

Review

A Review on Modification Methods of Adsorbents for Naphthalene in Environment

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Abstract: Naphthalene is one of the most hazardous polycyclic aromatic hydrocarbons to public health. This paper comprehensively summarized the recent development of modification methods of adsorbents for naphthalene removal in the environment. Various modification methods used in the adsorbent were summarized, mainly including acid oxidation modification, salt modification, doping modification, amino modification, microwave modification, and plasma modification. These methods enhance the adsorption performance of naphthalene mainly by changing the pore size and the oxygen content on the surface of the adsorbent. The modification parameters and their effects on naphthalene removal as well as the advantages and disadvantages of each method are described in detail. This review provides the necessary inspiration and guidance for the researchers who develop polycyclic aromatic hydrocarbons adsorption materials in the environment.

Keywords: naphthalene; modification methods; adsorbents



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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants widely distributed in the environment, most of which are colorless, white, or light yellow solid [1] almost all of the PAHs have stable chemical structure, high lipophilicity, and low water solubility. It mainly originates from the incomplete combustion of fuels that produces compounds with two or more benzene rings [2]. The source of combustion can be natural and anthropogenic, in which the amount of the latter is far greater than that of the former [3–5]. PAHs in the environment can be transported and transformed into the hydrosphere, soil sphere, and biosphere. Particularly, although most PAHs in the environment are insoluble in water, the PAHs with low molecular weight ones are also soluble [6–8], and in recent years, researchers found that the concentrations of PAHs in soil [9], atmospheric air [10], and water is increasing [11–13]. Due to the stable chemical property of PAHs, they can continue to accumulate in the environment, thus causing serious harm to human health and the environment. In general, human's exposure to PAHs through diet, breathing, and skin contact [14] can cause a variety of symptoms, such as loss of appetite, vomiting, skin itching, and diarrhea [15]. In addition, some compounds in PAHs have been listed as carcinogens by the International Agency for Research on Cancer (IARC) [16], and long-term exposure to PAHs increases the risk of lung cancer, stomach cancer, skin cancer, scrotal cancer, esophageal cancer, prostate cancer, and kidney cancer [15].

Naphthalene (Nap), one of the simplest PAHs [13], is a bright white flake crystal with a melting point of 80.5 °C and a boiling point of 218 °C, which is easy to sublimate. It is mainly extracted from coal tar and is the most abundant compound in coal tar, approximately 8–12%. It is widely used in industry to make dyes, chemical solvents, resins, and other raw materials, but it also can be used to prepare insect repellents and other supplies (such as mothballs or sanitary balls). The discharge of wastewater in the process of coal tar

extraction and the after-sale treatment of mothballs in daily life have caused the pollution of Nap in the environment, which seriously threatens the safety of human life.

Currently, Nap has become the main pollutant in many industrial pollution sites and is listed as one of the priority control pollutants by the United States Environmental Protection Agency with a carcinogenicity rating of 2B [17]. Additionally, it is well known that Nap has suppressive effects on the immune system and is suspected of being an endocrine disruptor [18–20]. More detailed properties and their carcinogenic potential are shown in Table 1. To reduce the harm of Nap to the local ecosystem and human health, various methods for removing Nap have been investigated. The processes removal and degradation studies of Nap in the environment have attracted considerable attention in the past, including biodegradation [21–23], photocatalysis [24,25], adsorption, etc. [26,27]. The advantages and disadvantages of the above-listed approaches are shown in Table 2. Nowadays, adsorption technology is more and more widely used to remove persistent organic pollutants because of its simple approach, low investment cost, and the fact that it is not easy to produce secondary pollution [28,29].

Table 1. Characteristic of Nap.

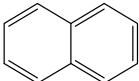
Formula	Structure	λ	Molecular Weight (g/mol)	Melting Point (K)	Boiling Point (K)	Log Kow	Possibly Carcinogenic to Humans
C ₁₀ H ₈		254	128.16	354.15	491.05	3.36	2B

Table 2. Methods for removal Nap.

