

Review

Nanomaterials with Tailored Magnetic Properties as Adsorbents of Organic Pollutants from Wastewaters

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Abstract: Water quality has become one of the most critical issue of concern worldwide. The main challenge of the scientific community is to develop innovative and sustainable water treatment technologies with high efficiencies and low production costs. In recent years, the use of nanomaterials with magnetic properties used as adsorbents in the water decontamination process has received considerable attention since they can be easily separated and reused. This review focuses on the state-of-art of magnetic core-shell nanoparticles and nanocomposites developed for the adsorption of organic pollutants from water. Special attention is paid to magnetic nanoadsorbents based on silica, clay composites, carbonaceous materials, polymers and wastes. Furthermore, we compare different synthesis approaches and adsorption performance of every nanomaterials. The data gathered in this review will provide information for the further development of new efficient water treatment technologies.

Keywords: adsorption; magnetic separation; nanotechnology; water treatments

1. Introduction

The deterioration of water quality by organic pollutants has become a global issue of concern that requires an effective solution. According to the European Environmental Agency Report, only around 40% of surface waters (rivers, lakes, and transitional and coastal waters) are in a good ecological status, and 38% are in a good chemical status [1]. Another report, on the quality of 100 rivers from 27 European countries concluded that only about 10% of the river water samples analyzed could be classified as “very clean” in terms of chemical pollution [2]. Pollutants present in water are classified as organic and inorganic and can reach surface waters and groundwaters mainly through industrial effluents, agricultural runoff, sewage plants and other human activities. In general, organic pollutants including aromatic compounds, dyes, pesticides, and antibiotics are toxic and/or resistant to microbial degradation. Once these organic pollutants enter the water bodies, water is no longer safe for drinking purpose and sometimes the complete removal of these pollutants from the water is a very difficult process.

Dyes are released by various industries, such as food, cosmetics and especially textiles [3,4]. According to incomplete statistics, over 35,000 metric tons of dyes are released into the environment [5]. Emerging contaminants, as pharmaceutical and personal care products, pesticides, food additives,

surfactants, etc., are present in different water resources in the range of ng L^{-1} – $\mu\text{g L}^{-1}$ [6]. These compounds are generally non-biodegradable or poorly biodegradable, thus becoming stable and persistent compounds when released into surface and groundwaters [7]. On the other hand, aromatic compounds, as phenols, anilines and polycyclic aromatic compounds, are also environmentally relevant contaminants and can be widely found in the effluents from dyestuffs, pharmaceuticals, petrochemicals, and other industries [8]. In recent years, there has been growing concern about the presence of these compounds in the aquatic environment due to their wide distribution and potential adverse health effects even at low concentration [8,9].

Various water treatment processes have been developed to reduce organic compounds' levels in waters, such as photocatalysis, ozonolysis, electrolysis, membrane process and adsorption. Among these methods, adsorption is one of the most promising techniques in water remediation due to its low cost, easy operation, the possibility of regeneration and feasibility of application in field conditions [3,6,10,11]. The overall adsorption process consists of the following key steps: (a) pollutant adsorption (b) recovery of the adsorbent for further reuse (c) adsorbent regeneration, and (d) management of both the regeneration solution and the saturated adsorbent. Adsorbent regeneration is a crucial economic factor for industrial applications [5]. Part of the cost that affects the application of the adsorption process lies in the possibility of reusing the adsorbent material several times. Therefore, the adsorbent material must have a good affinity to remove contaminants, be stable (i.e., not lose some of its components by leaching or bleeding) and must be regenerated and used in various adsorption/desorption cycles. To guarantee the reuse of the adsorbent, the separation process of the adsorbents from the aqueous medium is a key step to achieve a good performance and cost-effective treatment. Filtration or centrifugation techniques are often used for the separation process, but both techniques are not cost-effective and are difficult to handle when large volumes of water are used [11]. Moreover, adsorbents may lead to blockage of the filters or loss of adsorbent. To overcome these problems, the use of magnetic nanoadsorbents has been proposed [12,13]. 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 [14]. For the reasons outlined above, magnetic adsorbents have emerged as a new generation of materials for decontamination processes [15]. In particular, the most commonly employed magnetic carriers for environmental applications are magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles, because they are easy to synthesize, environmentally friendly, and have high saturation magnetization. The magnetic properties of iron oxide nanoparticles, in particular of those commonly used in environmental applications, are well documented and reviewed elsewhere and are beyond the scope of this review [16,17]. Bare magnetic iron oxide nanoparticles undergo oxidation/dissolution, especially in acid solutions [15,18], and co-aggregation because of their high surface energy [10,18], and even in environmental conditions their chemical stability can be affected [19], which limits the large-scale application of magnetic iron oxide nanoparticles. Therefore, a large number of functionalized magnetic nanoparticles and magnetic nanocomposites with new structures and surface properties have been produced to overcome the deficiencies of magnetic nanoparticles, provide more active sites and improve their aqueous stability and versatility. Currently, many different materials have been used in combination with magnetic nanoparticles to manufacture magnetic nanoadsorbents, such as silica, activated carbon, carbon nanotubes, polymers, metal–organic frame works, and clays, showing varying extents of effectiveness in removing the organic pollutants from water. Each type of adsorbent nanomaterial has different surface properties, surface chemical groups, and specific areas and pore size. The selection of the appropriate material represents a critical factor to guarantee efficient removal of the organic pollutant.

This review was designed to provide an overview of the synthesis methods, surface properties and application in organic pollutant removal of different magnetic nanoadsorbents. We will present recent scientific progress on the preparation of magnetic core–shell nanoparticles and nanocomposites paying special emphasis on materials with high adsorption capacities. Although there are many review

articles in the literature that cover the application of magnetic nanomaterials in the environmental field [13,14,17,20–24], we believe that more specific data gathering is still needed on the synthesis methods and properties of magnetic nanoadsorbents that have been developed so far, and their efficiencies and limitations in the water treatments. This information will contribute to the field of rational design of nanomaterials for water treatment and will help in designing more efficient water treatment technologies to guarantee adequate water quality.

2. Silica-Based Materials

Silica (chemically SiO_2) has a three-dimensional network structure that consists of SiO_4 and ends with oxygen through siloxane groups (Si–O–Si) or silanol groups (Si–OH) [25]. Silanol groups offer a rich surface chemistry useful in the adsorption process, since they can complex some molecules and metal cations. This interaction can be improved by modifying the pH, due to their acid-basic behavior. In consequence, bare silica can be used as an efficient adsorbent for pollutants, such as dyes, heavy metals and aromatic compounds [26]. Silica nanoparticles can be porous or non-porous. Mesoporous silica (mSiO_2) is a unique class of synthetic porous material, with a pore size between 2 and 50 nm. Because of its porosity and higher surface area, mesoporous silica is often preferred as an adsorbent rather than non-porous silica. The highly adjustable structure, versatile surface chemistry, low production cost and simple synthesis procedure are the primary benefits that encourage their application in adsorption. Moreover, silanol groups allow the introduction of a wide variety of functional groups to the silica surface. Therefore, many surface functionalization methods, post-synthesis or during synthesis, have been developed to improve the adsorption capacity and selectivity of mesoporous silica [26–31]. The incorporation of iron and iron oxides, such as magnetite and maghemite, to the silica structure is usually carried out by two approaches. One method consists in covering a core of iron oxide nano- or micro-particles with a shell of non-porous silica or mesoporous silica to produce hierarchical structures known as “core–shell” particles (Figure 1A,B). These structures have the additional advantage of protecting the iron-based core from leaching and oxidation in water [32] and, at the same time, of reducing the tendency of aggregation of the particles. In the other method, magnetic particles are dispersed onto mesoporous silica. Wang and co-workers [33] prepared magnetite by the hydrothermal method and they covered with a non-porous silica shell via the Stöber method. The obtained $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ nanoparticles were tested for the removal of anionic dye Congo Red. As expected, the adsorption results were strongly pH dependent. The silanol groups at low pH values are protonated allowing electrostatic interactions between $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ nanoparticles and Congo Red molecules, which leads to a higher dye removal performance. These core–shell type particles can be further modified in different ways. Recently, Cao’s group [34] used the polymer polyvinylpyrrolidone (PVP) to provide affinity to hydrophobic substances to $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ particles. They prepared magnetic cores by the miniemulsion method, then covered them with non-porous silica shell and finally with PVP. The resulted adsorbent ($\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-PVP}$) was tested for the hydrophobic compound phenanthrene. The adsorption reaches the equilibrium fast (10 min), and the maximum adsorption capacity was high compared to previous PAH adsorption reports [35].

