to produce hierarchical structures known as "core-shell" nanoparticles.[38] These structures have the additional advantage of protecting the iron oxide core from leaching and oxidation in water and, at the same time, reducing the tendency of aggregation of the particles. Recently, Zhang et al.[39] developed core-shell magnetic silica microspheres ($Fe_3O_4$@m$SiO_2$) using the amphiphilic co-polymer polystyrene-block-poly (4-vinylpyridine) as a templating agent. The obtained material showed large mesopores (10 nm), high specific surface area (244 $m^2$ $g^{-1}$) homogenous core-shell morphology and good adsorption performance of organophosphorus pesticide fenthion (Figure 2A and 2B). **2)** Ordered mesoporous materials loaded with magnetic NPs inside the porous channels. This approach consists in inserting iron oxide nanoparticles into a mesoporous silica matrix. For instance, monodisperse and hierarchically mesoporous silica microspheres embedded with maghemite nanoparticles (Figure 2C).[40] More recently, Fuentes-García and co-workers[41] dispersed magnetite nanoparticles in a silica matrix to study their magnetic properties (Figure 2D).

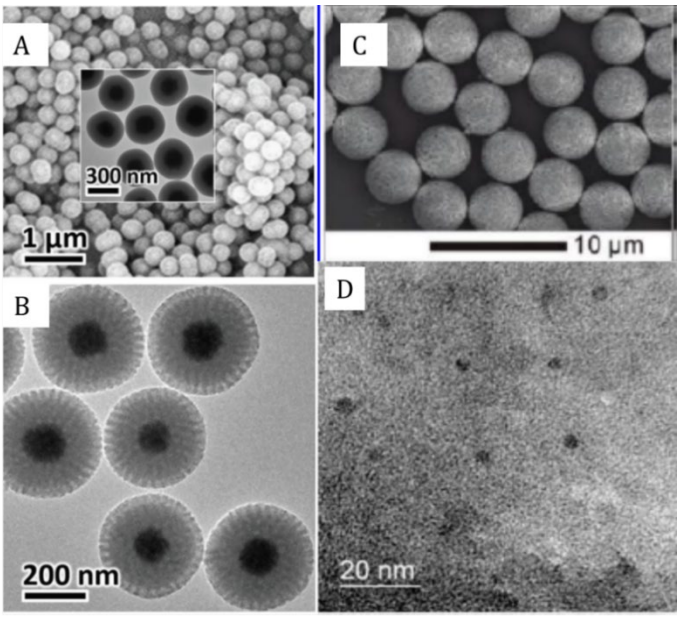



**Figure 2.** SEM (A) and TEM (B) images of core-shell magnetic silica microspheres. Adapted from reference 39. SEM image (C) of maghemite embedded mesoporous silica. Adapted from reference 40. TEM image (D) of magnetite dispersed in a silica matrix, adapted from reference 41.

nZVI can also provide magnetic properties to mesoporous silica materials.[42] However, it is more common to use nZVI as a catalyst because of its strong reduction capability against heavy metals, organochlorine compounds and nitroaromatic compounds.[43,44] In order to maximize the reactive surface area and reduce particle aggregation, nZVI can be embedded in porous materials. The most reported procedure consists in adding an iron source, like iron salts, which diffuse inside the pores, followed by reduction under hydrogen atmosphere or chemical reduction with sodium borohydride. Tang et al.[45] immobilized nZVI on SBA-15 surface. Also, nZVI was successfully loaded inside the channels of mesoporous silica nanoparticles by means of iron impregnation using hexane as a solvent followed by chemical reduction with $NaBH_4$.[46]

### 2.2. Carbon based materials

Mesoporous carbons are other key mesoporous materials for the removal of organic contaminants from water. Activated carbon (AC) is one of the most used supporting materials and one of the most ancient and studied adsorbents. It exhibits specific areas of 500 - 2000 $m^2/g$ and pore diameters generally in the micro- and meso-pore region.[47] AC is obtained from vegetable carbon sources submitted to an activation process (Figure 3). This process consists of a two-step calcination, where the raw material is carbonized at 500-800°C under inert atmosphere followed by activation at 700-1100 °C under $CO_2$ or $H_2O$ steam. Another way to achieve activation is through the use of dehydrating and oxidizing agents such as $ZnCl_2$, $CaCl_2$, KOH, NaOH, $H_2PO_4$ and simultaneous calcination at 400-900 °C.[47–51] The degree of mesoporous content depends on the type of activation and the nature of the chemical agent.[52] For instance, Hu and Srinivasan[52] reported the preparation of mesoporous activated carbons with mesopore contents above 70% by means of a simultaneous physical and chemical activation technique that utilize $CO_2$ and $ZnCl_2$. Ordered mesoporous carbons (OMC) are another family of adsorbents and supporting materials. The first OMC were obtained by Ryoo et al.[53] in 1999. This gave rise

to a series of synthesis process called "*hard template*" methods, where a carbon precursor solution is impregnated in the insides of a rigid silica template (Figure 4A). After this impregnation, carbonization creates the carbon structure inside the template, and the desired product is obtained when the silica is removed via acid dissolution.[54–56] Another approach to obtain OMC are the "*soft template*" methods. In this case, a phenol/formaldehyde resin is mixed with a try-block copolymer like Pluronic P123 or F127 and polymerized at temperatures close to 100-150°C to form a solid ordered structure, then this solid is carbonized to obtain the final OMC (Figure 4B).

