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Chapter

Nanoporous Carbon Composites for Water Remediation

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Abstract

Metal–organic frameworks (MOFs) are known for their superior surface properties such as surface area and porosity. Thermal decomposition of MOFs may lead to nanoporous carbon composites. These composites can be further used in various application areas. Environmental remediation is one of the most popular areas for using these composites. Nowadays, nanoporous carbon composites are used generally in supercapacitors, lithium-ion batteries, and sensors. Besides the aforementioned application areas, these materials can be used as adsorbents, photocatalysts, and nanomotors. In this review, the preparation methods of nanoporous carbon materials will be explained and their use in environmental remediation will be summarized. The future perspectives of nanoporous carbon composites will be also discussed.

Keywords: metal–organic frameworks, nanoporous carbon composites, water remediation, organic pollutants

1. Introduction

Carbon finds its place in every new developing technological field. Carbon materials are used as drug delivery agent in biotechnological and pharmaceutical researches. They are used as electrode materials for developing new battery systems. Also, different kinds of carbon materials are used in sensor applications. Environmental engineering is another field that makes use of carbon materials as adsorbents or catalysts.

Nanoporous carbon materials are critically important for environmental remediation processes. The physicochemical properties of nanoporous carbon materials are especially suitable for water treatment operations. The specific surfaces area and porosity of carbon materials are very high [1]. Furthermore, different functional groups can be grafted to the surface of carbonaceous materials. Carbon materials are of a wide variety. Activated carbons, carbon nanotubes, graphene, and graphite can be mentioned as some important examples. Particularly, activated carbons derived from organic materials have been mostly used in water purification processes [2, 3].

In the last decade, metal–organic frameworks (MOFs) and their carbon derivatives have triggered strong interest from researchers. MOFs are formed by the combination of metal ions or clusters and organic linkers. The ranges of porosity and surface area of MOFs are quite wide compared to those of the other materials...
used for environmental remediation. The crystal motifs of MOFs are coordinated as periodically organometallic 3D structures [4]. The carbon structures derived from MOFs are prepared by pyrolysis method. Before the pyrolysis step, physical or chemical treatments are applied to the organic precursors [5]. The diversity of MOFs provides the potential to achieve numerous different kinds of nanoporous carbon materials. These materials can be used for different application areas.

The purpose of this chapter is to introduce the reader in the field of MOF-derived nanoporous carbon materials and their applications to environmental engineering. Firstly, MOF structures, preparation methods, and properties will be defined, and then nanoporous carbon composites (NCCs) will be presented. Additionally, the application areas of NCCs will be reviewed.

2. Metal-organic frameworks (MOFs)

Metal-organic frameworks are built by the combination of organic and inorganic sites. Several examples of MOFs are given in Figure 1 (the structures were drawn using Mercury 4.2.0 software [6, 7]).

As shown in Figure 1, metal ions are connected by organic linkers. Different kinds of organic linkers can be used for preparation of MOFs. Terephthalic acid, trimesic acid, fumaric acid, and oxalic acid are only a few examples of organic linkers. A wide range of MOFs can be produced with a large number of different metal-organic sequences. MOFs have some advanced properties compared to traditional porous materials. Flexibility, regular structure, and ability of design are some of the most important properties. The crystalline structure of MOFs facilitates the characterization steps. X-ray diffraction analysis proves the structure of MOFs [11]. MOFs can be modified during the synthesis step and/or after synthesis. Synthesis media of MOFs can be easily controlled, so that some modifications can be operated by simply changing the media. For example, acid modulation is a preferred method for defecting MOFs and obtaining higher porosity. Also, organic linkers can be used to functionalize MOFs [11]. Nitroterephthalic acid and 2-aminoterephthalic acid are used for preparation of modified MOFs.

MOFs have a wide range of application areas. Gas storage and gas adsorption are very well-known application areas of MOFs. Also, sensors, catalysts, drug delivery agents, and biotechnological applications in general can be listed as applications of MOFs [12].