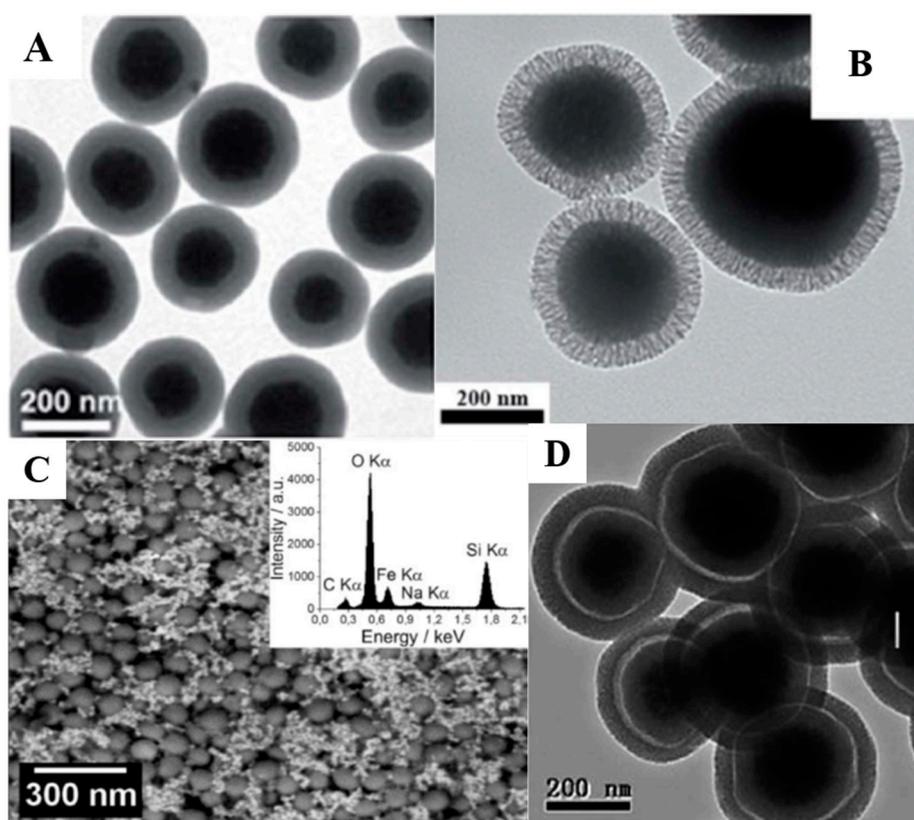


Figure 1. (A) TEM image of non-porous silica covering Fe_3O_4 nanoparticles (reproduced with permission from [36], published by Royal Society of Chemistry, 2015); (B) TEM image of mesoporous-silica covering Fe_3O_4 nanoparticles (reproduced from [37], published by Royal Society of Chemistry, 2018); (C) SEM images of Raspberry-like supraparticle system (reproduced with permission from [38], published by ChemNanoMat, 2019); and (D) TEM micrographs of $\text{Fe}_3\text{O}_4@SiO_2@h\text{-mSiO}_2$ (reproduced with permission from [36], published by Royal Society of Chemistry, 2015).

The incorporation of silane groups is one of the most common procedures to provide affinity and versatility to an adsorbent for a specific target pollutant [39]. A silane is a group that consists in a central silicon atom bonded to alkoxy groups (usually methoxy and ethoxy) and at least a different moiety with a specific group, such as amino, thiol, hydroxy, vinyl, aliphatic chains, aromatic chains, etc. In a silanization reaction, the surface hydroxyl groups of the solid (e.g., Si-OH in SiO_2 or Fe-OH in Fe_3O_4) react with the alkoxy groups of the silane and form a covalent bond (Si-O-Si in SiO_2 and Fe-O-Si in Fe_3O_4). The work of Sasaki and Tanaka [40] is an example of a simple silanization procedure. They covered commercial magnetite with phenyltrimethoxysilane (PTMS) and studied the adsorption mechanism with several aromatic compounds. The new functionality incorporated by a silane allows further modifications. For instance, the incorporation of vinyl groups by grafting of 3-(methacryloxypropyl)trimethoxysilane (MPS) to $\text{Fe}_3\text{O}_4@SiO_2$ nanoparticles allows a radical polymerization reaction to obtain a polymer covering the nanoparticles [41,42]. Jiaqi and co-workers [43] lately proposed a dendritic-like structure to enlarge the magnetic silica nanoparticles area and thus improve their adsorption performance. For this, 3-chloropropyltriethoxysilane (CPTES) were grafted to $\text{Fe}_3\text{O}_4@SiO_2$ NPs; then a substitution reaction with ethylenediamine and finally a chemical reaction with maleic anhydride were performed. The obtained carboxylated ethylenediamine functionalized nanoparticles ($\text{Fe}_3\text{O}_4@SiO_2\text{-EDA-COOH}$) show remarkable magnetic saturation and high sorption capacity of cationic dye methylene blue and can be reused five cycles. However, the reported maximum sorption capacity of 43.15 mg g^{-1} corresponds to a relatively high pH of 10.

Wang's group [44] developed a novel MOF-based smart adsorbent named $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{UiO}-67$ for the simultaneous selective recognition, detection and removal of organophosphorus pesticide glyphosate for the first time. The prepared adsorbent contains Zr–OH groups with high affinity for phosphate groups, endowing it with an outstanding adsorption capacity for glyphosate. Furthermore, the adsorbent was able to be reused four times with no significant adsorption capacity decrease.

Other types of magnetic silica-based materials use nanoscale zero-valent iron (nZVI) instead of iron oxides as a core. nZVI is commonly applied as a catalyst because of its strong reduction capability. However, there are a few reports of their use to provide magnetic properties to silica-based materials. Li et al. [35] synthesized nZVI nanoparticles coated with silica and polydopamine using a two-step process. The obtained adsorbent ($\text{Fe}@\text{SiO}_2@\text{PDA}$) was applied in the removal of anthracene and phenanthrene from aqueous media, achieving maximum adsorption capacities of 0.185 and 0.367 mg g^{-1} , respectively. Interestingly, the adsorption efficiency of $\text{Fe}@\text{SiO}_2@\text{PDA}$ barely decreased after 10 cycles.

Recently, a novel particle system, so-called raspberry-like supraparticles, consisting in magnetite/maghemite and amorphous silica nanoparticles, was studied in the adsorption of methyl blue dye [38]. For the synthesis of these nanoparticles, the method of spray-drying was used: droplets from nanoparticle dispersions were generated in a hot chamber and the solvent was evaporated, forcing the remaining nanoparticles in the droplets together to form supraparticles. The supraparticle system consisted of nanoparticles of 10 nm diameter (Figure 1B) and showed a maximum adsorption capacity of 93 mg g^{-1} . Though this adsorption capacity is comparable or lower than previous reports, the adsorption kinetics results to be outstandingly fast, reaching equilibrium within 60 s. Further, the system can be regenerated either thermally or by acid treatment and can be reused consecutively with a slight loss in adsorption capacity.

Currently, it is of interest to have alternative silica sources rather than synthetic reactants, e.g., from industrial waste, to prepare silica-based materials and adsorbents. This approach could contribute to minimize waste and to apply more economic methods. For instance, silica were obtained from rice husk by calcination and acid leaching and with microwave assistance [45,46]. Additionally, solid waste coal gasification fine slag as the silica source successfully produced mesoporous glass microspheres with a specific surface area of 364 $\text{m}^2 \text{g}^{-1}$ and an adsorption capacity of 140.57 mg g^{-1} in methylene blue removal [47]. Recently, silica obtained from rice husk has been used to incorporate an amorphous silica shell onto magnetite obtaining core–shell nanoparticles [45]. These particles were then amino-functionalized with (3-aminopropyl)trimethoxysilane (APTMS) and tested in the adsorption of methylene red dye.

The preparation of core–shell magnetic mesoporous silica is generally a multi-step procedure: synthesis of magnetic nanoparticles, coating with mesoporous silica, removal of template, and functionalization of the mesoporous silica shell. Among the many synthesis procedures for mesoporous silica [28], the hydrothermal method, based on the sol–gel Stöber method, is the most frequently reported for adsorbent preparation. This process consists in the polymerization of a silica precursor (e.g., TEOS) directed by micelles of a templating agent that lead to a mesoporous silica covering formerly prepared magnetic cores in a perpendicularly aligned pore arrange. Then, the templating agent remaining inside the pores is usually removed by calcination [37] or reflux in ethanol/acid water mix [48]. The pore size, particle size and morphology of mesoporous silica can be adjusted by selecting different template agents, by controlling pH and by using additives [29]. For instance, the synthesis of MCM-41 typically involves the cationic surfactant cetyltrimethylammonium bromide (CTAB); meanwhile, the neutral co-polymer with larger molecular weight Pluronic P-123 is used in preparation of SBA-15 [30]. Adding a co-solvent, like trimethylbenzene (TMB), to expand the micelle formed by the templating agent is another way to obtain wider pores [49]. Finally, the functionalization of mesoporous silica can be done post-synthesis or even during synthesis.

Zhang and co-workers [37] prepared these kinds of magnetic silica-based particles functionalized with cyclodextrins and they tested them as an adsorbent of the antibiotic doxycycline (DOX).