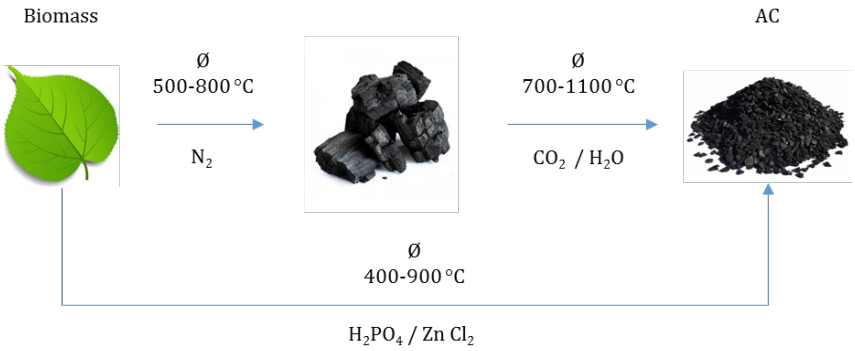



**Figure 3.** Schematic route for activated carbon synthesis.

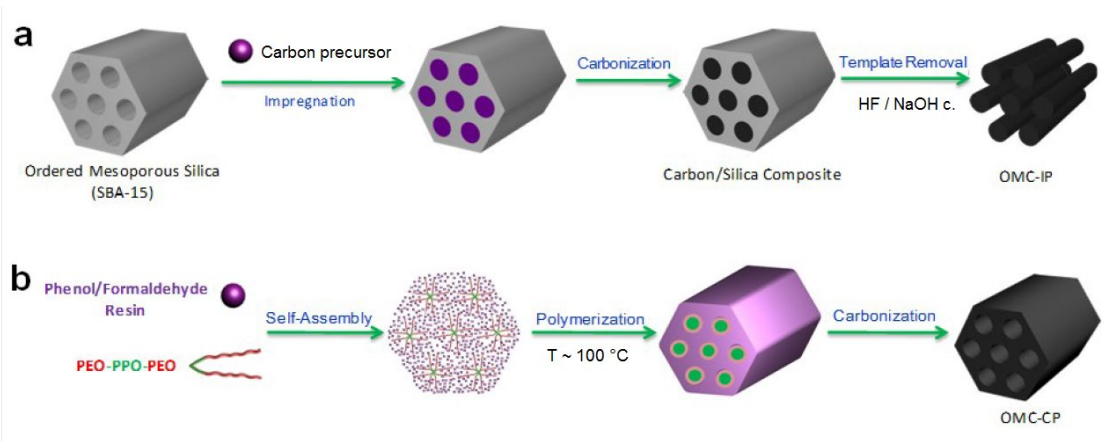



**Figure 4.** OMC synthesis routes: (A) Hard template and (B) Soft template. Adapted from reference 57.

The typical magnetic mesoporous carbon-based MNs for environmental application consist of nZVI supported on the mesoporous carbon matrix and rattle-type magnetic mesoporous hollow carbon materials. These magnetically separable materials show improved adsorption capacities,[45,58,59] can be used as chemical reductors and can serve as catalyst for Fenton like reactions.[60–63] nZVI supported on mesoporous carbon can be broadly classified into three groups: 1) iron supported on unordered mesoporous carbon (UMC), as activated carbon, biochar, etc.;[58,64] 2) iron supported on ordered mesoporous carbon, as CMK and FDU types; 3) other materials that fall out of these two categories, as "core-shell" materials and others.[65–67] The synthesis procedure of the first two mesoporous materials consists of two steps: first mesoporous carbon is subjected to a wet impregnation with iron salts. In this way, the iron precursors are incorporated into the mesopores of the material. The second step involves the reduction of the iron precursors to $Fe^0$ by means of a chemical agent, such as $NaBH_4$, or by calcination at temperatures between 500 and 1000 °C under $N_2$ or $H_2$ atmospheres (Figure 5).[68,69]

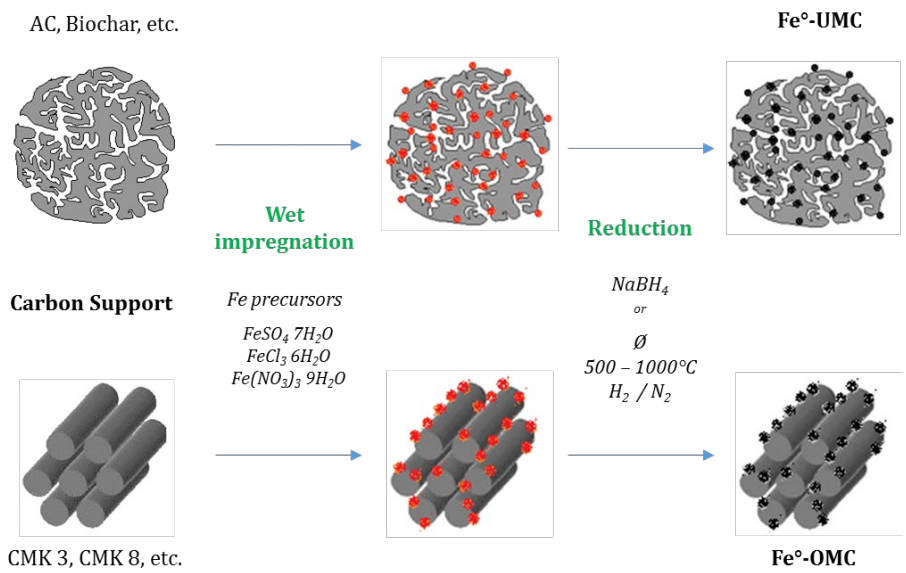



**Figure 5.** Iron loading on carbon matrix through wetness impregnation.

Core-shell materials are obtained in a process that combines carbon precursors such as glucose with iron salts, typically $Fe(NO_3)_3$. These species are dissolved and brought into contact by

agitation for a certain period of time and then subjected to hydrothermal treatment at temperatures between 150 and 300 °C for times ranging from 1 to 18 h. Finally, the obtained solid is subjected to a final calcination step at temperatures between 300 and 800 °C in an inert atmosphere. Examples of this process can be found in the literature, where glucose and olive mill wastes were used as carbon sources.[65,66] On the other hand, rattle-type magnetic mesoporous hollow carbon materials have shown great promise as adsorbents for water treatment.[67] This kind of materials are prepared through a hard template approach, which involves encapsulation of phenol-formaldehyde resin in the mesopores of preformed hard template of $Fe_3O_4$@$SiO_2$@m$SiO_2$, followed by carbonization and silica removal.[70,71]

## 3. Application of magnetic mesoporous NMs in remediation processes.

### 3.1. Adsorption.

Adsorption is one of the most promising techniques to be applied in water remediation because of its low cost, ease procedure, possibility of regeneration and highly efficient removal of target pollutants. Different steps must be considered in the adsorption process: a) adsorption of the pollutant b) recovery of the adsorbent for further reuse c) adsorbent regeneration, and d) management of both the regeneration solution and the saturated adsorbent. The great challenge is developing highly efficient and reusable adsorbents.

Due to their high specific surface area, pore volume, adaptable structure, functionalizable surface and ease separation, magnetic mesoporous NMs have attracted great attention for adsorption applications. In this section, we summarized recent advances on the application of mesoporous silica- and carbon-based materials for the adsorption of different families of organic pollutants (Table 1). Among organic pollutants, cationic dyes (such as methylene blue or crystal violet) and anionic dyes (like acid orange 10 or methyl orange) are the most frequently reported in adsorption assays. Liu et al.[72] prepared a magnetic bimodal mesoporous carbon via hard-

template method with Fe and Ni (Fe/Ni-OMC) as magnetic precursors and tested this NMs for the adsorption of dyes. As expected, alkaline pH was favourable for cationic dye methylene blue adsorption and acid pH was better for anionic dye methyl orange. The maximum adsorption capacities were 959.5 mg $g^{-1}$ and 849.3 mg $g^{-1}$, respectively. The adsorbent was able to be used up to 7 cycles using ethanol as the regeneration solvent. As was stated before, adsorbent regeneration is a significant step for adsorption process cost as well as the final disposition of pollutant. The most common way for regeneration is by using an eluent (e.g. ethanol, acid or basic aqueous solution, acid or basic organic solution) to desorb the adsorbate. Then, if the adsorbate has no commercial value, a degradation process (like oxidation, reduction or calcination) can be performed. Mesoporous silica-based materials were also tested for dyes adsorption. In the study performed by Brigante *et al.*[73], cationic dye malachite green and humic acids were adsorbed onto core-shell magnetic mesoporous silica ($Fe_3O_4$@m$SiO_2$) with different magnetite and silica ratio. For both species, adsorption showed a dependence with pH. They proposed that the adsorption of HA takes place by hydrogen bonds between their functional groups and the active sites of the magnetite. For malachite green, the most relevant interaction proposed were electrostatics among dye positive charge and negative-charged silanol groups.