MOFs and MOF-based technologies have been started to be used as commercial products. The number of patents granted by different countries has been increasing in the last decade [13]. Different application types can be generated based on MOFs.

Figure 1.
(a) MIL-100 (Al) [8], (b) UiO-66 (Zr) [9], and (c) MOF-5 (Zn) [10].
MOFs can be transformed further to nanoporous carbon structures. Pyrolyzed MOFs have gained special attention in the last decades. This chapter focuses on NCCs. Preparation methods and application areas of NCCs are summarized.

3. Nanoporous carbon composites (NCC) derived from MOFs

Porous nanomaterials represent one of the most important classes of solid materials. Especially, nanoporous carbons have advanced chemical and physical features. Thermal and chemical stabilities of nanoporous carbons are remarkable so that these materials are very important for a wide range of technological areas. Many researchers reported that nanoporous carbon materials are very important for solving of the global environmental issues [1]. Nanoporous carbons are generally prepared by pyrolysis of an organic material [5].

Nanoporous carbons are very light, and they have high surface area and porosity. These properties represent important advantages [1]. Different organic materials can be used as precursor of nanoporous carbons. Generally, some templates are used in pyrolysis for obtaining ordered porous carbons [14]. Hard template and soft template methods have been used to prepare ordered nanoporous carbons. However, the stability of porous carbons prepared by hard template method is not appropriate. Also, this method is not economic and the process is very long. Soft template method is often not preferred by researchers due to it is difficult to find a suitable template for pyrolysis [14]. MOFs are newly used precursors for this purpose. The nanoporous carbons derived from MOFs provide different functionalities to the final product. Magnetic properties, oxygen and nitrogen doping, and metal or metal oxides on nanoporous carbons are some examples of functionalities [15].

Examples of application areas for nanoporous carbon composites are as follows: electrode materials, catalysts, and adsorbents [15].

The research studies on the topic of NCCs have been rapidly increasing in the last decade. As shown in Figure 2, the research activities have been increasing exponentially in the last 5 years.

According to the pyrolysis method, three different types of MOF structures can be obtained. Figure 3 describes the three structures. Carbons and different types of metal compounds can be prepared by pyrolysis of MOFs under different conditions.
Metal carbides, metal oxides, and metal sulfides are some of the metal structures. These materials are generally used as heterogeneous catalysts [16].

The pyrolysis temperature and post- or pretreatments on MOFs can affect the obtained products. Some examples are given below.

As listed in Table 1, reaction conditions are very important for the final product. Furfuryl alcohol treated MOF-5 has different values of surface area in dependence of temperature. For IRMOF-1, IRMOF-3, and IRMOF-8, the total pore volume of MOFs increases. The total pore volume of IRMOF-1 increases from 1.45 to 4.06 cm$^3$/g; similarly, the total pore volume of IRMOF-3 increases from 0.90 to 2.01 cm$^3$/g [1]. Different carbon sources and different templates can be added to MOFs so that a wide variety of materials can be produced. Furfuryl alcohol is an example for this purpose. Zhang et al. [17] used glucose+ZIF-7 for preparing carbon structures. Glucose is a green carbon source and also ensures the removal of metals from the derived carbon structure. The additives for MOFs and derived products from these types of structures can be classified as follows (Figure 4).

MOFs have metal ions in their crystal structures. Direct pyrolysis under N$_2$ or Ar atmosphere cannot remove all metal compounds. According to the required structure,

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
MOFs & BET surface area (m$^2$/g) & Pyrolysis conditions & Derived structure & BET surface area (m$^2$/g) & Reference \\
\hline
CO$_3$(NDC)$_6$(DMF)$_4$ & - & Calcination at 600°C in air & \text{Co$_3$O$_4$} & 5-3 & [18] \\
\hline
\end{tabular}
\caption{Examples of MOF-derived carbon composites.}
\end{table}
MOFs are modified before pyrolysis. For this purpose, different templates can be used. Xia et al. [18] prepared a catalyst for oxygen reduction reaction. They used a Co-based MOF for this purpose to prepare Co@Co$_3$O$_4$@C core@bshell nanoparticles. In the mentioned study, the authors used MOF as a metal source, obtaining highly porous carbon structure. Also, they prepared Co@Co$_3$O$_4$ by controlled oxidation.