Cyclodextrins (CDs) are a class of macrocyclic molecules with a hydrophilic exterior and a lipophilic interior cavity, and they can form inclusion complexes with organic molecules, which can be trapped in the hydrophobic cavity through multiple interactions, including inclusion interactions, hydrophobic interactions, electrostatic attractions, and π - π interactions. First, magnetite was prepared via the solvothermal method and later these particles were covered with a non-porous silica layer through a modified Stöber method. The as-prepared $\text{Fe}_3\text{O}_4@SiO_2$ microspheres were put in a water solution of CTAB and triethanolamine; then, TEOS was added and a mesoporous silica layer covering the microspheres was formed. After calcination, $\text{Fe}_3\text{O}_4@SiO_2@mSiO_2$ microspheres were obtained (Figure 1C). To introduce covalently bound cyclodextrins, the $\text{Fe}_3\text{O}_4@SiO_2@mSiO_2$ microspheres were added to a basic water/ethanol solution containing APTMS and monochlorotriazinyl β -cyclodextrin (MCT- β -CD). The obtained $\text{Fe}_3\text{O}_4@SiO_2@mSiO_2$ -CD microspheres showed a maximum DOX adsorption capacity of 78 mg g^{-1} at initial pH of 3.8. The pH of the DOX solution significantly affected the adsorption process, which is spontaneous at 298 K. The contact time required for antibiotic adsorption using this adsorbent is short compared to activated carbon.

In order to develop a simple synthesis procedure amenable to scale-up, some authors propose the functionalization of mesoporous silica during synthesis. One method consists in the co-condensation reaction adding a silane along with the primary silica precursor in the presence of a surfactant, thus obtaining structures known as periodic mesoporous organosilicas [50]. Cai's group reported the first one-pot synthesis of functionalized magnetic mesoporous silica composites for the adsorption removal of organic dyes from water [51]. The adsorption of methyl blue on the obtained adsorbent, here termed as $\text{Fe}_3\text{O}_4@mSiO_2$ -C18, has a negligible influence of solution pH in the range of 4.5–9.5 with an optimal at pH 7.5 and a maximum adsorption capacity of 363 mg g^{-1} according to the Langmuir model. Furthermore, the adsorption equilibrium was achieved within a relatively short period of time (20 min), because of the high surface area and short adsorption path of mesoporous solid. Another approach is the work of Keller's group [52] in which the surfactant 3-(trimethoxysilyl)propyl-octadecyldimethyl-ammonium chloride (TPODAC) was used as a templating agent to prepare permanently confined micelle array core-shell nanoparticles. Maghemite cores were surrounded by TPODAC and TMB as a micelle-swelling agent, and then TEOS was added to covalently bind the surfactant onto the magnetic cores. Three different TMB:TPODAC weight ratio were tested. The authors studied the adsorption performance of the as-prepared nanoparticles ($\gamma\text{-Fe}_2\text{O}_3@mSiO_2$ -TPODAC) on methyl orange, sulfamethoxazole, gemfibrozil, acenaphthene and phenanthrene. It was found that larger amounts of TMB (TMB:TPODAC 60%) results in a noteworthy higher sorption kinetic rate as well as slightly higher sorption capacity. In addition, the core-shell nanoparticles showed good adsorption capacity after five regeneration cycles. The nanoparticles show relatively low surface area and magnetic saturation; however, they proved to be a versatile adsorbent for dyes, ECs and PAHs.

Composites consisting of magnetic nanoparticles dispersed in a mesoporous silica matrix were also developed and applied as adsorbents. Ghanei [53] prepared iron oxide nanoparticles embedded in SBA-15 mesoporous silica functionalized with 3-methacryloxypropyltrimethoxysilane followed by a polymerization with acrylic acid monomer. The obtained adsorbent M-SBA-15/CPAA proved to have a noteworthy adsorption capacity towards Acid Blue 25 dye. However, the adsorption process proved to be strongly pH-dependent and the maximum corresponds to highly acid conditions (pH 2). Other composites functionalized via polymerization onto silica surface were used for removal of the dyes [54].

Hollow mesoporous silica spheres (Figure 1D), in contrast with conventional mesoporous silicas such as MCM-41 and SBA-15, have some additional features including low density, high adsorption capacity, high storage capacity and permeability, turning them into promising materials for applications in drug delivery, catalysis and adsorption [36]. Thus, the preparation of nanocomposites with magnetic cores inside the cavities of hollow mesoporous silica spheres, namely rattle-type or yolk-shell magnetic mesoporous silica nanocomposites, is of great interest for a variety of environmental applications. The study of Jin and co-workers [55] is the first report about the adsorption capacity of rattle-type

nanoparticles. The synthesis consists in preparation of magnetic particles, covering with silica and a sacrificial template (resorcinol-formaldehyde resin polymer), a further layer of mesoporous silica and calcination to remove the organic matter. The prepared spheres, here named γ -Fe₂O₃@SiO₂@h-mSiO₂, present a similar fast removal rate of methyl blue to mesoporous MCM-41. The adsorption capacity increase with the pH, with a value of 41 mg g⁻¹ at pH 7.2.

Table 1 summarizes the adsorption capacities and some physicochemical properties of the silica-based nanocomposites described in this section.

Table 1. Application of magnetic silica-based nanoadsorbents for organic pollutants removal from water.

Adsorbent	Surface Area (m ² g ⁻¹)	Magnetic Saturation (emu g ⁻¹)	Organic Pollutant	Adsorption Capacity (mg g ⁻¹)	Ref.
Fe ₃ O ₄ @SiO ₂	-	48.06	Congo red	50.54	[33]
Fe ₃ O ₄ @SiO ₂ -PVP	60.82	30.89	Phenanthrene	18.84	[34]
Fe ₃ O ₄ @SiO ₂ -VTEOS-DMDAAC	-	-	Methylene blue	109.89	[41]
Fe ₃ O ₄ @SiO ₂ -EDA-COOH	-	58.7	Methylene blue	43.15	[43]
Fe ₃ O ₄ @SiO ₂ @Zn-TDPAT	-	>20	Methylene blue Congo red	58.67 17.73	[56]
Fe ₃ O ₄ @SiO ₂ @UiO-67	-	20.9	Glyphosate	256.54	[44]
Fe@SiO ₂ @PDA	-	51.98	Anthracene Phenanthrene	0.484 0.184	[35]
Fe ₃ O ₄ /SiO ₂ 10 nm SP	193	>25	Methylene blue	93	[38]
Fe ₃ O ₄ @SiO ₂ -NH ₂	-	>40	Methylene red	81.39	[45]
Fe ₃ O ₄ @SiO ₂ @mSiO ₂ -CD	119	30.99	Doxycycline	78	[37]
Fe ₃ O ₄ @SiO ₂ -C18	303	22.62	Methylene blue	363.64	[51]
γ -Fe ₂ O ₃ @mSiO ₂ -TPODAC	1.63	7.09	Methyl orange	104	[52]
			Gemfibrozil	50	
			Sulfamethoxazole	50	
			Acenaphthene	0.83	
			Phenanthrene	0.95	
mMCM-41-g-p(GMA)-TAEA	185	19.6	Direct blue-6	142.7	[54]
			Direct black-38	79.9	
M-SBA-15/CPLAA	159	2.68	Acid blue 25	909.09	[53]
γ -Fe ₂ O ₃ @SiO ₂ @h-mSiO ₂	329	-	Methylene blue	41	[55]
MNCM-1	576	2.9	Methylene blue	248	[57]

3. Clay-Based Composites

Clays are naturally occurring adsorbents, although their hydrophilic character and natural negative charge limits the adsorption capacity of many hydrophobic organic pollutants and anionic compounds [4,58,59]. Despite this, their swelling capacity and ability to interleave and/or graft different substances makes them as a very attractive option to develop different composites. Several techniques, such as the incorporation of organic cations, polymers and metals using pillaring, have been used to modify the surface and structural properties of clays [60–63]. Adsorption studies using modified clay minerals as adsorbents have shown remarkable results [60,64,65]; however the small particle size and low density of these materials makes it difficult to separate them from the aqueous solution [66]. Therefore, conferring magnetic properties to clay minerals could open a wide range of possibilities for water treatment. The preparation of magnetic clay mineral composites has been the subject of various studies [3,4,6,10,11,67,68]. The interlayer space, channels, siloxane surfaces and edges of the clay minerals provide hosting sites to stabilize magnetic NPs, thus leading to the formation of magnetic nanoparticles/clay mineral nanocomposites [18]. Typical synthesis routes to prepare magnetic clay minerals nanocomposites are pillaring, coprecipitation and intercalation (Figure 2). Pillaring represents a simple synthesis route where two strategies are possible; the combination of magnetic NP and

pillared clay mineral, where the pores of the pillared clay minerals host the magnetic NPs (route A1, Figure 2), or the use of magnetic NPs as pillars to expand the interlayer space of clay mineral in order to create magnetic pillared clay mineral nanocomposite (route A2, Figure 2). Co-precipitation is the other simple and widely used route of synthesis, based on the in-situ formation of the magnetic NPs in an aqueous dispersion of clay mineral (route B, Figure 2). The intercalation method is usually used in two ways; on the one hand, using surfactant-modified magnetic NP, which is stabilized into clay mineral (route C1, Figure 2), and on the other hand, the inclusion of magnetic NP into surfactant intercalated clay mineral, where the surfactants change the surface and expand the interlayer space of the clay minerals to match and facilitate the entrance of the magnetic NPs (route C2, Figure 2).