Mesoporous carbon and organo-functionalized silica were studied as adsorbents of PAHs from aqueous media. Sharma *et al.*[74] tested the removal of 2-naphthol and naphthalene from water with mesoporous carbon coated superparamagnetic $ZnFe_2O_4$ nanoparticles (UMC-$ZnFe_2O_4$). The results revealed higher adsorption capacity ($q_{max}$ = 40.27 mg $g^{-1}$) of polar 2-naphthol than non-polar naphthalene ($q_{max}$ = 24.44 mg $g^{-1}$). The adsorbent was able to be used after 4 washing cycles with alkaline ethanol solution. Furthermore, the mesoporous carbon was prepared from date palm seed waste, which contributes for the adsorbent low-cost.

Tang et al. [45] reported the removal of 2,4-dicholorophenoxyacetic acid (2,4-D), a widely used herbicide, by ordered mesoporous carbon prepared via hard-template method, functionalized with carboxyl groups and magnetized with the deposition of iron oxide nanoparticles inside the

pores (OMC-IONPs). The adsorption of 2,4-D on OMC-IONPs resulted in a fast pseudo-second order kinetics, a Langmuir-type isotherm ($q_{max}$ = 310.78 mg $g^{-1}$) and a decrease of the adsorption capacity with temperature and pH. The adsorbent was regenerated with ethanol, retaining percentage of removal up to 50% after 6 cycles of reuse. Recently, the performance of biochar supported nZVI (Biochar-nZVI) in the removal of glyphosate was studied for the first time.[58] Biochar was prepared from palm by calcination and then was used in a liquid-phase reduction process to obtain the absorbent. The adsorption process showed a pseudo second order kinetics, pH dependence and a Langmuir model behaviour. The authors proposed various mechanisms involving the removal process: pore-filling, hydrogen bonding, complexation, and electrostatic interactions. The low-cost adsorbent presented a high adsorption capacity (80 mg $g^{-1}$ at pH 4), however no reuse experiments were performed.

Huang et al.[75] prepared a particular permanently confined micelle array core-shell nanoparticles to use as adsorbent. Maghemite cores were surrounded by 3-(trimethoxysilyl)propyl-octadecyldimethyl-ammonium chloride (TPODAC) surfactant with 1,3,5-trimethyl benzene (TMB) as micelle swelling agent, then TEOS was added to covalently bind the surfactant (which has reactive methoxy group) onto the magnetic cores. Three different TMB:TPODAC weight ratio were used to prepare the adsorbent nanoparticles. In this work, the authors studied the adsorption performance of the as prepared nanoparticles ($\gamma$-$Fe_2O_3$@$SiO_2$-TPODAC) on methyl orange, sulfamethoxazole, gemfibrozil, acenaphthene and phenanthrene. It was found that larger amounts of TMB results in noteworthy higher sorption kinetic rate as well as slightly higher sorption capacity to ECs and PAHs. In addition, the core-shell nanoparticles showed good adsorption capacity after 5 regeneration cycles employing methanol as regeneration solvent.

**Table 1.** Application of magnetic mesoporous nanomaterials as adsorbents for pollutants removal from water.

| Material | Pollutant | Adsorption capacity (mg $g^{-1}$) | Regeneration solvent and reuse cycles | Ref. |
|---|---|---|---|---|
| Fe/Ni-OMC | methylene blue<br>methyl orange | 959<br>849 | EtOH<br>7 cycles | 72 |
| $Fe_3O_4$@m$SiO_2$ | malachite green | - | HCl<br>3 cycles | 73 |
| UMC-$ZnFe_2O_4$ | 2-naphthol<br>naphtalene | 40<br>24 | NaOH-EtOH<br>4 cycles | 74 |
| OMC-IONPs | 2,4-D | 310 | EtOH<br>6 cycles | 45 |
| Biochar-nZVI | glyphosate | 80 | - | 58 |
| $Fe_3O_4$@m$SiO_2$ | Fenthion | 440 | - | 39 |
| γ-$Fe_2O_3$@$SiO_2$-TPODAC | Methyl orange<br>Sulfamethoxazole<br>Phenanthrene | 104<br>50<br>0.95 | MeOH<br>5 cycles | 75 |

### 3.2. Reduction.

Magnetic mesoporous NMs frequently used in reductive treatments to degrade organic pollutants are mainly made up of nZVI nanoparticles embedded into de mesopores of a solid matrix. It has been proven that nZVI is very effective for the removal and degradation by reductive pathways of a wide variety of chemicals, including nitrated organic compounds, chlorinated organic compounds, organophosphates, nitro amines, PCBs, and organic dyes.[76] The chemical reduction of the pollutant induced by $Fe^0$ typically requires the contaminant to be adsorbed on or near to the surface of the solid.[77] The mesoporous nanocomposites described in this section seek to combine the adsorbent capacities of the mesoporous structure with the reactive characteristics of nZVI. In this section we will describe recent literature results of magnetic mesoporous NMs applied for the removal of organic pollutant from waters by reductive pathways (Table 2).

Tang et al.[78] obtained nZVI dispersed on SBA-15 nanoparticles (Fe-SBA15-WI) by wet impregnation of SBA-15 mesoporous silica and studied the reduction of p-nitrophenol (PNP). They observed a significant dependence of the PNP degradation with the pH, achieving 96% and 16% removal at pH 3 and 9, respectively, by using 400 mg/L solutions of PNP and 5 g/L solid dose. They also found almost no iron leaching from the remaining supernatants. Zhang et al.[79] developed a nanocomposite where nZVI was dispersed inside the SBA-15 mesopores (Fe-SBA15-IWI) using two different types of SBA-15 through incipient wetness impregnation of iron precursors and $H_2$ reduction. Reduction capacity was studied on 20 mg/L solutions of nitrobenzene (NB) achieving 94% and 84% removal for the two different composites and 57% for unsupported bare nZVI. Similarly, Lu et al.[46] studied NB reduction by nZVI incorporated inside the channels of monodisperse mesoporous silica nanospheres (nZVI-MSN) under different experimental conditions such as pH, presence of typical anions, solid dose, etc. and evaluated reusability and stability in successive removal experiments. They obtained a 99 to 74% removal from pH 3 up to 11. Ions including $Na^+$, $K^+$, $Cl^-$, $NO_3^-$ and $SO_4^{2-}$ showed no effect on NB degradation, while $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$ showed a slight inhibitory effect. Moreover, after seven cycles of reduction the removal efficiency of NB remained higher than 86%. On the other hand, nZVI supported on ordered mesoporous silica (Fe-MCM41) was evaluated for n-dimethylnitrosamine removal from water.[80] Unlike other studies, these authors found a maximum removal around neutral pH, in particular they reached 70%, 90% and 80% removal at pH 4, 7 and 9 respectively. Chen et al.[81] prepared core-shell nanoparticles of nZVI core with a mesoporours silica shell (Fe@m$SiO_2$) by the synthesis of bare nZVI directly followed by mesoporous silica condensation using CTAB and TEOS. Surface charge, dispersion stability and mobility in sand columns were studied. The Fe@m$SiO_2$ nanoparticles were used for treatment of 1,1,1-trichloroethane in water and real groundwater samples obtained from a pesticide factory site.