The ordered metal-free nanoporous carbon structures can be prepared by acid leaching [19] or by adding different materials such as glucose, etc. Graphene, carbon nanotubes, and other organic templates are used as extra carbon sources. Carbon sources provide larger surface areas for the required product. The surface area of furfuryl alcohol+MOF-5 can be given as an example.

The facile production of MOFs and MOF composites and also of nanoporous carbon composites derived from MOFs is very important for researchers. This is the easiest way for producing new catalysts and adsorbents. In the last 5 years, the researchers have prepared new derived materials and generally used them as catalysts in the energy field. In the present review, the uses of these derived materials in the area of water remediation are presented.

4. Application areas of nanoporous carbon composites

Electrochemical and energy areas are generally the most preferred applications for nanoporous carbon composites. The research group of Prof. Yusuke Yamauchi is one of the most active groups on this subject. For instance, they synthesized Zn$^{2+}$/Co$^{3+}$ hybrid MOFs at room temperature, using deionized water as solvent [20]. After the pyrolysis of the hybrid material and activation with KOH (for increasing the surface area), they used the derived material for electrical double-layer capacitors and pseudocapacitors [20]. The nanoporous carbon composites are also used in oxygen reduction reaction [21], selective fluorescence sensor [22], and Li-ion battery applications [23]. Yamauchi et al. [24] prepared ZIF-8 nanoparticles and transformed it to nanoporous carbon to use as intracellular drug (cisplatin) delivery carriers.

Water remediation studies of MOF-derived nanoporous carbon composites are presented herein further.

Water is the most essential source of life for all living things. The greater part of water is salty, so a low percent of water is actually reachable and useful for livings. Even less, about 0.3% of water in the world can be used for human being [25]. Reaching clean water and cleaning the polluted water represent the biggest problem of the entire world. Carbon materials have been used for remediation of polluted water for a long time. New engineered materials are very promising. MOF-derived nanoporous carbon composites are one of these engineered materials. Some of these materials have started to be used in the last decade especially in the energy field. However, they have very huge potential for water remediation applications. The researchers show more and more interest to this purpose [5].
Different kinds of MOF-derived nanoporous carbon composites have been reported in water remediation studies. Some of these studies are introduced and listed below:

Li et al. [26] prepared nanoporous carbon from the derivation of MOF-5. The surface area value of the nanoporous carbon is 1731 m²/g. They used the obtained material as an adsorbent for the removal of sulfamethoxazole, bisphenol A, and methyl orange from water. The maximum adsorption capacities ($q_m$) of these organic pollutants are 625 mg/g, 757 mg/g, and 872 mg/g, respectively. These values show that the nanoporous carbon composites are really effective for such organic pollutants. As the authors stated “these $q_m$ values are 1.0–3.2 times higher than single-walled carbon nanotubes (SWCNTs) and powder active carbon (PAC) under the same conditions”; the reported results are truly remarkable.

Bhadra et al. [27] used metal azolate frameworks for the preparation of nanoporous carbons. After 24 h of thermal treatment, the surface area of nanoporous carbon reached 1906 m²/g. The adsorption studies were carried out to remove aromatic hydrocarbons such as naphthalene, anthracene, pyrene, and benzene by means of this carbon. The $q_m$ values are 150 mg/g for benzene, 240 mg/g for naphthalene, 280 mg/g for anthracene, and 310 mg/g for pyrene.

Zhang et al. [28] chose a bimetallic ZIF for the preparation of nanoporous carbon composites. ZIF (Zn/Co) was used as the precursor. The thermal conditions were 900°C, the atmosphere was Argon, and the reaction duration was of 5 h. The obtained surface area is of 398 m²/g. This material was used for Rhodamine B adsorption. The maximum adsorption capacity was found as 116.2 mg/g. This value is competitive compared to the results in literature.