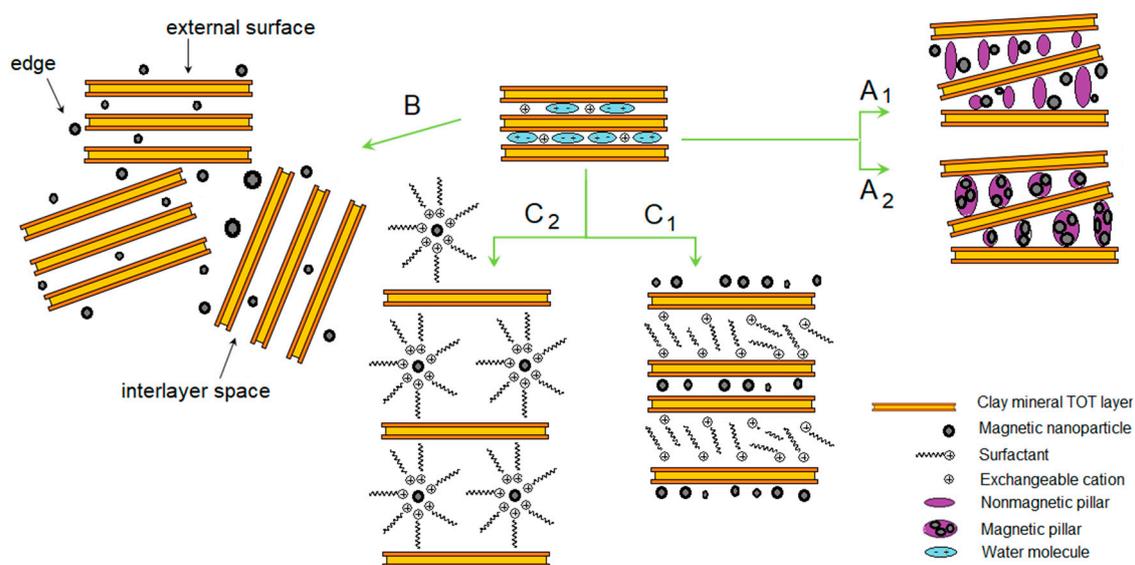


Figure 2. Scheme of typical synthesis routes to obtain magnetic nanoparticle/clay mineral 2:1 type (MNP/CM) nanocomposites: (A1) pillaring with nonmagnetic pillar; (A2) pillaring with magnetic pillar; (B) coprecipitation; (C1) intercalation of MNP into surfactant intercalated clay mineral; (C2) intercalation of surfactant-modified MNP into clay mineral.

Expansible and non-expansible clay minerals have been used to prepare magnetic nanocomposites. Magdy et al. [10] prepared magnetic nanocomposites of kaolin and magnetite ($\text{Fe}_3\text{O}_4/\text{kaolin}$) by the co-precipitation method in one step, and tested the prepared nanocomposites as adsorbents in the removal of the anionic Direct Red 23 dye. They achieved a complete removal of dye under the following set of operating conditions: initial dye concentration = 20 mg L^{-1} , adsorbent mass = 0.75 g , $T = 25^\circ\text{C}$ and $\text{pH } 7$. Additionally, the adsorption followed the Langmuir isotherm with a maximum adsorbent capacity of 22.88 mg g^{-1} . On the other hand, Chang et al. [4] prepared magnetic nanocomposites from montmorillonite (Mt) and magnetite ($\text{Fe}_3\text{O}_4/\text{Mt}$) by a co-precipitation method. This study revealed that Fe_3O_4 nanoparticles are present on the surface of Mt. The magnetic nanocomposite showed a good adsorption efficacy (99.47%) in methylene blue removal.

Another possibility of very interesting modification results from the preparation of magnetic clay mineral nanocomposites with the incorporation of one or more extra components to improve some of the mentioned properties or incorporate new ones. Mu et al. [69] developed several magnetic nanocomposites combining in-situ intercalation, polymerization and coprecipitation techniques. They polymerized aniline molecule, during the synthesis of Fe_3O_4 in a suspension of Mt, obtaining polyaniline (PANI) and Fe_3O_4 supported on the surface of Mt ($\text{Mt/PANI/Fe}_3\text{O}_4$). They tested these materials in the adsorption of three dyes, methylene blue, brilliant green and congo red. One of the developed nanocomposites removes 99.6%, 96.2% and 98.1% of methylene blue, brilliant green and congo red, respectively, from 100 ppm dye solutions, with nanocomposite dosages of 1 g L^{-1} , at 25°C .

They also studied the reuse of Mt/PANI/Fe₃O₄ using BM, and after five cycles the adsorption capacity did not decrease (in all cases it was close to 100%).

Arya and Philip [6] incorporated powdered-activated carbon, chitosan and sodium tripolyphosphate as a binding agent to magnetite nanoparticles supported in bentonite, with the aim of developing a new adsorbent compound capable of removing anionic, cationic, hydrophilic or hydrophobic contaminants. They studied the efficiency of this adsorbent to remove atenolol, ciprofloxacin and gemfibrozil from aqueous systems. The authors found a high removal of atenolol and ciprofloxacin (85% and 95% respectively, with an adsorbent dosage of 1.5 g L⁻¹), which can be attributed to the hydrophilic nature and the interchange capacity of clay–chitosan, since both pollutants are predominantly cationic at the working pH. On the other hand, the hydrophobic nature of activated carbon may be the main factor in the adsorption of gemfibrozil (90% removal).

Diagboya and Dikio [11] developed magnetic adsorbent composites with feldspar clay (FLC), pericarp of oak fruits (PER) and magnetic nanoparticles. The nanocomposites were prepared by the co-precipitation method in the presence of FLC free of organic matter and sieved PER; then, the product obtained was pyrolyzed at 250 °C for 4 h. Magnetic adsorbents (BMF-0.5 and BMF-1) were used to study the removal of methylene blue. The authors performed three adsorption/desorption cycles of methylene blue; they observed that the adsorption capacity decreases in each cycle. The second cycle was lower than the first by approximately 7% for both nanocomposites and the third cycle decreased by a similar proportion.

On the other hand, Fizir et al. [68] developed magnetic halloysite nanotubes (MHNTs) by the method of co-precipitation followed by polymer grafting onto the nanocomposites, to adsorb norfloxacin. Combining the advantages of the high adsorption capacity and the magnetic properties of this biocompatible clay nanotube and the advantage of the polymer shell in improving the controlled and sustained release of the drug, they formulated a novel bioactive agent.

Beé et al. [3] used an extrusion method to obtain a magnetic adsorbent that was prepared by trapping maghemite nanoparticles (γ -Fe₂O₃) and montmorillonite (MMT) in cross-linked chitosan (CS) beads, in order to obtain an efficient adsorbent for cationic and anionic contaminants. They prepared pearls with different clay contents and performed adsorption experiments with methylene blue. They observed that the adsorption capacity of methylene blue increased as the amount of clay increased and the increase occurred over the entire pH range studied (3–12). The maximum uptake of methylene blue (82 mg g⁻¹ at pH 9.9) was obtained with the material that had the highest proportion of clay; this indicates that the adsorption properties of the clay were not affected by encapsulation in the beads. Table 2 summarizes the adsorption capacities of the magnetic-clay-based nanocomposites described in this section.

Table 2. Application of magnetic clay-based nanoadsorbents for organic pollutants' removal from water.

Adsorbent	Surface Area (m ² g ⁻¹)	Magnetic Saturation (emu g ⁻¹)	Organic Pollutant	Adsorption Capacity (mg g ⁻¹)	Ref.
Clay:chitosan:PAC:MNP	95	1.91	Atenolol	15.6	[6]
			Ciprofloxacin	39.1	
			Gemfibrozil	24.8	
Fe ₃ O ₄ /Mt	148	-	Methylene blue	106.4	[4]
Magnetic chitosan/clay beads	-	-	Methylene blue	82	[3]
MSEP	112	31.8	Atrazine	1.79	[67]
MHNTs	-	42.87	Norfloxacin	99.6	[68]
Fe ₃ O ₄ /kaolin	32	12.32	Direct red 23	22.88	[10]
Fe ₃ O ₄ -Sep	81	26.22	Bisphenol A	-	[66]
BMF-1	-	-	Methylene blue	14.93	[11]
BMF-0.5	-	-	Methylene blue	12.35	[11]
Mt/PANI/Fe ₃ O ₄ -2	-	36.52	Methylene blue	184.5	[69]

4. Carbon-Based Materials

Different carbon-based materials have been utilized for adsorption of pollutants, including activated carbon, graphitized carbon black, porous carbon, graphene oxide (GO) and carbon nanotubes (CNTs), due to the versatility of types of interactions that can accomplish with pollutants, such as electrostatic, hydrophobic and π - π interactions [70]. These materials differ in their structures and physicochemical characteristics, as pore size/shape, pore volume, surface area and surface functionality. For instance, CNTs can be considered as hollow graphitic nanomaterials comprising one (single-walled carbon nanotubes, SWNTs) or multiple (multiwalled carbon nanotubes, MWNTs) layers of graphene sheets, while GO is a derivative of graphene, which has abundant active functional groups such as carboxyl, hydroxyl and epoxy [71].