Methods	Advantages	Disadvantages	Ref.
Biodegradation	Good efficiency Less expensive	Refractory high molecular weight PAHs Long incubation time PH sensitive	[30,31]
Photocatalysis	Good efficiency	Toxic products Requires skilled operator	[32]
Physical and chemical processes	Good efficiency	High operation cost Corrosion Secondary pollution	[33]
Membrane filtration	High removal efficiency	High initial and operating cost Membrane fouling	[34,35]
Advanced oxidation processes	High removal efficiency Strong oxidation Easy operation control	High cost Instability High requirements for reaction equipment	[36–38]
Adsorption	High efficiency Simple operation Low processing cost	Labor intensive Poor removal of fine emulsions	[39,40]

The adsorption mechanism of adsorbent for Nap can be summarized as physical adsorption and chemical adsorption. If the adsorption process is dominated by the Johannes Diderik van der Waals force and the adsorption process is reversible, it can be depicted as

physical adsorption, while the adsorption behavior controlled by the action of chemical bonds belongs to chemical adsorption; both these two adsorption processes can occur simultaneously or alternately [41]. Additionally, the pore size of the adsorbent is an important factor in its physical adsorption process, and the chemisorption is mainly affected by the functional groups on the surface of the adsorbent. Therefore, the adsorption capacity of the adsorbent can be enhanced by adjusting the pore structure of the adsorbent or adding more functional groups to the surface of the adsorbent. Currently, activated carbon (AC) adsorption as a high removal efficiency adsorbent has been widely used for Nap removal [42–44]. However, the ACs in practical application face some problems such as high operating cost, large loss of adsorbent, and poor regeneration, which hinder its further development [45]. At present, many researchers have developed new adsorbents to replace activated carbon, but the specific surface area of most adsorbents is low, and the surface oxygen functional groups are less, which leads to the poor removal ability of Nap. Therefore, some modification methods were used to change the pore size structure of the adsorbent and/or increase the oxygen-containing functional group on the surface of the adsorbent to enhance the adsorption capacity of the adsorbent for Nap [36,46,47]. Figure 1 summarizes the detailed classification of adsorbents and modification methods of adsorbents commonly used for Nap removal.

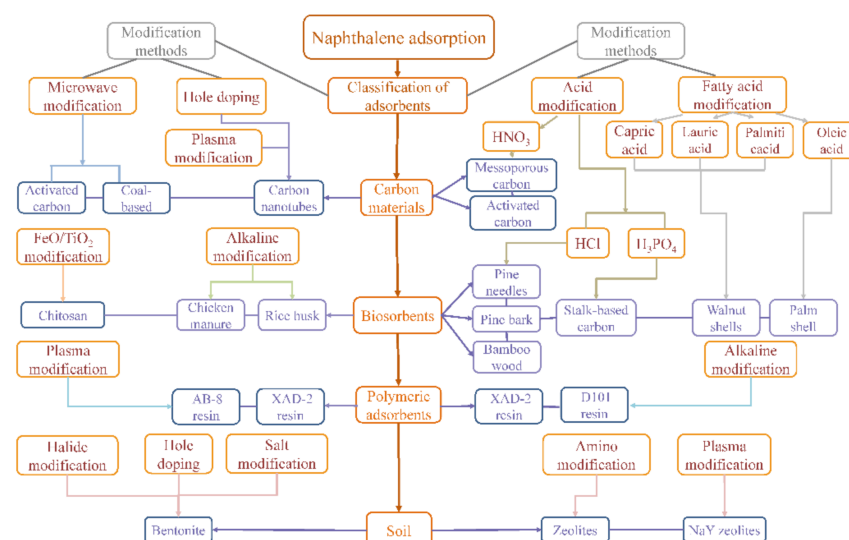


Figure 1. The detailed classification of adsorbents and modification methods of adsorbents commonly used for Nap.