Xu et al. [29] used ZIF-8 and a carbon sources to prepare nanoporous carbon. The carbon sources were sucrose and dicyanamide. Carbonization conditions were 950°C under Argon atmosphere, and the obtained product was nitrogen-doped nanoporous carbon composites. The chosen adsorbate for this carbon was methylene blue. The highest value for the surface area is of 1796 m²/g with dicyanamide treated ZIF-8. The $q_m$ value is 1160.5 mg/g. According to literature, this value is outstanding.

Jin et al. [30] synthesized (Ni^{2+}/Zn^{2+}) + H3BTC MOFs to prepare further nanoporous carbon composites. Ni/Zn MOF was calcinated at 910°C under nitrogen flow. The surface area was measured as 999 m²/g. The adsorption of malachite green, Congo red, rhodamine B, methylene blue, and methyl orange was carried out. Maximum adsorption capacities of organic dyes were found as 898, 818, 395, 312, and 271 mg/g, respectively.

Bhadra and Jhung [15] prepared MAF-4-, MAF-5-, and MAF-6-derived nanoporous carbon composites for the removal of emerging contaminants from water. The carbonization conditions were 800°C, under nitrogen flow for a 6-h period. The surface areas of carbonized products were found as 1176, 938, and 1642 m²/g, respectively. The chosen contaminants are salicylic acid, clenfenac acid, diclofenac sodium, bisphenol A, and oxybenzone. In the case of oxybenzone, the adsorption capacity of carbonized MAF-4 was 898 mg/g, 818 mg/g for carbonized MAF-5, and 440 mg/g for carbonized MAF-6.

Liu et al. [31] chose ZIF-8 (Zn) for carbonization. They added another carbon source to their MOFs. Furfuryl alcohol is generally used for carbon sources in such studies. The heat treatment temperature was 900°C under N2 flow. They used the obtained adsorbent for dispersive solid phase extraction of benzoylurea insecticides (diflubenzuron, triflumuron, hexaflumuron and teflubenzuron). The importance of this study resided in the very low pollution concentration range, 0.10–0.23 ng/L, the reported carbon getting very successful adsorption values.

Mg-MOF-74 is another template for using carbonization studies. Lv et al. [32] carried out the calcination at 800°C for 1 hour, under inert conditions. The product was
MgO/C composite. The surface area of Mg-MOF-74 was found as 18 m$^2$/g, yet the carbonized product has a significantly higher surface area, 296 m$^2$/g. The aim of producing this composite consisted in uranium (VI) adsorption. The adsorption capacity of the carbonized product was found as 777 mg/g, whereas the adsorption capacity of raw Mg-MOF-74 was of only 110 mg/g. In the literature, U (VI) adsorption capacity of activated carbon was given as 28 mg/g. This result outlines the huge potential of engineered nanoporous carbon composites for water remediation studies.

The carbonization process provides additional physical properties to carbon composites. Magnetization is one of them. Ahsan et al. [33] carbonized Fe-benzenedicarboxylate MOFs at 800°C under Ar for 1 h. The obtained product was magnetic C/Fe composite. They used this composite for 4-nitrophenol and methyl orange degradation. Reaction yields reached 99.59% for 4-nitrophenol and 98% for methyl orange. The composites can be regenerated and used at least four times for this purpose. Lin et al. [34] prepared magnetic composite by carbonization of ZIF-67 and used this composite for caffeine reduction.

Bhadra et al. [35] carbonized and annealed Bio-MOF-1 (adenine, biphenyl-4,4′-dicarboxylic acid, and Zn$^{2+}$) at 1000°C (N$_2$ atmosphere) for different values of reaction time (6, 12, and 24 h). After 12 h, the maximum surface area was of 1449 m$^2$/g. Bisphenol A adsorption was carried out with this composite. The maximum adsorption capacity was found as 710 mg/g using 12-h annealed composite.