During the last decade, much effort has been devoted to developing efficient synthetic routes to shape-controlled, highly stable, and well-defined magnetic carbon hybrid nanocomposites. Several methods including the filling process, template-based synthesis, chemical vapor deposition, the hydrothermal/solvothermal method, the pyrolysis procedure, the sol-gel process and the self-assembly method can be used for the synthesis of high-quality magnetic carbon nanocomposites [72].

A list of magnetic carbon-based nanocomposites with their adsorption capacity for organic contaminants and some physicochemical properties has been summarized in Table 3. In some cases, the magnetization of the carbon-based materials enhances the adsorption properties when compared to the pristine carbon material. This is explained considering that magnetic nanoparticles can increase the porosity of carbon materials, which favor the diffusion of contaminants to more available adsorption sites.

Fe₃O₄ supported on reduced Grapheme Oxide (rGO) nanocomposite for the removal of harmful pesticides, namely simazine, simeton, atrazine, prometryn, and ametryn, was synthesized by Boruah et al. [73] using an eco-friendly in-situ solution chemistry approach, GO was synthesized from graphite powder and reduced to the rGO sheet using ascorbic acid as a reducing agent. Then, Fe₃O₄ nanoparticles were synthesized adopting the chemical co-precipitation method in the presence of rGO, yielding Fe₃O₄/rGO nanocomposite. Their study reveals that Fe₃O₄/rGO nanocomposite exhibits excellent adsorption performance towards the adsorption of the five pesticide molecules, compared to Fe₃O₄ nanoparticles and rGO sheets. The corresponding adsorption efficiencies for simazine, atrazine, prometryn, ametryn, and simeton were found to be 88%, 75%, 91%, 93% and 81%, respectively.

In general, carbon-based nanomaterials have a unique π - π electronic structure that provides excellent properties to be used as adsorbents for the removal of aromatic compounds [74,75]. Yang

et al. [76] compared the adsorption capacity of aromatic compounds (1-naphthylamine, 1-naphthol and naphthalene) between reduced graphene oxide/iron oxide composites (GO/Fe₃O₄) and multi-walled carbon nanotube/iron oxide composites (MWCNTs/Fe₃O₄). They found that electron–donor–acceptor (EDA) interaction was the primary adsorption mechanism and the higher polarity of adsorbates lead to higher adsorption capacity. In particular, GO/Fe₃O₄ showed better adsorption capacity than MWCNTs/Fe₃O₄, probably due to GO/Fe₃O₄ presenting more available and abundant adsorption sites.

Fan et al. [77] prepared magnetic β -cyclodextrin–chitosan/graphene oxide materials (MCCG) via a chemical route to remove methylene blue from aqueous solution. In this synthesis procedure, the carboxyl group of GO chemically reacts with the amine group of the magnetic β -cyclodextrin–chitosan composite to yield the magnetic carbon-based sorbent. MCCG showed excellent sorbent properties, benefiting from the high surface area of graphene oxide, hydrophobicity of β -cyclodextrin and the abundant amino and hydroxyl functional groups of chitosan. The maximum adsorption capacity of MCCG was 84.3 mg g⁻¹, which was higher than those reported for other adsorbents such as graphene/magnetite composite (43.8 mg g⁻¹), pyrophyllite (4.2 mg g⁻¹), carbon nanotubes (46.2 mg g⁻¹), exfoliated graphene oxide (17.3 mg g⁻¹) and β -cyclodextrin–chitosan (50.12 mg g⁻¹) [78–80]. Among other magnetic carbonaceous materials with high sorption capacity to remove methylene blue, magnetic graphene sponge, (Fe₃O₄-GS) synthesized using a simple method, in which Fe₃O₄ nanoparticles are mixed with GO and subsequently lyophilized to obtain Fe₃O₄-GS, was reported by Yu et al. [81] This magnetic graphene sponge presents quite high adsorption capacity for MB (526 mg g⁻¹) and facile regeneration.

Alizadeh Fard and Barkdoll [82] prepared magnetic carbon nanotubes (MCN) to remove six micropollutants (Metolachlor, Bisphenol-A, Tonalide, Triclosan, Ketoprofen and Estriol) from water. In this work, to prevent the formation of other species of iron oxide, the synthesis of MCNs was performed separately: first, the magnetic nanoparticles were produced by a simple hydrothermal method. Then, the magnetic nanoparticles were mixed with the HNO₃-treated CNTs. MCN presented good adsorption capacity in which Bisphenol-A, Ketoprofen and Tonalide were the most effectively removed micropollutants, with 98%, 96% and 96% removal within 47 min, respectively.

Gong et al. [83] developed magnetic multi-wall carbon nanotube (MMWCNT) nanocomposite using a modified sol–gel process. The negatively charged MMWCNT surface over a wide pH range is one of the main characteristics that allows the removal of cationic pollutants. The adsorption properties of this adsorbent were examined using cationic dyes (methylene blue, neutral red and brilliant cresyl blue). They observed that dye adsorption capacity increased when pH increased from 3 to 7, while beyond 7, the adsorption capacity was not significantly altered. The comparison of the adsorption results with MWCNT and activated carbon indicated that MMWCNT nanocomposite showed the main advantage of the convenience of separation compared to the adsorption treatment in aqueous media. By using another synthesis strategy, Zhao et al. [84] prepared MWCNTs decorated with Fe₃O₄ nanoparticles modified with polyaniline (MWCNTs/Fe₃O₄/PANI) and used this material to test the adsorption of methyl orange and Congo red. The MWCNTs/Fe₃O₄/PANI showed high adsorption capacity toward the tested dyes (446.25 mg g⁻¹ for methyl orange and 417.38 mg g⁻¹ for congo red). The nitrogen containing functional groups of PANI, along with the synergistic effect between MWCNT π -conjugated bonds and PANI π -conjugated bonds, contribute to boosting the effective adsorption sites and thus increase the adsorption capacity toward MO and CR. Another important result obtained from the authors is that the presence of PANI prevented Fe₃O₄ nanoparticles from dissolving, and hence improved the stability of MWCNTs/Fe₃O₄/PANI in solution. In order to confer more carboxyl groups to magnetic carbon nanotube nanocomposites, Deng et al. [85] prepared carbon dot-modified magnetic carbon nanotubes (CMNTs) by three consecutive steps including the preparation of MWNTs, the synthesis of carbon dots and the surface modification of MWNTs using carbon dots. This adsorbent has a moderately high adsorption capacity of carbamazepine (65 mg g⁻¹ at pH 7) and can be regenerated and reused up to six times with capacity loss less than 2.2%.

Liu et al. [86] assembled activated carbon and Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4/\text{AC}$) by a facile one-step thermal decomposition process and tested $\text{Fe}_3\text{O}_4/\text{AC}$ for the adsorption of rhodamine B and methyl orange. $\text{Fe}_3\text{O}_4/\text{AC}$ showed a high surface area (about $1200 \text{ m}^2 \text{ g}^{-1}$), which was much higher than pure AC (about $750 \text{ m}^2 \text{ g}^{-1}$), and wide pore size distribution. These properties benefit the adsorption and the rapid inter-diffusion of the dye molecules through interconnected channels. The obtained magnetic composite exhibited better adsorption of the dyes than its pure AC counterpart. Another approach to assemble Fe_3O_4 nanoparticles with activated carbon was reported by Shan et al. [87] through the ball milling method. They obtained two ultrafine magnetic activated carbon ($\text{Fe}_3\text{O}_4/\text{AC}$) and biochar ($\text{Fe}_3\text{O}_4/\text{BC}$) hybrid materials. The use of biochar drastically increased the surface area of the magnetic composite, while in case of AC the surface area decreased, probably because some pores in AC are blocked by the Fe_3O_4 nanoparticles produced in the milling process. However, in both cases, the authors obtained a higher adsorption capacity than pristine carbon materials using two pharmaceuticals as model contaminants (i.e., carbamazepine and tetracycline). On the other hand, Yu et al. [88] reported a higher sorption capacity of tetracycline (473 mg g^{-1}) using a magnetic graphene oxide sponge ($\text{Fe}_3\text{O}_4\text{-GOS}$) as sorbent. The material was prepared by lyophilizing the dispersion of Fe_3O_4 nanoparticles and graphene oxide (GO).