Among nZVI-UMC composites, Choi et al.[82] synthesised granular activated carbon impregnated with reactive iron/palladium bimetallic nanoparticles (Fe/Pd-AC) through traditional wetness

impregnation method with $NaBH_4$ reduction, coupled to an additional step of Pd doping. They tested this material against 2-chlorobiphenyl and obtained almost complete dechlorination of 4 mg/L solutions within 1 day at 20 g/L of Fe/Pd-AC. Wang et al.[83] obtained nZVI supported on granular AC (Fe-AC) to reduce various nitrosamines to their corresponding amines, nitrate and nitrite. They also studied the influence of various anions, cations and humic acids (HA), and found that all of this coexisting species had a negative effect on the total reduction obtained. Similarly, Zhang et al.[84] used a traditional wet impregnation method followed by a post annealing treatment (T~ 105-700°C under $N_2$ for 2 h) in order to increase crystallinity and improve electron mobility inside the iron phase of Fe-AC nanocomposites. Dechlorination of trichloroethane, trichloroethylene and tetrachloroethene by Fe-AC reached 95% after 300 min of treatment. They found a negative effect of $Na^+$, $Ca^{2+}$, $SO_4^{2-}$ , $NO_3^-$ and HA, on the substrates dechlorination rate, but no effect on the final dechlorination degree. Wang et al.[85] studied Metronidazole degradation using nZVI supported on non-porous carbon spheres (Fe-CSS). With 1 g/L dose of Fe-CSS under aerobic conditions they observed 94% degradation in 6 min, compared with 36% for bare nZVI in the same time. On the other hand, Ling et al.[86] studied the reduction of nitrobenzene using a nZVI supported on ordered mesoporous carbon (Fe-OMC) prepared from a soft template route and wet impregnation. They observed a 92 % removal of 80 mg/L solutions of NB using a 0.5 g/L of Fe-OMC, compared with a 49% removal for unsupported nZVI under the same conditions.

**Table 2.** Application of magnetic mesoporous nanomaterials in reductive treatments.

| Material | Load | Pollutant | Conc. | %Removal | Ref. |
|---|---|---|---|---|---|
| Pd/Fe-AC | 20 g $L^{-1}$ | 2-chlorobiphenyl | 4 mg $L^{-1}$ | 100 | 82 |
| Fe-AC | 2 g $L^{-1}$ | Nitrosamines | 0.2 mg $L^{-1}$ | 80-100 | 83 |
| Fe-AC | 7 g $L^{-1}$ | Trichloroethylene Tetrachloroethylene | 80 mg $L^{-1}$ | 95 | 84 |
| Fe-CSS | 0.8 g $L^{-1}$ | Metronidazole | 60 mg $L^{-1}$ | 90 | 85 |
| Fe-OMC | 0.5 g $L^{-1}$ | Nitrobenzene | 80 mg $L^{-1}$ | 90 | 86 |
| Fe-SBA15-WI | 5 g $L^{-1}$ | p-nitrophenol | 400 mg $L^{-1}$ | 96 | 78 |
| Fe-SBA15-IWI | 1 g $L^{-1}$ | Nitrobenzene | 20 mg $L^{-1}$ | 94 | 79 |
| Fe-MSN | 2.3 g $L^{-1}$ | Nitrobenzene | 20 mg $L^{-1}$ | 100 | 46 |
| Fe-MCM41 | 0.02 g $L^{-1}$ | N-dimethylnitrosamide | 1 ug $L^{-1}$ | 90 | 80 |
| Fe@m$SiO_2$ | 3.9 g $L^{-1}$ | 1,1,1-trichloroethane | 4.5 mM | 77 | 81 |

### 3.3. Oxidation.

Magnetic mesoporous NMs have recently attracted attention in oxidation processes, such as Fenton processes, for the removal of organic pollutants. The Fenton processes is an Advanced Oxidation Process (AOP) that has gained vast acceptance for its high removal efficiency of organic pollutants. In the Fenton reaction, $H_2O_2$ oxidizes $Fe^{2+}$ to $Fe^{3+}$ producing hydroxyl radical ($HO^{\bullet}$), which is the key reactive specie involved in the degradation of the pollutants.[87] In particular, when ZVI is used in the treatment, ZVI naturally oxidizes upon reaction with $H_2O$ and $O_2$, leading to the formation of oxidation products such as $HO^{\bullet}$ radicals, superoxide radical, ferryl ion species and $H_2O_2$.[88] These reaction products can subsequently degrade organic contaminants through oxidative reactions. Moreover, external addition of $H_2O_2$ cause an efficient pollutant degradation treatment commonly named ZVI-assisted Fenton systems.[89] Immobilizing the nZVI on mesoporous NMs can effectively increase the contact area with pollutants, and prevent the agglomeration of nZVI. Duan et al.[60] investigated ordered mesoporous carbon supported nZVI catalysts (Fe/OMC-300) in Fenton-like degradation of 4-chlorophenol. Under optimal conditions, the authors found 96.1% of 4-chlorophenol and 47.4% of total organic carbon (TOC) removal after 270 min of treatment (at 30°C, initial pH of 3 and 6.6 mmol/L

$H_2O_2$). Shao et al.[90] obtained a complete phenol degradation (>99%) with remarkable low iron leaching by using nZVI embedded within ordered mesoporous carbon (Fe-OMC) as heterogeneous Fenton catalysts in a fixed-bed reactor operated under continuous-flow condition. On the other hand, Zheng et al.[63] demonstrate that surface hydrophilic modification of OMC with uniform dispersed γ-$Fe_2O_3$ nanoparticles (H-$Fe_2O_3$/OMC) showed enhanced adsorption and degradation performance of methylene blue (MB) in heterogeneous Fenton treatment. Wang et al.[61] found that Fe-$Fe_2O_3$ nanoparticles supported on ordered mesoporous carbon (Fe-$Fe_2O_3$/OMC) degrade 98.1% of 100 mg $L^{-1}$ of Acid Orange II in the presence of $H_2O_2$ (0.5 g $L^{-1}$) at neutral pH and nearly room temperature. They also found an improved catalytic activity for Fe-$Fe_2O_3$/OMC over Fe/OMC and γ-$Fe_2O_3$/OMC; this effect is explained by an efficient electron transfer between the iron and the iron oxide, which leads to an acceleration of the $Fe^{3+}/Fe^{2+}$ cycle.