In previous studies, many modification methods have been developed, such as acid and alkaline modification, fatty acid modification, halide modification, hole doping, amino modification, microwave, and plasma modification [38]. To provide some useful information for researchers in this field, this article reviews various adsorbents modification methods for Nap adsorption. The main process parameters, adsorption performance of Nap, and the advantages and disadvantages of various modification methods were summarized and introduced.

2. Acid and Alkaline Modification

2.1. Acid Modification

Acid modification often belongs to oxidative modification. The type and content of oxygen-containing functional groups such as carbonyl, carboxyl, and ester are increased by the reaction of the added strong oxidant with the surface of the adsorbent. In addition, the strong oxidant enhanced the polarity and hydrophilicity of the adsorbent, and also improved its adsorption capacity [48]. HNO_3 , H_2SO_4 , HCl , H_3PO_4 , etc. are commonly used acid solvents. Different oxidants cause different amounts of oxygen-containing functional

groups on the surface of the adsorbent. The higher degree of acid oxidation, the greater the number of functional groups generated when reacting with the adsorbent. The raw adsorbents, the modified reagents, their concentration, the Nap removal efficiency, and the adsorption capacity of modified adsorbents are listed in Table 3.

Anbia et al. [49] used 15 mL of HNO_3 solution to treat mesoporous carbon (MC) for 1 h at 80 °C under refluxing to introduce oxygen-containing functional groups on the surface of the carbon to prepare the chemically oxidized mesoporous carbon (COMC). They found that the adsorption capacity of the COMC for Nap was significantly enhanced [50,51]. The results showed that the HNO_3 oxidation modification reduced the specific surface area and pore volume of MC by 2.5% and 9.5%, respectively, while the pore size distribution of MC (3.4 nm of average pore size) and COMC (3.1 nm of average pore size) was almost the same. On the other hand, during the process of modification, the HNO_3 solution reacts with C atoms on the carbon surface and forms C-OH and/or -COOH, which increases the active sites on the surface of the adsorbent; this plays an important role in the process of Nap adsorption [52]. In addition, the experiment also investigated the best adsorption effective at a pH range of 5–7. Qiu et al. [53] prepared modified mesoporous carbon by adding 5 g MC samples into 50 mL of nitric acid with a concentration of 35–85% and preserved the mixture at 40–80 °C for 1–5 h. The competitive adsorption of Nap and phenanthrene in HNO_3 oxidation-modified coal tar pitch-based MC was studied. It was found that the surface of the MCs becomes smoother, and the external pore size was enlarged after oxidation modification. At the same time, the specific surface area decreases, while the number of mesopores, the densities of carboxylic and lactonic groups, and the total acidity were found to increase sharply. The adsorption performance of activated carbon is significantly enhanced, which is attributed to the increase in acidic oxygen-containing functional groups on the surface of the adsorbent. The higher the HNO_3 concentration and the oxidation temperature, the more the number of acidic oxygen functional groups connected to the adsorbent surface.