Torad et al. [36] prepared magnetic cobalt nanoparticles (Co/nanoporous carbon composites) by the carbonization of ZIF-67 crystals. The obtained Co nanoparticles were used for methylene blue adsorption. Two different values of temperature were chosen for carbonization, 600°C and 800°C, under N$_2$ flow. The authors also used HCl solutions for controlling the magnetization. The surface area of the MOF carbonized at 800°C was measured at 345 m$^2$/g. The maximum adsorption capacity is of 502.5 mg/g.

Fe(III)-modified MOF-5 was prepared by Chen et al. [37] The carbonization temperature was 500°C in the reported study. The product was used for the adsorption of atrazine, carbamazepine, bisphenol A, norfloxacin, and 4-nitrophenol.

Sarker et al. [38] designed different MOFs for carbonization. They prepared ZIF-8 + ionic liquid composites. Then, the composite was carbonized at 1000°C, under nitrogen flow for 10 h. The surface area of this pyrolysis product is of 1468 m$^2$/g. The chosen adsorbents were two toxic herbicides diuron and 2,4-D. The $q_m$ values were found as 284 mg/g for diuron and 448 mg/g for 2,4-D. Bhadra et al. [39] adsorbed ibuprofen and diclofenac by ZIF-8-derived nanoporous carbon. Li et al. [40] also chose ZIF-8 for carbonization and adsorbed ciprofloxacin antibiotic from water. They showed a very good adsorption capacity of 416.7 mg/g.

In this section, some applications of MOF-derived nanoporous carbons in the field of water remediation were described. Generally, organic pollutants were chosen by researchers for adsorption studies. Only a few heavy metal adsorption studies were reported in literature. Organic dyes, personal care products, some drugs, and antibiotics were studied with only a few different MOFs. The investigations show that these materials have huge research potential for water remediation studies.

5. Conclusion

The properties of metal-organic frameworks and MOF-derived nanoporous carbon composites were discussed in this mini-review chapter. The structures of MOFs were explained. The preparation methods and the kinds of nanoporous carbons were mentioned.
The carbonization of MOFs represents the main method for preparing nanoporous carbon composites. The chosen temperature, the reaction media, and the reaction time are very important for the obtained product. MOFs can be calcinated under air atmosphere. Metal and metal oxides are the products. If inert atmosphere (N₂, Ar) is chosen, then carbon, carbon/metal, and carbon/metal oxides nanoparticles can be obtained. Also, some carbon sources can be used to provide higher surface areas, such as furfuryl alcohol, glucose, and sucrose. Some other templates can be used such as carbon nanotube, graphene, and other graphene structures. Different shapes and sizes of products can be synthesized. According to the chosen metal ions, the obtained nanoporous carbon composites can have magnetic properties. This property is very useful for adsorption processes.

The nanoporous carbons and carbon composites have been used for water remediation studies especially in the last 5 years. Generally, organic pollutants have been studied until now. Some organic dyes, personal care products, some drugs, herbicides, and antibiotics have been adsorbed from aqueous solutions using nanoporous carbon composites. According to the reported results, the adsorption efficiency of nanoporous carbon composites is very promising.

Having excellent physical and chemical properties, MOF-derived nanoporous carbon composites may lead to the development of countless different products. All these new products can be functionalized by various chemicals according to requirements. This new family of nanoporous materials provides large perspectives especially in the field of wastewater treatment. The summary presented herein above shows that highly featured MOF-derived composites have not been adequately used for water treatment so far. In the context of to the nowadays global problem of clean water scarcity, the future of MOF-derived nanoporous carbon composites emerges bright.

6. Future perspectives

The nanoporous carbon composites derived from MOFs are brand new materials. The surface area and porosities are very high. Such properties favor these carbon materials for adsorption and catalysis processes. Generally, energy applications and sensors have been studied with these carbon materials. Water remediation approaches based on nanoporous carbon composites are very promising.

Preparation methods of nanoporous carbons, diversifying the MOF structures before carbonization, enrich the research options. Further, these options open the perspectives for new products and new application areas. Water treatment activities will be positively influenced by this rich range of products. Engineered nanoporous carbon composites may be a significant milestone in solving the global environmental problems.

Conflict of interest

The authors declare no conflict of interest.
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