## 4. Conclusions and future prospect

In this review, we have outlined various methodologies for the synthesis of magnetic mesoporous nanomaterials, especially silica- and carbon-based materials, with applications in water treatment. We have provided updated examples of their applications in adsorption, reduction and oxidation processes for organic pollutant removal. It was shown that the resulting nanomaterials from magnetic iron and iron oxides encapsulated within or supported on the mesoporous matrices have excellent properties to be used in different water treatments. In particular, magnetic mesoporous nanomaterials are versatile frameworks that can be functionalized with various active compounds to create multifunctional materials. Also, magnetic separation is an environmentally friendly alternative for the separation and recovery of nanomaterials, since it minimizes the use of solvents and auxiliaries, reduces the operation time, and is a cost-effective method compared to conventional separation processes as filtration or centrifugation. However, there are still several issues and challenges to achieve highly efficient

magnetic separation designs that avoid the loss of nanomaterials in the separation step with possible release to the environment.

Finally, it is necessary the development of simple and low-cost synthesis methods. Further research should be devoted to designing cost-effective and highly efficient nanomaterials. The use of green synthesis routes for nanomaterials, such as the use of waste materials as precursors, and the application of these eco-friendly nanomaterials will reduce the overall production cost and help reducing the environmental impact.

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## References

(1) Leng, W.; Barnes, H. M.; Yan, Q.; Cai, Z.; Zhang, J. Low Temperature Synthesis of Graphene-Encapsulated Copper Nanoparticles from Kraft Lignin. Mater. Lett. **2016**, 185, 131–134.
(2) Chelme-Ayala, P.; El-Din, M. G.; Smith, D. W. Kinetics and Mechanism of the Degradation of Two Pesticides in Aqueous Solutions by Ozonation. Chemosphere **2010**, 78 (5), 557–562.
(3) Li, R.; Zhang, L.; Wang, P. Rational Design of Nanomaterials for Water Treatment. Nanoscale **2015**, 7 (41), 17167–17194.
(4) Madhura, L.; Singh, S.; Kanchi, S.; Sabela, M.; Bisetty, K.; Inamuddin. Nanotechnology-Based Water Quality Management for Wastewater Treatment. Environ. Chem. Lett. **2019**, 17, 65-121..
(5) Santhosh, C.; Velmurugan, V.; Jacob, G.; Jeong, S. K.; Grace, A. N.; Bhatnagar, A. Role of Nanomaterials in Water Treatment Applications: A Review. Chem. Eng. J. **2016**, 306, 1116–1137.
(6) Adeleye, A. S.; Conway, J. R.; Garner, K.; Huang, Y.; Su, Y.; Keller, A. A. Engineered Nanomaterials for Water Treatment and Remediation : Costs , Benefits , and Applicability. **2016**, 286, 640–662.
(7) Cai, Z.; Dwivedi, A. D.; Lee, W. N.; Zhao, X.; Liu, W.; Sillanpää, M.; Zhao, D.; Huang, C. H.; Fu, J. Application of Nanotechnologies for Removing Pharmaceutically Active Compounds from Water: Development and Future Trends. Environ. Sci. Nano **2018**, 5 (1), 27–47.
(8) Wu, Z.; Zhao, D. Ordered Mesoporous Materials as Adsorbents. Chem. Commun. **2011**, 47 (12), 3332–3338.
(9) Holden, P. A.; Gardea-Torresdey, J. L.; Klaessig, F.; Turco, R. F.; Mortimer, M.; Hund-Rinke, K.; Cohen Hubal, E. A.; Avery, D.; Barceló, D.; Behra, R.; Cohen, Y.; Deydier-Stephan, L.; Ferguson, P. L.; Fernandes, T. F.; Herr Harthorn, B.; Henderson, W. M.; Hoke, R. A.; Hristozov, D.; Johnston, J. M.; Kane, A. B.; Kapustka, L.; Keller, A. A.; Lenihan, H. S.; Lovell, W.; Murphy, C. J.; Nisbet, R. M.; Petersen, E. J.; Salinas, E. R.; Scheringer, M.; Sharma, M.; Speed, D. E.; Sultan, Y.; Westerhoff, P.; White, J. C.; Wiesner, M. R.; Wong, E. M.; Xing, B.; Steele Horan, M.; Godwin, H. A.; Nel, A. E. Considerations of Environmentally Relevant Test Conditions for Improved Evaluation of Ecological Hazards of Engineered Nanomaterials. Environ. Sci. Technol. **2016**, 50 (12), 6124–6145.
(10) Wu, J.; Zhu, G.; Yu, R. Fates and Impacts of Nanomaterial Contaminants in Biological Wastewater Treatment System: A Review. Water. Air. Soil Pollut. **2018**, 229 (1).
(11) Rossi, L. M.; Costa, N. J. S.; Silva, F. P.; Wojcieszak, R. Magnetic Nanomaterials in Catalysis: Advanced Catalysts for Magnetic Separation and Beyond. Green Chem. **2014**, 16 (6), 2906.
(12) Mohammed, L.; Gomaa, H. G.; Ragab, D.; Zhu, J. Particuology Magnetic Nanoparticles for Environmental and Biomedical Applications : A Review. Particuology. **2017**, 30, 1–14.
(13) Yang, R.; Li, H.; Huang, M.; Yang, H.; Li, A. A Review on Chitosan-Based Flocculants and Their Applications in Water Treatment. Water Res. **2016**, 95 (2015), 59–89.