Zhou et al. [54] used 68% HNO_3 of analytical grade to soak at 60 °C for 3 h to oxidize and modify activated carbons (ACs). The samples prepared by treating ACC (ACs purchased from Calgon, Pittsburgh, PA, USA) and ACNU (ACs purchased from Westvaco, Richmond, VA, USA) with HNO_3 were recorded as NO-ACC and NO-ACNU, respectively. The ACC and ACNU were oxidized at 400 °C and 350 °C, the heating rate is 58 °C min^{-1} , and then, 5 vol% O_2 flows under N_2 to modify for 3 h were recorded as O-ACC and O-ACNU, respectively. Comparing their adsorption properties, it is found that the adsorption performance of adsorbents showed an ascending order: ANCU < O-ACC < O-ACNU < ACC < NO-ACC < NO-ACNU. The increased adsorption performance of HNO_3 -modified adsorbents is mainly attributed to the increase in the acid oxygen-containing functional groups of COO on the ACC surface. However, the surface of ACC modified by oxygen oxidation tends to form a C=O functional group. Oxidation modification significantly changed the adsorption capacity of the adsorbent, and HNO_3 oxidation modification is an effective method to improve the adsorption performance of AC samples. Wen et al. [55] and Ania et al. [56] prepared adsorbents with a similar pore structure but different surface chemical properties for Nap removal. The products obtained from the physical activation of coal as the original adsorbent were oxidized with different concentrations of HNO_3 (20% and 60%) and ammonium persulfate. The results showed that the specific surface area and total pore volume of the adsorbent decrease after oxidation modification. In addition, the microporosity of the adsorbent after HNO_3 modification was more significant, indicating that new pores were generated during the oxidation modification process and the number of micropores increased. Both HNO_3 and ammonium persulfate modification changed the properties of the adsorbent surface and introduced a large amount of oxygen-containing groups. Nitric acid modification can introduce more functional groups on the surface of the adsorbent, while ammonium persulfate forms a more acidic carboxylic acid. The adsorption properties of different polar adsorbents for Nap in solution were studied: B > BS > BN20 > BN60 (B: activated carbon; BS: prepared by ammonium persulfate; BN20 and

BN60: prepared by wet oxidation with nitric acid at 20% and 60% concentrations), and they investigated how the polarity of the solution affects the interaction between the surface groups on the adsorbent. In a water medium, although the adsorbent is nonpolar, the surface acidity will also reduce its adsorption performance.

Xi et al. [57] prepared the adsorbent by using the acid hydrolysis method to modify bamboo, pine, pine needle, and pine bark plant residues to remove PAHs. The relationship between the adsorption of PAHs and the structural characteristics of biosorbents was studied. The results showed that the original skeleton of the material was not damaged by HCl modification, and the surface morphology of the modified adsorbent was more uneven and rougher than that of untreated BW (bamboo wood) and PN (pine needles). It indicated that the acid hydrolysis method removes polysaccharides from plant residues and increases the oxygen-containing functional groups of -COOH and -OH on the adsorbent surface, which improves the adsorption capacity of the adsorbent. The use of acid modification consumes the cellulose component of the plant residue adsorbent, which can significantly improve the adsorption capacity of the hydrolyzed biological adsorbent because the polar component of the plant-based adsorbent seriously inhibits the adsorption of polycyclic aromatic hydrocarbons by the adsorbent. Kong et al. [58] prepared soybean stalk-based carbons under different carbonization temperatures by using phosphoric acid activation and discussed the removal efficiency by the prepared carbon for phenanthrene, Nap, and acenaphthene. The results showed that the soybean stalk-based carbon adsorbents prepared by impregnation in 1 mol L⁻¹ phosphoric acid solution for 6 h and carbonization at 700 °C had a large specific surface area, which greatly increased the removal efficiency of Nap and showed a removal efficiency of Nap up to 100%.

Table 3. Summary of modification reagents, adsorption efficiency, and Nap adsorption capacity of raw and modified adsorbents.

Raw Adsorbent	Modification Reagents	Modified Adsorbents' Name	Nap Adsorption Efficiency	Adsorption Capacity (μg g ⁻¹)	Ref.
MC	HNO ₃	COMC	/	1.6 × 10 ³	[49]
MC	HNO ₃	Oxidized MC	100%	/	[53]
ACC/ ACNU	HNO ₃ /O ₂	NO-ACC/NO- ACNU/O-ACC/O- ACNU	100%	/	[54]
MCs	H ₂ SO ₄ /(NH ₄) ₂ S ₂ O ₈	MCS-S/MCS- N/MCS-NS	10%	/	[55]
B	HNO ₃ /(NH ₄) ₂ S ₂ O ₈	BN20/BN60/BS	/	4.7 × 10 ⁵	
BW/PW/PN/PB	HCl	BW-DS/PW-DS/PN- DS/PB-DS	/	2.8 × 10 ³	[57]
Soybean stalk-based carbon	H ₃ PO ₄	/	100%	3.02 × 10 ⁴	[58]
Bentonite	DPC	Organoclays	The K _d value of Nap increased from 0.151 to 1.675 L g ⁻¹ when the amount of DPC increased to 2.00 times the CEC.	1.75 × 10 ³	[59]
Kaolinite and Halloysite	HDTMA	-	When the HDTMA was 42% of CEC, the K _d of Nap increased from 0.9 to 109.	About 9.0 × 10 ²	[60]