In the study performed by Lompe et al. [89] the adsorption capacity for nine micropollutants (Diclofenac, Fluoxetine, Estradiol, Norethindrone, Atrazine, Carbamazepine, Deethylatrazine, Sulfamethoxazole and Caffeine) on fresh and aged magnetic powdered activated carbon (MPAC) was investigated. They demonstrated that MPAC produced via co-precipitation can be customized with respect to its magnetic properties without compromising its adsorption capacity beyond the reduction expected for lower powdered activated carbon (PAC) contents. Maximum adsorption capacities of PAC and MPAC for all pollutants ranged between 1 and 80 mg g^{-1} .

Table 3. Application of magnetic carbon-based nanoadsorbents for organic pollutant removal from water.

Adsorbent	Surface Area (m ² g ⁻¹)	Magnetic Saturation (emu g ⁻¹)	Organic Pollutant	Adsorption Capacity (mg g ⁻¹)	Ref.
GO/Fe ₃ O ₄	272	-	1-Naphthylamine 1-Naphthol Naphthalene	2.85 2.70 2.63	[76]
MWCNTs/Fe ₃ O ₄	77	-	1-Naphthylamine 1-Naphthol Naphthalene	1.45 1.13 1.05	[76]
Magnetic-cyclodextrin-chitosan/graphene oxide	402	55.1	Methylene blue	84.3	[77]
Fe ₃ O ₄ -GS	-	4.4	Methylene blue	526	[81]
MWCNT	61	-	Methylene blue Neutral red Brilliant cresyl blue	15.9 20.5 23.0	[83]
Fe ₃ O ₄ /AC	1200	16.5	Rhodamine B Methyl orange	182.4 150.3	[86]
MWCNTs/Fe ₃ O ₄ /PANI	-	42.9	Methyl orange Congo red	446.2 417.4	[84]
Fe ₃ O ₄ /BC	365	19.0	Carbamazepine Tetracycline	62.7 94.2	[87]
Fe ₃ O ₄ /AC	486	20.8	Carbamazepine Tetracycline	135.1 45.3	[87]
Fe ₃ O ₄ -GOS	-	1.1	Tetracycline	473	[88]
CMNTs	184	5.6	Carbamazepine	65	[85]
MPAC	430–780	5–30	Diclofenac, Fluoxetine, Estradiol, Norethindrone, Atrazine, Carbamazepine, Deethylatrazine, Sulfamethoxazole and Caffeine	1–80	[89]
MCN	-	-	Metolachlor, Bisphenol A, Tonalide, Triclosan, Ketoprofen and Estriol	18–28	[82]

5. Polymer-Based Materials

Polymers can be chemically anchored or physically adsorbed on magnetic nanoparticles to form a core-shell structure, acting as a protective layer and simultaneously providing active sites to adsorb pollutants. The core-shell structured can be synthesized by using the seed polymerization method and surface-modified Fe₃O₄ particles as the seeds [90]. This method allows the development of novel porous materials with high surface area and porosity to improve their adsorption performances [91].

Fe₃O₄@polyaniline, a typical Fe₃O₄-based magnetic core-shell material, was synthesized for the removal of pollutants such as humic acid, separation of organic dye, extraction and analysis of phenolic compounds and analysis of pyrethroids in tea drinks and polycyclic aromatic hydrocarbons [92]. As a magnetic core-shell material, polyaniline shows great promise, because it can effectively decrease the chance of aggregation, enhance the adsorption properties for organic pollutants via π - π and van der Waals interactions, and improve the stability of magnetic core-shell composites. However, the most appropriate composition of core-shell structure demands that the ratio between magnetic core and shell dimensions be optimized, since insufficient core magnetic oxide could determine a limited magnetic response and insufficient polymer component could result in poor adsorption capacity. Furthermore, to increase the maximum adsorption capacity and the versatility of the nanomaterials, several functional

groups such as carboxylate, phosphate, sulfate, hydroxyl, amino and amide groups have been explored for the modification of conventional adsorbents. Hou et al. [93] prepared a core-shell nanoadsorbent based on Fe_3O_4 nanoparticles surface-modified with a copolymer, using 2,4-diaminophenol and formaldehyde for the adsorption of anionic dyes (amaranth, orange II and acid red 18) and obtained good adsorption capacities, fast adsorption processes and high saturation magnetization.

Liu et al. [94] reported the synthesis of magnetic nanospheres functionalized with β -cyclodextrin (β -CD) by the one-pot solvent thermal method using β -CD immobilized Fe_3O_4 magnetic nanoparticles with tetra-fluoroterephthalonitrile as the monomer. This material showed fast adsorption kinetics for methylene blue, high dispersibility in aqueous phase, a short equilibrium time (5 min), high recovery and good recyclability (keeping the adsorption efficiency above 86% after five uses). The maximum adsorption capacity of methylene blue was 305 mg g^{-1} .

During the last decade, porous organic polymers, including polymers of intrinsic microporosity [95], metal-organic frameworks (MOFs) [96], covalent organic frameworks (COFs) [97], porous aromatic frameworks [98] and hyper-cross-linked polymers (HCPs) [99] have attracted extensive interest because they have the advantages of low density, excellent chemical and physical stabilities, high surface area, easy control of pore size and functional modification [100]. MOFs are coordination polymers with intriguing structural motifs that can be self-assembled from organic ligands and metal ions or clusters of metal ions. In the last years, MOFs have been developing rapidly and have actually attracted extensive attention in the field of porous materials due to their high surface areas, with a range from 1000 to $10,000 \text{ m}^2 \text{ g}^{-1}$, and a permanent porosity that is superior to those of porous materials such as activated carbon and zeolites [101]. While the use of MOFs as sorbents in gas phase is well-known, some MOFs show limitations in liquid phase adsorption due to their relatively low stability in water and their hydrophilic nature. However, in recent years, the development of water-stable MOFs has increased considerably [102]. Numerous different synthetic approaches, including slow diffusion, hydrothermal, electrochemical, mechanochemical, microwave-assisted heating and ultrasound can be applied to produce MOFs relying on the resulting structures and features [103]. Several magnetic adsorbents with MOF structure have been synthesized. Yang et al. [104] synthesized a new type of Fe_3O_4 @MOF magnetic porous composite material with a core-shell structure of Fe_3O_4 nanoparticles coated with petal-like ZIF-67 crystals (Zeolitic imidazolate framework-67), in which Co^{2+} firstly combines with SO_3^{2-} provided by poly-styrenesulfonate sodium salt to form nucleation. This adsorbent showed high adsorption capacity for methyl orange (anionic dye) owing to the nature of Lewis base coordinated Co(II) and its high porosity. The equilibrium adsorption capacity was as high as 738 mg g^{-1} , which was significantly higher than other adsorbents like coconut shell activated carbon (368 mg g^{-1}) and clay (300 mg g^{-1}) [91]. Hamedi et al. [105] produced a magnetic MOF for the elimination of malachite green and methyl red from wastewaters. Metal-organic framework (MIL-101(Fe)) was prepared from FeCl_3 and terephthalic acid. Moreover, they used an extremely tinny film of 3, 4-dihydroxy-L-phenylalanine (PDopa) as an eco-friendly and effective binder between MIL-101(Fe) and Fe_3O_4 nanoparticles, in order to prevent detachment of the MOF from the magnetic material. In this regard, the authors were able to obtain the perfect capacities of adsorption (833 and 1250 mg g^{-1} for malachite green and methyl red, respectively). Moreover, the MIL-101(Fe)@PDopa@ Fe_3O_4 adsorbent can be used almost four times to remove dyes. Wu et al. [106] prepared magnetic copper-based MOF (Fe_3O_4 /HKUST-1) as an effective and recyclable adsorbent for the removal of ciprofloxacin and norfloxacin (two fluoroquinolone antibiotics) from aqueous solutions. The maximum adsorption capacities of the magnetic composites toward ciprofloxacin and norfloxacin reached 538 mg g^{-1} and 513 mg g^{-1} , respectively, noticeably higher than those values of most of the reported adsorbents for these two compounds.

Covalent organic frameworks (COFs), an emerging class of ordered crystalline porous polymers, are constructed from light elements and linked to organic monomers by strong covalent bonds that have an ordered π -structure with pore uniformity. In general, COFs are derived from MOF. They show comparable surface areas, ordered channel structures, well defined pore apertures, low densities, and thermal and chemical stability [91]. COFs with various functionalities and high

crystallinity have been synthesized and several materials have been reported in the environmental field. Functionalized crystalline polyimide, polycationic and polyanionic COFs have been used for the removal of contaminants with varying physical and chemical properties. It is noteworthy that the size-sieving effect played a major role in the application of COFs for the removal of pollutants. Based on the literature, COFs' high surface areas (e.g., $3500 \text{ m}^2 \text{ g}^{-1}$) give COFs more potential as adsorbents than zeolites or activated carbon [107]. Strategies to obtain water-stable materials with highly ordered structures and large surface areas are reviewed. By means of post-synthetic modification approaches, pore surfaces can be tuned to target specific contaminants based on size-dependent separation and charge-selective separation. Immobilization of COFs on solid substrates is a strategy to improve stability and dispersibility, while taking advantage of the properties of all materials present in the composite [108]. Yi et al. [109] prepared core-shell-structured magnetic COF nanocomposites ($\text{Fe}_3\text{O}_4@\text{COFs}$) for the adsorption of triclosan and triclocarban in aqueous solutions. $\text{Fe}_3\text{O}_4@\text{COFs}$ was fabricated on the Fe_3O_4 nanoparticles using an in-situ growth strategy at room temperature via a condensation reaction of 1,3,5-tris(4-aminophenyl) benzene and terephthalaldehyde in the presence of dimethyl sulfoxide. The adsorption behaviors showed high adsorption capacity and fast adsorption of triclosan and triclocarban. Different magnetic COF composites were also reported for the extraction of bisphenols [110] and polycyclic aromatic hydrocarbons (PAHs) [111] from water.