(14) Husnain, S. M.; Um, W.; Woojin-Lee; Chang, Y. S. Magnetite-Based Adsorbents for Sequestration of Radionuclides: A Review. RSC Adv. **2018**, 8 (5), 2521–2540.
(15) Iqbal, A.; Iqbal, K.; Li, B.; Gong, D.; Qin, W. Recent Advances in Iron Nanoparticles: Preparation, Properties, Biological and Environmental Application. J. Nanosci. Nanotechnol. **2017**, 17 (7), 4386–4409.
(16) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism. Nature **1992**, 359 (6397), 710–712.
(17) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates. J. Am. Chem. Soc. **1992**, 114 (27), 10834–10843.
(18) Ryoo, R.; Kim, J. M.; Shin, C. H.; Lee, J. Y. Synthesis and Hydrothermal Stability of a Disordered Mesoporous Molecular Sieve. Stud. Surf. Sci. Catal. **1997**, 105, 45–52.
(19) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. Science **1998**, 279, 548-552.
(20) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. Nonionic Triblock and Star Diblock Copolymer and Oligomeric Sufactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures. J. Am. Chem. Soc. **1998**, 120 (24), 6024–6036.
(21) Nam, L.; Coll, C.; Erthal, L. C. S.; de la Torre, C.; Serrano, D.; Martínez-Máñez, R.; Santos-Martínez, M. J.; Ruiz-Hernández, E. Drug Delivery Nanosystems for the Localized Treatment of Glioblastoma Multiforme. Materials (Basel). **2018**, 11 (5).
(22) Slowing, I. I.; Vivero-Escoto, J. L.; Trewyn, B. G.; Lin, V. S. Y. Mesoporous Silica Nanoparticles: Structural Design and Applications. J. Mater. Chem. **2010**, 20 (37), 7924–7937.
(23) Lettow, J. S.; Han, Y. J.; Schmidt-Winkel, P.; Yang, P.; Zhao, D.; Stucky, G. D.; Ying, J. Y. Hexagonal to Mesocellular Foam Phase Transition in Polymer-Templated Mesoporous Silicas. Langmuir **2000**, 16 (22), 8291–8295.
(24) Lin, H.-P.; Mou, C.-Y. Salt Effect in Post-Synthesis Hydrothermal Treatment of MCM-41. Microporous Mesoporous Mater. **2002**, 55 (1), 69–80.
(25) Ge, S.; Geng, W.; He, X.; Zhao, J.; Zhou, B.; Duan, L.; Wu, Y.; Zhang, Q. Effect of Framework Structure, Pore Size and Surface Modification on the Adsorption Performance of Methylene Blue and $Cu^{2+}$ in Mesoporous Silica. Colloids Surfaces A Physicochem. Eng. Asp. **2018**, 539, 154–162.
(26) Wang, W.; Ren, X.; Yang, W.; Zhang, C.; Ru, H. Hierarchical Mesoporous Silica Microspheres Prepared by Partitioned Cooperative Self-Assembly Process Using Sodium Silicate as Precursor and Their Drug Release Performance. Microporous Mesoporous Mater. **2019**, 275, 50–60.
(27) Huo, Q.; Margolese, D. I.; Stucky, G. D. Surfactant Control of Phases in the Synthesis of Mesoporous Silica-Based Materials. Chem. Mater. **1996**, 8 (5), 1147–1160.
(28) Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. Silica-Based Mesoporous Organic-Inorganic Hybrid Materials. Angew. Chemie - Int. Ed. **2006**, 45 (20), 3216–3251.
(29) Wan, Y.; Zhao, D. On the Controllable Soft-Templating Approach to Mesoporous Silicates. Chem. Rev. **2007**, 107 (7), 2821–2860.
(30) Lira, E.; López, C. M.; Oropeza, F.; Bartolini, M.; Alvarez, J.; Goldwasser, M.; Linares, F. L.; Lamonier, J.-F.; Pérez Zurita, M. J. HMS Mesoporous Silica as Cobalt Support for the Fischer–Tropsch Synthesis: Pretreatment, Cobalt Loading and Particle Size Effects. J. Mol. Catal. A Chem. **2008**, 281 (1–2), 146–153.
(31) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. Templating of Mesoporous Molecular Sieves by Nonionic Polyethylene Oxide Surfactants. Science (80-. ). **1995**, 269 (5228), 1242–1244.
(32) Fellenz, N.; Perez-Alonso, F. J.; Martin, P. P.; García-Fierro, J. L.; Bengoa, J. F.; Marchetti, S. G.; Rojas, S. Chromium (VI) Removal from Water by Means of Adsorption-Reduction at the Surface of Amino-Functionalized MCM-41 Sorbents. Microporous Mesoporous Mater. **2017**, 239, 138–146.
(33) Brunella, V.; Jadhav, S. A.; Miletto, I.; Berlier, G.; Ugazio, E.; Sapino, S.; Scalarone, D. Hybrid Drug Carriers with Temperature-Controlled on-off Release: A Simple and Reliable Synthesis of PNIPAM-Functionalized Mesoporous Silica Nanoparticles. React. Funct. Polym. **2016**, 98, 31–37.
(34) Hegazy, M.; Zhou, P.; Wu, G.; Wang, L.; Rahoui, N.; Taloub, N.; Huang, X.; Huang, Y. Construction of Polymer Coated Core–shell Magnetic Mesoporous Silica Nanoparticles with Triple Responsive Drug Delivery. Polym. Chem. **2017**, 5852–5864.
(35) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. Periodic Mesoporous Organosilicas with Organic Groups inside the Channel Walls. Nature **1999**, 402 (6764), 867–871.
(36) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. Novel Mesoporous Materials with a Uniform Distribution of Organic Groups and Inorganic Oxide in Their Frameworks. J. Am. Chem. Soc. **1999**, 121 (41), 9611–9614.
(37) Ganiyu, S. O.; Bispo, C.; Bion, N.; Ferreira, P.; Batonneau-Gener, I. Periodic Mesoporous Organosilicas as Adsorbents for the Organic Pollutants Removal in Aqueous Phase. Microporous Mesoporous Mater. **2014**, 200, 117–123.