MC: mesoporous carbon; COMC: chemically oxidized mesoporous carbon; ACC: ACs purchased from calgon; ACNU: ACs purchased from Westvaco; B: activated carbon; BS: prepared by ammonium persulfate; BN20 and BN60: prepared by wet oxidation with nitric acid at 20% and 60% concentrations; BW: bamboo wood; PW: pine wood; PN: pine needles; PB: pine bark; DPC: dodecylpyridinium chloride; CEC: cation exchange capacity; HDTMA: hexadecyltrimethylammonium.

2.2. Fatty Acid Modification

Several attempts have been made to improve the adsorption performance of the adsorbents by chemical acid modifications, which are simple and promise outcomes. As we all know, chemical acid modification can increase the affinity for hydrocarbons, but there are few studies on the removal of PAHs from aqueous solutions using fatty acid [61]. Zhu et al. [62] studied the fatty acid-modified (including capric acid, lauric acid, palmitic acid, and oleic acid) walnut shell (WNS) as an effective biological adsorbent for the adsorption efficiency of Nap in polluted water, as listed in Table 4. The results show that the relationship between the structure partition coefficients guides the selection of high-efficiency adsorbents, and the polarity and aromaticity of the adsorbents have an important influence on their adsorption performance. Compared with capric acid, lauric acid, and palmitic acid modified walnut shell, oleic acid grafted walnut shell (OWNS) has a strong adsorption capacity that reached 7210 mg g^{-1} (the room temperature at 298 K, the OWNS dosage is 1 g L^{-1} , an initial pH is 7.0, and contact time is 40 h), which was 85.3% higher than the raw WNS sample. Kumar et al. [63] used oleic acid to modify palm shell-activated carbon (PSAC) to improve the adsorption capacity of Nap. The results showed that the adsorption performance of Nap on the modified PSAC was greatly improved under the conditions of initial Nap concentration of 5 mg L^{-1} , pH value of 2.0, the dosage of PSAC of 5.0 g L^{-1} , contact time set at 90 min, and the temperature at 30°C ; the maximum adsorption capacity of PSAC reached 44.87 mg g^{-1} .

2.3. Alkaline Modification

The OH ion in the alkaline conditions not only can increase the concentration of oxygenated basic complexes on the adsorbent surface but also reacts with the surface functional groups of the adsorbent and creates more positive charges on the surface of the adsorbent [64,65]. In previous studies, it was found that activated carbon treated by alkali can improve the specific surface area and increase the surface hydrophobicity, which is suitable for the purification of a hydrophobic volatile organic compound [66,67]. Recently, biochar (wood, crop residue, sewage waste, wood, etc.) has been widely used as a valuable adsorbent to adsorption pollutants [68]. However, the physical and chemical properties of the adsorbents prepared by different biochar and modified reagents are quite different. Among many alkaline agents, NaOH has been the most commonly used for alkaline modification. This may be due to the strong ability of the NaOH reagent to decompose the internal structure of lignocellulose components inside the biochar, thereby enhancing the pore structure of the adsorbent [69,70].

Peng et al. [69] modified biochars that were prepared from rice husk and chicken manure by NaOH activation. They found that the pore size of the modified rice husk and chicken manure biochars modified by NaOH was mainly concentrated at 2 nm and 10 nm, respectively, and the total pore volume and surface area are greatly increased. In addition, it can increase the aroma of rice husk biochar modified by NaOH agent, that is, increase the content of aromatic functional groups on the surface of bio-carbon, which provide more adsorption sites for rice husk biochar and thus improve its adsorption capacity. Liu et al. [70] prepared the modified biochar adsorbents from chicken manure by NaOH. The results showed that the content of the C=O functional group and the active sites were enriched, and the adsorption capacity of Nap was improved. In general, the aromatic functional groups formed on the surface of the adsorbent modified by NaOH are the main factors to enhance its adsorption performance.