Hyper-cross-linked polymers (HCPs) can be synthesized by using external crosslinker. The porosity can be improved by using various kinds of reactive monomers or different amounts of crosslinking. For instance, Hu et al. (2019) [100] have synthesized a magnetically hyper-cross-linked polymer using benzylamine and benzene as the reactive monomers, which combined the advantage of the amino-modified HCP (HCP-NH₂) and the magnetic Fe_3O_4 nanoparticles to adsorb organic pollutants such as tetracycline, ethyl orange, methylene blue, bisphenol A and 2,4-dichlorophenol in aqueous solution. The magnetic HCP presented high BET specific surface area ($532.62 \text{ m}^2 \text{ g}^{-1}$), well-developed mesoporous ($0.3786 \text{ cm}^3 \text{ g}^{-1}$) and good magnetic properties. The adsorption experiments indicated that the magnetic HCP-NH₂ showed highly efficient adsorption properties for organic contaminants. In particular, the maximum adsorption capacity of the magnetic HCP-NH₂ for tetracycline was 694 mg g^{-1} at 298 K, which was much higher than that of HCP-NH₂ (389 mg g^{-1}). Based on the adsorption performance, the authors propose that tetracycline removal was mainly driven by coordination interaction, cation exchange and hydrogen bonding interactions that involve polymer functional groups and magnetite surface groups.

Recently, various biomaterials based on natural polymers have been developed for improving adsorption capacities, increasing environmental compatibility and operating efficiently. Alginate-based composites have been extensively studied for applications in environmental sectors due to their biocompatible, nontoxic, and cost-effective properties [112]. Various alginate-based composites that enhanced adsorption performance have been reported for the removal of various pollutants including dyes, heavy metals, and antibiotics in water and wastewater. Environmental applications of alginate depend partly on the fact that the rich surface functional groups (e.g., carboxyl and hydroxyl) could capture metallic or cationic ions via ion exchange between the crosslinking cations and target pollutants. Alginate beads may serve as a stable matrix for other types of adsorbents that are too fine in particle size and too difficult to separate from aqueous solution. Magnetic adsorbents can be developed by encapsulating magnetic functionalized nanoparticles in alginate beads along with different covalently cross-linked agents, such as molecules of different sizes and structures, including adipic dihydrazide, lysine, and poly-(ethylene glycol)-diamines [113,114]. Talbot et al. [115] reported the synthesis of alginate/maghemite nanoparticles for the adsorption of methylene blue. A co-precipitation method in alkaline medium followed by oxidation of magnetite into maghemite led to a stable colloidal dispersion, which was added to sodium alginate solution in order to obtain the magnetic nanocomposite. The nanocomposites showed high adsorption capacity in a wide pH range and a reuse performance higher than 98% even after ten adsorption/desorption cycles. On the other hand, Mohammadi et al. [116] fabricated superparamagnetic sodium alginate-coated Fe_3O_4

nanoparticles by a co-precipitation method, obtaining good removal efficiency of malachite green (48 mg g^{-1}).

Chitosan is another biopolymer that is widely used in environmental applications, owing to its low-cost source and environment-friendly nature. It has abundant reactive amino and hydroxyl groups, which can serve as binding sites turning it a potential adsorbent for organic pollutant removal [117,118]. Solubility of chitosan in an acidic medium limits its wide application in water treatment; thus, various cross-linking agents such as glutaraldehyde [119], sodium tripolyphosphate [92], and epichlorohydrin [120] offer an important pathway to improve its chemical stability and extend its potential applications. Zheng et al. [121] prepared poly([2-(methacryloxy)ethyl] trimethylammonium chloride)-grafted magnetic chitosan microparticles via free radical polymerization to obtain novel superior adsorbents with a huge electrostatic “force field” for capturing food dyes. The nanocomposite morphology was nearly spherical with approximately $125 \mu\text{m}$ average diameters, with a specific surface area of $150 \text{ m}^2 \text{ g}^{-1}$ and average pore diameters of 33.8 \AA . Compared to unmodified adsorbents, the adsorption capacities toward Food Yellow 3 and Acid Yellow 23 were considerably enhanced after modification, indicating that the dyes were captured by electrostatic interaction and ion exchange. On the other hand, polymer-grafted magnetic microspheres (GMMs) were prepared by graft polymerization of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid onto the surface of chitosan/magnetite composite microspheres and were used as an adsorbent to remove methylene blue from aqueous solutions [122]. The authors reported a maximum adsorption capacity for methylene blue of 926 mg g^{-1} , which is notably higher than the reported values for other adsorbents. Table 4 shows the adsorption capacities of the polymer-based magnetic nanomaterials with higher organic pollutant uptake.

Table 4. Application of magnetic polymer-based nanoadsorbents for organic pollutants removal from water.

Adsorbent	Surface Area ($\text{m}^2 \text{ g}^{-1}$)	Magnetic Saturation (emu g^{-1})	Organic Pollutant	Adsorption Capacity (mg g^{-1})	Ref.
Bio-magnetic membrane capsules from PVA–alginate matrix	-	11.02	Malachite green	500	[123]
Magnetic nanocellulose from olive industry solid waste	-	21.4	Methylene blue	166.67	[124]
Fe_3O_4 -amine-functionalized chitosan with p-Benzoquinone	-	17.5	Diclofenac sodium	469.48	[125]
Magnetic β -cyclodextrin porous polymer nanospheres	70.63	44.8	Methylene blue	305.8	[94]
Magnetic porphyrin-based porous organic polymer	310	45.9	Phenylurea herbicides	Metoxuron = 1.13, Mono-linuron = 0.95, Chlorotoluron = 0.86, Buturon = 1.10	[92]
Magnetic copper based metal–organic frameworks (MOF)	327.9	44	Fluoroquinolone antibiotics	Ciprofloxacin = 538 Norfloxacin = 513	[106]
Magnetic polyimide-Mg-Fe layered double hydroxides core–shell composite		26.38	Tetracycline 2,4-dichlorophenol Glyphosate	185.53 176.06 190.84	[126]
Magnetic mesoporous lignin from date palm pits	640	37.81	Diesel Gasoline	Diesel = 22370 Gasoil = 21010	[127]

6. Waste-Based Materials

Within the framework of the circular economy, several efforts have been made to add value to wastes, converting them into renewable raw material for the production of fine, bioplastic and auxiliary

chemicals for technological and environmental applications. In particular, the modification of different industrial and household wastes into adsorbent materials has been the subject of much research, since it represents an economically sustainable method of waste valorization [128–130]. Among them, the most common are agricultural residues, for example the skin of different fruits and vegetables, remnants of branches and leaves, remnants of rice, corn, olive and many others. The reuse of waste from the paper industry, the metallurgical industry, cement and sludge from water treatment plants has also been studied [131].

For the synthesis of waste-derived magnetic materials, most studies use magnetite nanoparticles as the magnetic agent to modify the starting adsorbent sourced from wastes. Safarik and co-workers published two short studies in which they synthesized magnetic adsorbents by putting a stable suspension of magnetite in contact with powdered peanut husk and pine sawdust, respectively [132,133]. They tested these materials against a broad spectrum of organic dyes, obtaining, in particular, maximum adsorption capacities for crystal violet of 80.9 and 51.2 mg g⁻¹. Zuorro et al. [134] achieved remarkable adsorption performance for a waste-derived magnetic material obtained from a similar procedure, in which a suspension of coffee silverskin wastes was mixed with magnetite ferrofluid for 1 h at room temperature. This magnetic adsorbent was tested for methylene blue adsorption, achieved an adsorption capacity of 556 mg g⁻¹ within 2 h at pH 6, and showed good reusability potential, with only a 14% decrease in adsorption after eight regeneration cycles with HCl. Minh et al. [135] also obtained a magnetic adsorbent from ground coffee wastes with an adsorption capacity toward methylene blue of 128 mg g⁻¹. On the other hand, Stan et al. [136] studied four different magnetite–starch materials prepared through an environmentally friendly synthetic route which consist of a co-precipitation method using water as the solvent and sodium bicarbonate as the precipitating agent. One of the four materials was made using bare magnetite and the other three used magnetite synthesized with fruit waste vegetable extract as surfactant. Removal efficiencies of optilan blue dye were between 72% and 89% for these materials. The authors also found that the use of fruit extract in the magnetite synthesis did not improve adsorption performance.