(38 Suteewong, T.; Sai, H.; Lee, J.; Bradbury, M.; Hyeon, T.; Gruner, S. M.; Wiesner, U. Ordered Mesoporous Silica Nanoparticles with and without Embedded Iron Oxide Nanoparticles: Structure Evolution during Synthesis. J. Mater. Chem. **2010**, 20 (36), 7807.
(39) Zhang, Y.; Yue, Q.; Yu, L.; Yang, X.; Hou, X. F.; Zhao, D.; Cheng, X.; Deng, Y. Amphiphilic Block Copolymers Directed Interface Coassembly to Construct Multifunctional Microspheres with Magnetic Core and Monolayer Mesoporous Aluminosilicate Shell. Adv. Mater. **2018**, 30 (26), 1–10.
(40) Wang, Y.; He, J.; Chen, J.; Ren, L.; Jiang, B.; Zhao, J. Synthesis of Monodisperse, Hierarchically Mesoporous, Silica Microspheres Embedded with Magnetic Nanoparticles. ACS Appl. Mater. Interfaces **2012**, 4 (5), 2735–2742.
(41) Fuentes-García, J. A.; Diaz-Cano, A. I.; Guillen-Cervantes, A.; Santoyo-Salazar, J. Magnetic Domain Interactions of Fe3O4nanoparticles Embedded in a SiO2matrix. Sci. Rep. **2018**, 8 (1), 2–11.
(42) Li, J.; Zhou, Q.; Liu, Y.; Lei, M. Recyclable Nanoscale Zero-Valent Iron-Based Magnetic Polydopamine Coated Nanomaterials for the Adsorption and Removal of Phenanthrene and Anthracene. Sci. Technol. Adv. Mater. **2017**, 18 (1), 3–16.
(43) Zou, Y.; Wang, X.; Khan, A.; Wang, P.; Liu, Y.; Alsaedi, A.; Hayat, T.; Wang, X. Environmental Remediation and Application of Nanoscale Zero-Valent Iron and Its Composites for the Removal of Heavy Metal Ions: A Review. Environ. Sci. Technol. **2016**, 50 (14), 7290–7304.
(44) Raychoudhury, T.; Scheytt, T. Potential of Zerovalent Iron Nanoparticles for Remediation of Environmental Organic Contaminants in Water: A Review. Water Sci. Technol. **2013**, 68 (7), 1425–1439.
(45) Tang, L.; Zhang, S.; Zeng, G.-M.; Zhang, Y.; Yang, G.-D.; Chen, J.; Wang, J.-J.; Wang, J.-J.; Zhou, Y.-Y.; Deng, Y.-C. Rapid Adsorption of 2,4-Dichlorophenoxyacetic Acid by Iron Oxide Nanoparticles-Doped Carboxylic Ordered Mesoporous Carbon. J. Colloid Interface Sci. **2015**, 445, 1–8.
(46) Lu, H.; Wen, C.; Gao, S.; Dong, Y.; Zhang, M.; Li, B.; Hu, W.; Dong, J. Incorporation of Nanoscale Zero-Valent Iron Particles in Monodisperse Mesoporous Silica Nanospheres: Characterization, Reactivity, Transport in Porous Media. Colloids Surfaces A Physicochem. Eng. Asp. **2018**, 553, 28–34.
(47) Carrott, P. J. M.; Carrott, M. M. L. R. Lignin – from Natural Adsorbent to Activated Carbon : A Review. **2007**, 98, 2301–2312.
(48) Nor, N. M.; Chung, L. L.; Teong, L. K.; Mohamed, A. R. Journal of Environmental Chemical Engineering Synthesis of Activated Carbon from Lignocellulosic Biomass and Its Applications in Air Pollution Control — a Review. Biochem. Pharmacol. **2013**, 1 (4), 658–666.
(49) Mohan, D.; Pittman, C. U. Activated Carbons and Low Cost Adsorbents for Remediation of Tri- and Hexavalent Chromium from Water. **2006**, 137, 762–811.
(50) Ioannidou, O.; Zabaniotou, A. Ã. Agricultural Residues as Precursors for Activated Carbon Production — A Review. **2007**, 11, 1966–2005.
(51) Dias, J. M.; Alvim-ferraz, M. C. M.; Almeida, M. F.; Sa, M. Waste Materials for Activated Carbon Preparation and Its Use in Aqueous-Phase Treatment : A Review. **2007**, 85, 833–846.
(52) Hu, Z.; Srinivasan, M. P. Mesoporous High-Surface-Area Activated Carbon. Microporous Mesoporous Mater. **2001**, 43 (3), 267–275.
(53) Ryoo, R.; Joo, S. H.; Jun, S. Synthesis of Highly Ordered Carbon Molecular Sieves via Template-Mediated Structural. **1999**, 103 (37).
(54) Ryoo, B. R.; Joo, S. H.; Kruk, M.; Jaroniec, M. Ordered Mesoporous Carbons Adv. Mater., **2001**, 13, 677-681.
(55) Vinu, A.; Miyahara, M.; Ariga, K. Preparation and Pore Size Control of Cage Type Mesoporous Carbon Materials and Their Application in Protein Adsorption, **2005**, 158, 971–978.
(56) Vinu, A.; Streb, C.; Murugesan, V.; Hartmann, M. Adsorption of Cytochrome C on New Mesoporous Carbon Molecular Sieves, **2003**, 8297–8299.
(57) Liang, Y.; Chen, L.; Cai, L.; Liu, H.; Fu, R.; Zhang, M. Strong Contribution of Pore Morphology to High-Rate Electrochemical Performance of Lithium-Ion Battery. Chem. Commun. **2016**, 52, 803-806.
(58) Jiang, X.; Ouyang, Z.; Zhang, Z.; Yang, C.; Li, X.; Dang, Z.; Wu, P. Mechanism of Glyphosate Removal by Biochar Supported Nano-Zero-Valent Iron in Aqueous Solutions. Colloids Surfaces A Physicochem. Eng. Asp. **2018**, 547, 64–72.
(59) Tan, P.; Jiang, Y.; Liu, X.; Sun, L. Magnetically Responsive Porous Materials for Efficient Adsorption and Desorption Processes. Chinese J. Chem. Eng. **2019**, 27(6), 1324-1338.
(60) Duan, F.; Yang, Y.; Li, Y.; Cao, H.; Wang, Y.; Zhang, Y. Heterogeneous Fenton-like Degradation of 4-Chlorophenol Using Iron / Ordered Mesoporous Carbon Catalyst. J. Environ. Sci. **2014**, 26 (5), 1171–1179.
(61) Wang, J.; Liu, C.; Qi, J.; Li, J.; Sun, X.; Shen, J.; Han, W.; Wang, L. Enhanced Heterogeneous Fenton-like Systems Based on Highly Dispersed Fe 0 -Fe 2 O 3 Nanoparticles Embedded Ordered Mesoporous Carbon Composite Catalyst. Environ. Pollut. **2018**, 243, 1068–1077.
(62) Wang, Y.; Zhao, H.; Zhao, G. Applied Catalysis B : Environmental Iron-Copper Bimetallic Nanoparticles Embedded within Ordered Mesoporous Carbon as Effective and Stable Heterogeneous Fenton Catalyst for the Degradation of Organic Contaminants. Applied Catal. B, Environ. **2015**, 164, 396–406.
(63) Zheng, C.; Cheng, X.; Yang, C.; Zhang, C.; Li, H.; Kan, L.; Xia, J.; Sun, X. Hydrophilic Modification of Ordered Mesoporous Carbon Supported Fe Nanoparticles with Enhanced Adsorption and Heterogeneous Fenton-like Oxidation Performance. RSC Adv. **2015**, 5 (120), 98842–98852.