3. Salt Modification

Currently, many researchers have used salt modification methods to improve some adsorbents' performance because of their good chemical stability. Halides are representative of salt modification, and halogen and chlorine are the most widely used in the salt modification of adsorbent materials. Numerous investigations have demonstrated that halides modification can greatly enhance the adsorption capacity of adsorbents for Nap [59,71–73].

Table 4 summarizes the relevant information including the modification reagents, the name of the raw and modified adsorbents, the adsorption efficiency of Nap, and the maximum adsorption capacity of raw and modified adsorbents.

3.1. Bromide Modification

The brominated modified adsorbents can enhance the adsorption capacity to remove Nap from the aqueous solution. Hydrogen bromide, potassium bromide, ammonium bromide, and liquid bromine are the commonly used bromide reagents. However, the utilization of the bromide reagents to modified adsorbents to adsorb Nap has been rarely studied. Shi et al. [72] used dodecyl trimethyl ammonium bromide (DTAB) and sodium dodecylbenzenesulfonate (SDBs) to modify the crude bentonite. The results showed that the layered silicate structure of the bentonite was unaltered after modification, and the binding of dodecyl trimethyl-ammonium cation and dodecyl sulfonate anion to bentonite improves the adsorption capacity and removal efficiency for Nap, which were 0.604 mg g^{-1} and 99.1%, respectively. Gan et al. [73] selected anion–cation (hexadecyl trimethyl ammonium bromide: tetramethyl ammonium bromide = 3:1) to modify bentonite. The results prove that the modified bentonite adsorbs Nap up to 99.4%, and its cation exchange capacity increases by 1.6 times.

Table 4. Summary of the modification reagents, the name of the raw and modified adsorbents, the adsorption efficiency of Nap, and the maximum adsorption capacity of modified adsorbents.

Raw Adsorbent	Modification Reagents	Name of Modified Adsorbents	Nap Adsorption Efficiency	Adsorption Capacity	Ref.
WNS	fatty acid	OWNS/CWNS/LWNS/PWNS	85.3%	7210 mg g^{-1}	[62]
PSAC	oleic acid	/	/	44.87 mg g^{-1}	[63]
bentonites	DTAB/SDBs	modified bentonite	99.1%	0.604 mg g^{-1}	[72]
bentonite	ammonium bromide	modified bentonite	99.4%	/	[73]
bentonite	DPC	CEC	55–60%	1.675 L g^{-1}	[59]
zeolite	APTMS	NH_2 -zeolite	93.95%	1.88 mg g^{-1}	[74]
SWNTs	hole doping	(10, 0) SWNTs	/	/	[75]
c-HAp	DP	10 DP-HAp	/	7.22 mg g^{-1}	[76]
SBA-15	NH_2	NH_2 -SBA-15	79.3%	1.92 mg g^{-1}	[11]
un-Ch	FeO/TiO_2	Ch- FeO/TiO_2	90%	149.3 mg g^{-1}	[77]

WNS: walnut shells; OWNS: oleic acid-grafted walnut shell; PSAC: palm shell-activated carbon; DTAB: dodecyl trimethyl ammonium bromide; SDBs: sodium dodecylbenzenesulfonate; DPC: dodecylpyridinium chloride; APTMS: 3-aminopropyltrimethoxysilane; SWNTs: single-wall carbon nanotubes; c-HAp: converted hydroxyapatite, DP: dodecylphosphate; SBA-15: SBA-15 mesoporous silica; un-Ch: unmodified chitosan; Ch- FeO/TiO_2 : chitosan beads modified with iron oxide (FeO) and titanium dioxide (TiO_2).