Another method to prepare waste-derived magnetic materials consists in the synthesis of magnetite nanoparticles in an aqueous system where the adsorbent is previously dissolved. Aydin and co-workers used a high-alkaline waste which is produced by the Bayer process in aluminum production called “red mud” and used it along with Fe(II) and Fe(III) salts to synthesize a magnetic-red mud material for adsorption of organophosphorus pesticides and antibiotics [137,138]. With an isoelectric point near eight, this material showed relatively low adsorption capacity towards pesticides, in the order of µg g⁻¹, and good performance against antibiotics with a maximum adsorption capacity of 200 mg g⁻¹ for ciprofloxacin. Madrakian et al. [139] used the solid fraction of tea leaves previously washed and boiled, and tested the obtained magnetic adsorbent performance for seven common cationic and anionic organic dyes. The maximum adsorption capacities for the seven dyes were between 82 and 128 mg g⁻¹. Similar results were obtained by Madrakian et al. [140] using *Platanusorientalis* tree leaves as a raw material for the production of waste-derived magnetic materials. The adsorption capacities of five dyes were between 89 and 133 mg g⁻¹. The authors claim there is no significant loss in adsorption capacity after ten adsorption–desorption cycles for this material. Jodeh et al. [124] prepared magnetic cellulose-based materials from olive industry solid waste and tested the adsorption performance of these materials with methylene blue. In this study, the cellulose was extracted in a powder form by a multistep pulping and bleaching process. The extracted powder cellulose was converted to nanocrystalline cellulose (NCs) by acid hydrolysis and finally dispersed in an aqueous solution of Fe(II) and Fe(III) to obtain magnetic cellulose nanocrystalline through a co-precipitation method. The magnetic material showed good methylene blue adsorption capacity, ranging from 148 to 196 mg g⁻¹. Sun et al. [141] synthesized a magnetic material from wastes of *Vallisneria natans*, a widespread fast-growing aquatic plant, using a chemical co-precipitation method. This material achieved an outstanding methylene blue adsorption capacity (474 mg g⁻¹), almost constant in a wide range of pH values (from 5 to 9).

Yu et al. [142] prepared magnetic modified biomass from beer yeast and tested the adsorption potential by using methylene blue and basic violet as model dyes. The magnetic material was prepared by two steps that included the preparation of pyromellitic dianhydride (PMDA)-modified biomass in *N,N*-dimethylacetamide solution and the preparation of magnetic PMDA-modified biomass by a co-precipitation method under the assistance of ultrasound irradiation. The modified biomass achieved maximum adsorption capacities of 609 and 521 mg g⁻¹ for methylene blue and basic violet, more than six times higher than the unmodified biomass adsorbent. Increasing pH showed a positive effect on adsorption capacities, showing values above 300 mg g⁻¹ over a pH range between 3 and 9.

Core-shell magnetite nanoparticles, using soluble organic matter extracted from urban public park trimming and home gardening residues as a covering material, were used as sustainable and removable magnetic adsorbent materials [143–145]. The soluble organic matter (SBO) was obtained through 230 days of green residues composting followed by alkaline digestion and ultrafiltration of the soluble matter. Magnacca et al. [143] used the obtained Fe₃O₄-SBO nanoparticles for crystal violet removal from waters, and the results showed a good adsorption capacity (244 mg g⁻¹) at pH 7. On the other hand, Nistico et al. [144] studied the removal of polycyclic aromatic hydrocarbons (PAHs) by using Fe₃O₄-SBO nanoparticles. They found that a thermal treatment at 550 °C under nitrogen atmosphere of the Fe₃O₄-SBO nanoparticles enhance their adsorption performance towards PAHs.

Liu et al. [146] developed a synthesis procedure that uses iron mud. This procedure consist of a simple co-precipitation method where iron mud, previously dissolved with 2% HNO₃ overnight, acts as an Fe(III) source, and the addition of ascorbic acid (AA) reduces part of the Fe(III) to Fe(II) needed for the formation of magnetite at alkaline conditions. Increasing the AA/Fe³⁺ ratio during synthesis resulted in increased saturation magnetization values, crystallite size and reduced BET specific area. To further reduce the production cost, acid wastewater from a propylene plant was used to replace nitric acid in digestion of iron mud. Samples with higher crystallite size exhibited less BET specific surface area and less adsorption capacity. Results yield maximum methylene blue adsorption capacities of 87 mg g⁻¹ for the material synthesized with a 0.1 AA/Fe³⁺ ratio. A list of magnetic waste-based nanomaterials with their adsorption capacity for organic contaminants is summarized in Table 5.

Table 5. Application of magnetic waste-based nanoadsorbents for organic pollutants removal from water.

Adsorbent	Surface Area (m ² g ⁻¹)	Magnetic Saturation (emu g ⁻¹)	Organic Pollutant	Adsorption Capacity (mg g ⁻¹)	Ref.
Magnetic Sawdust	-	-	Crystal violet	51.2	[132]
Magnetic Peanut husk	-	-	Acridine orange Bismark brown Crystal violet Safranin O	71.4 95.3 80.9 86.1	[133]
Fe ₃ O ₄ -Coffe Skin	-	-	Methylene blue	556	[134]
Fe ₃ O ₄ -Ground coffe waste	-	-	Methylene blue	128	[135]
Fe ₃ O ₄ -Starch	62	51	Optilan blue	119	[136]
Fe ₃ O ₄ -Av1-Starch	78	43		111	
Fe ₃ O ₄ -Wm-Starch	63	49		63	
Fe ₃ O ₄ -Red mud	84	12	Diazinon Malathion Parathiion Chlorpyrifos	1.9 1.7 2.9 3.9	[137]
Fe ₃ O ₄ -Red mud	84	12	Ciprofloxacin	200	[138]
Fe ₃ O ₄ -Tea Waste	-	-	Neutral red Reactive blue Congo red Janus green Methilene blue Crystal violet Thionine	127 88 83 130 119 114 128	[139]
Fe ₃ O ₄ -Tree leaves	-	-	Malachite green Neutral red Methylene blue Crystal violet Methyl violet	89 101 128 117 133	[140]
Fe ₃ O ₄ -Olive cristal cellulose	-	21	Methylene blue	166	[124]
Fe ₃ O ₄ -Acuatic Plant	7	3	Methylene blue	474	[141]
Fe ₃ O ₄ -Beer Yeast	-	-	Methylene blue Basic violet	609 521	[142]
Fe ₃ O ₄ -SBO	35	51	Crystal violet	244	[143]
Fe ₃ O ₄ (MP-10)	70	9	Methylene blue	99.4	[144]
Fe ₃ O ₄ (MP-3)	176	5	Methylene blue	87.3	[146]
Fe ₃ O ₄ (MP-3w)	119	4		56.7	

7. Conclusions and Future Perspective

Magnetic core–shell nanoparticles and nanocomposites containing iron oxide nanoparticles are a very attractive option to be used in water treatment, due to their advantages in terms of improving some of the properties of unmodified materials for the adsorption of pollutants, namely: (i) a synergistic combination of adsorbent materials where a material is chemically anchored or physically adsorbed on magnetic nanoparticles; (ii) the use of low-cost materials; (iii) facilitation of the separation of the aqueous medium by a simple magnetic process, reducing the overall cost of the process; (iv) the possibility of being reused successively; (v) potential for change in the physicochemical properties of the nanoparticles and nanocomposites surface just by adjusting the experimental conditions, offering a high versatility to be applied to a wide range of contaminants (anionic, cationic, hydrophilic or hydrophobic). Therefore, nanoadsorbents with magnetic response has shown several advantages that could be used in the development water treatment technologies. In this review, the adsorption capacities of magnetic nanomaterials based on silica, clay, carbonaceous materials, polymers and waste

were highlighted in order to provide valuable information related to their efficiency of various organic pollutants' removal.

Although magnetic core–shell nanoparticles and magnetic nanocomposites possess different structural characteristics and different removal mechanisms of organic molecules, their adsorption capacities for various organic pollutants are similar. It is worth mentioning that there are some cases where ultra-high adsorption uptake of organic contaminants was achieved. On the other hand, the preparation of nanoadsorbents by combining magnetic iron oxide nanoparticles with materials such as clays, carbon or polymers enable to control the aggregation of the magnetic nanoparticles and improve their performance in aqueous media.

Despite the growing interest in the synthesis of magnetic nanoadsorbents for water treatment in last years, nowadays there are few industrial applications and most of the research work is based on small-scale studies. We believe that further studies are needed to address large-scale applications, taking into account design aspects related to stability, adsorbent regeneration, and separation from the aqueous medium. This could help to identify the key operating conditions to achieve low-cost removal of the contaminant with minimal environmental impact. Along with these studies, the efficient production of magnetic nanomaterials at large scale must be investigated further, taking into consideration the environmental impact of manufacturing these materials.

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