(64) Shang, J.; Zong, M.; Yu, Y.; Kong, X.; Du, Q.; Liao, Q. Removal of Chromium ( VI ) from Water Using Nanoscale Zerovalent Iron Particles Supported on Herb-Residue Biochar. J. Environ. Manage. **2017**, 197, 331–337.
(65) Calderon, B.; Smith, F.; Aracil, I.; Fullana, A. Green Synthesis of Thin Shell Carbon-Encapsulated Iron Nanoparticles via Hydrothermal Carbonization. ACS Sustain. Chem. Eng. **2018**, 6, 7995–8002.
(66) Sun, H.; Zhou, G.; Liu, S.; Ang, H. M.; Tade, M. O.; Wang, S. Nano-$Fe^0$ Encapsulated in Microcarbon Spheres : Synthesis , Characterization, and Environmental Applications. ACS Appl Mater Interfaces. **2012,** 4(11), 6235-6241.
(67) Kalantari, M.; Yu, M.; Noonan, O.; Song, H.; Xu, C.; Huang, X.; Xiang, F.; Wang, X.; Yu, C. Chemosphere Rattle-Type Magnetic Mesoporous Hollow Carbon as a High- Performance and Reusable Adsorbent for Water Treatment. Chemosphere **2017**, 166, 109–117.
(68) Chen, W. F.; Yan, C. C.; Wang, Q.; Pan, L.; Chen, L. F. Carbothermal Synthesis of Activated Carbon-Supported Nano Zero Valent Iron: Effects of Temperature, Characterization, and Reactivity. Desalin. Water Treat. **2016**, 57 (20), 9520–9529.
(69) Bleyl, S.; Kopinke, F.; Mackenzie, K. Carbo-Iron ® — Synthesis and Stabilization of Fe ( 0 ) -Doped Colloidal Activated Carbon for in Situ Groundwater Treatment. Chem. Eng. J. **2012**, 191, 588–595.
(70) Liu, J.; Qiao, S. Z.; Hu, Q. H.; Lu, G. Q. Magnetic Nanocomposites with Mesoporous Structures: Synthesis and Applications. Small **2011**, 7 (4), 425–443.
(71) Zhang, Y.; Xu, S.; Luo, Y.; Pan, S.; Ding, H.; Li, G. Synthesis of Mesoporous Carbon Capsules Encapsulated with Magnetite Nanoparticles and Their Application in Wastewater Treatment. J. Mater. Chem. **2011**, 21 (11), 3664–3671.
(72) Liu, Y.; Zeng, G.; Tang, L.; Cai, Y.; Pang, Y.; Zhang, Y.; Yang, G.; Zhou, Y.; He, X.; He, Y. Journal of Colloid and Interface Science Highly Effective Adsorption of Cationic and Anionic Dyes on Magnetic Fe / Ni Nanoparticles Doped Bimodal Mesoporous Carbon. J. Colloid Interface Sci. **2015**, 448, 451–459.
(73) Brigante, M.; Pecini, E.; Avena, M. Magnetic Mesoporous Silica for Water Remediation: Synthesis, 0Characterization and Application as Adsorbent of Molecules and Ions of Environmental Concern. M0icroporous Mesoporous Mater. **2016**, 230, 1–10.
(74) Sharma, A.; Siddiqi, Z. M.; Pathania, D. Adsorption of Polyaromatic Pollutants from Water System Using Carbon/ZnFe2O4nanocomposite: Equilibrium, Kinetic and Thermodynamic Mechanism. J. Mol. Liq. **2017**, 240, 361–371.
(75) Huang, Y.; Fulton, A. N.; Keller, A. A. Optimization of Porous Structure of Superparamagnetic Nanoparticle Adsorbents for Higher and Faster Removal of Emerging Organic Contaminants and PAHs. Environ. Sci. Water Res. Technol. **2016**, 2 (3), 521–528.
(76) Das, S.; Chakraborty, J.; Chatterjee, S.; Kumar, H. Prospects of Biosynthesized Nanomaterials for the Remediation of Organic and Inorganic Environmental Contaminants. Environ. Sci. Nano **2018**, 2784–2808.
(77) Tesh, S. J.; Scott, T. B. Iron Nanoparticles for Water Treatment: Is the Future Free or Fixed? In Iron Oxides; D. Faivre (Ed.), Ed.; **2016**; pp 473–522.
(78) Tang, L.; Tang, J.; Zeng, G.; Yang, G.; Xie, X.; Zhou, Y.; Pang, Y.; Fang, Y.; Wang, J.; Xiong, W. Rapid Reductive Degradation of Aqueous P-Nitrophenol Using Nanoscale Zero-Valent Iron Particles Immobilized on Mesoporous Silica with Enhanced Antioxidation Effect. Appl. Surf. Sci. **2015**, 333, 220–228.
(79) Zhang, R.; Li, J.; Liu, C.; Shen, J.; Sun, X.; Han, W.; Wang, L. Colloids and Surfaces A : Physicochemical and Engineering Aspects Reduction of Nitrobenzene Using Nanoscale Zero-Valent Iron Confined in Channels of Ordered Mesoporous Silica. Colloids Surfaces A Physicochem. Eng. Asp. **2013**, 425, 108–114.
(80) Publishing, I. W. A.; Science, W.; Supply, W. Adsorption / Reduction of N -Dimethylnitrosamine from Aqueous Solution Using Nano Zero-Valent Iron Nanoparticles Supported on Ordered Mesoporous Silica Xiaodong Xin , Shaohua Sun , Mingquan Wang , Qinghua Zhao , Yan Chen. **2017**, 1097–1105.
(81) Chen, S.; Bedia, J.; Li, H.; Yao, L.; Naluswata, F.; Belver, C. Nanoscale Zero-Valent Iron @ Mesoporous Hydrated Silica Core-Shell Particles with Enhanced Dispersibility , Transportability and Degradation of Chlorinated Aliphatic Hydrocarbons. Chem. Eng. J. **2018**, 343, 619–628.
(82) Choi, H.; Agarwal, S.; Al-Abed, S. R. Adsorption and Simultaneous Dechlorination of PCBs on GAC/Fe/Pd: Mechanistic Aspects and Reactive Capping Barrier Concept. Environ. Sci. Technol. **2009**, 43 (2), 488–493.
(83) Wang, W.; Wang, J.; Guo, Y.; Zhu, C.; Pan, F.; Wu, R.; Wang, C. Science of the Total Environment Removal of Multiple Nitrosamines from Aqueous Solution by Nanoscale Zero-Valent Iron Supported on Granular Activated Carbon : Influencing Factors and Reaction Mechanism. Sci. Total Environ. **2018**, 639, 934–943.
(84) Zhang, W.; Xiao, T.; Liu, N.; Ying, W. The Removal of Chlorinated Aliphatic Hydrocarbons from Water Using Reactive Activated Carbon : The Influence of Synthesis Factors and Reaction Environments. Environ. Technol. **2018**, 39, 1328-1339.
(85) Wang, X.; Du, Y.; Ma, J. Applied Surface Science Novel Synthesis of Carbon Spheres Supported Nanoscale Zero-Valent Iron for Removal of Metronidazole. **2016**, 390, 50–59.
(86) Ling, X.; Li, J.; Zhu, W.; Zhu, Y.; Sun, X.; Shen, J.; Han, W.; Wang, L. Chemosphere Synthesis of Nanoscale Zero-Valent Iron / Ordered Mesoporous Carbon for Adsorption and Synergistic Reduction of Nitrobenzene. Chemosphere **2012**, 87 (6), 655–660.

(87) Carlos, L.; Fabbri, D.; Prevot, A. B.; Capparelli, A. L. Primary Yields and Intermediate Distributions in Nitrobenzene Degradation with Fenton Reagent . Chemosphere. **2008**, 72, 952–958.
(88) Donadelli, J. A.; Carlos, L.; Arques, A.; García Einschlag, F. S. Kinetic and Mechanistic Analysis of Azo Dyes Decolorization by ZVI-Assisted Fenton Systems: PH-Dependent Shift in the Contributions of Reductive and Oxidative Transformation Pathways. Appl. Catal. B Environ. **2018**, 231, 51–61.
(89) Yoon, I.-H.; Yoo, G.; Hong, H.-J.; Kim, J.; Kim, M. G.; Choi, W.-K.; Yang, J.-W. Kinetic Study for Phenol Degradation by ZVI-Assisted Fenton Reaction and Related Iron Corrosion Investigated by X-Ray Absorption Spectroscopy. Chemosphere **2016**, 145, 409–415.
(90) Shao, Y.; Chen, H. Heterogeneous Fenton Oxidation of Phenol in Fixed-Bed Reactor Using Fe Nanoparticles Embedded within Ordered Mesoporous Carbons. Chem. Eng. Res. Des. **2018**, 132, 57–68.

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