3.2. Chloride Modification

Compared to bromide, chloride is less active than bromide, but chloride has proved to be a stable, cheap, and effective chemical reagent that can be used for adsorbents modified to adsorb PAHs. Therefore, many researchers use chloride to modify adsorbents to adsorb Nap in the environment.

Changchaivong et al. [59] modified bentonite by dodecylpyridinium chloride (DPC). Specifically, eight organoclays were prepared by adding different levels of 0.25–2.00 times the cation exchange capacity (CEC) into sodium-rich bentonite and dodecylpyridinium chloride. The results indicated that the BET-specific surface areas of the eight organoclays were lower than that of the bentonite, while the adsorption capacity onto organoclays increased when the amount of DPC increased from 0.25 to 1.25 times the CEC. In addition, the adsorption isotherms of Nap indicated that the K_d value of Nap increased from 0.151 to

1.675 L g⁻¹ when the amount of DPC increased to twice that of the CEC. Bouiahya et al. [76] synthesized new hydrophobic surface apatite nanoparticles by grafting dodecylphosphate (DP). The results showed that the DP addition did not change the original substrate structure of the hydroxyapatite, but it enhanced their hydrophobicity and adsorption performance. It can be seen from the right of Figure 2a, initially, that the hydroxylapatite is hydrophilic because the OH groups on the particles form hydrogen bonds in the solution and then sink under their weight. After the introduction of the DP molecules, as shown in Figure 2b, the DP molecules are grafted onto the surface of the hydroxylapatite, reducing the OH contact with the aqueous solution, thus enhancing its hydrophobicity, which can also be verified in the left of Figure 2a; 10 DP-HAp is floating in aqueous solution and has good hydrophobicity. In addition, the hydroxyapatite has a higher adsorption performance of Nap after DP modification. In addition, the adsorption experimental results show that the equilibrium adsorption capacity of 10 DP-HAp to Nap is 7.22 mg g⁻¹, which is much higher than that of the raw HAp (2.84 mg g⁻¹), which proves that the DP addition greatly enhances the adsorption capacity of hydroxyapatite.

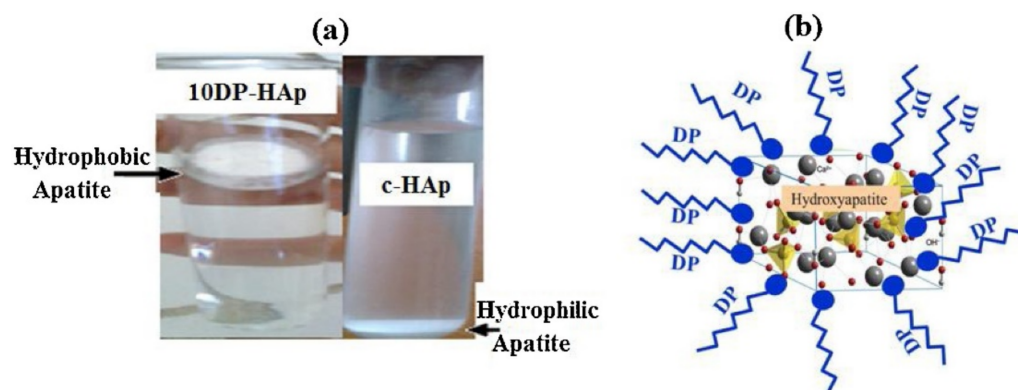


Figure 2. (a) Picture showing the transformation of the surface properties of the material, going from a totally hydrophilic character for the pure c-HAp (right) to a hydrophobic surface-modified behavior for the 10 DP-HAp hybrid material (left). (b) Schematic showing the hydrophobic surface modification of the Hap nanoparticles with a DP coupling agent.

4. Amino Modification

It was found that increasing the number of amino functional groups on the surface of the adsorbents could increase the number of positive charges in the adsorbents that enhance the adsorbents' capacity [74]. As we all know, positive and negative electrons can build up weak interaction, and this interaction usually leads to the formation of charge transfer complexes that can be used to adsorb aromatic pollutants [11].

Wang et al. [74] prepared five kinds of amino functionalized hydrophobic zeolite adsorbent by using 3-aminopropyltrimethoxysilane to modify the natural clinoptilolite. It is found that water vapor adsorption on 20% amino functionalized zeolite samples is lower than on the unmodified zeolite sample, which indicated that the hydrophobicity significantly improves after amino modification. In addition, the specific surface area of 20% amino functionalized zeolite decreased compared with that of the raw zeolites, but the chemical functional groups on the surface increased. The constants n and KF of Freundlich for the raw zeolites (0.382 and 0.241) are much lower than that of 20% amino functionalized zeolite (0.717 and 3.043), and the adsorption experiment showed that the adsorption performance and removal efficiency of Nap was rising from 1.63 mg g⁻¹ and 81.67% to 1.88 mg g⁻¹ and 93.95%, respectively. This illustrated that implanting amino groups on the surface of the zeolite can enhance the adsorption capacity and removal efficiency.

Figure 3 shows the modification process of natural zeolite and the adsorption process of chromate and Nap on amino-functionalized hydrophobic zeolite. The amino functionalized hydrophobic zeolite was formed by reacting the -OCH₃ group in 3-

aminopropyltrimethoxysilane with the -OH group on zeolite. At acidic pH, the amino group can be ionized and thus positively charged. In addition, the surface of zeolite shows good hydrophobicity due to the hydrocarbon chain of the silane coupling agent. This amino-functionalized hydrophobic zeolite can be used to remove anions (such as chromate ions) and hydrophobic pollutants (such as Nap), which is proved by adsorption experiments.

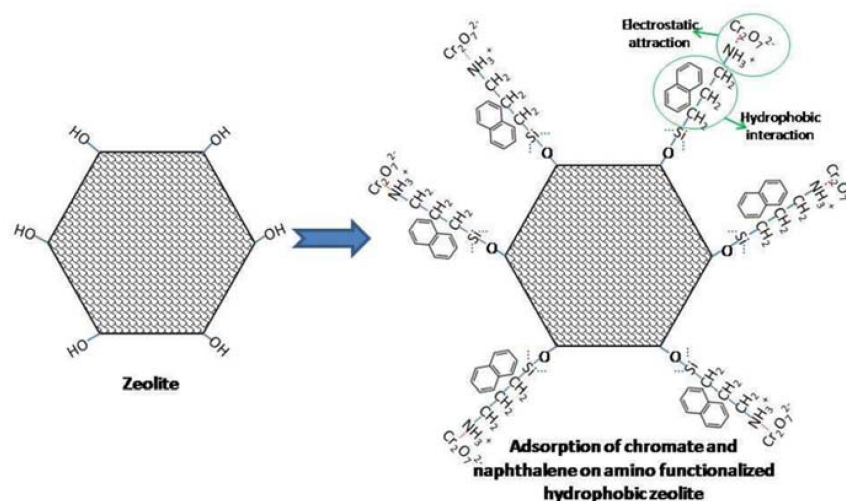


Figure 3. Schematic diagram of the modification of natural zeolite and the adsorption process of on chromate and Nap on the amino functionalized hydrophobic zeolite.

Hashemi et al. [11] grafted NH_2 onto the SBA-15 mesoporous silicon to enhance the adsorption capacity of PAHs, and the XRD results indicate that NH_2 modification does not damage the $P6$ mm hexagonal structure. In addition, the FTIR results confirmed that amine groups were incorporated in the silicate frameworks after NH_2 modification. After NH_2 modification, the adsorption capacity of NH_2 -SBA-15 to Nap, acenaphthene (ACN), and phenanthrene (PHN) followed $\text{Nap} > \text{ACN} > \text{PHN}$. Under the same conditions (initial PAH concentration of 18 mg L^{-1} , pH 5, dosage of 3 g L^{-1} , and temperature of 25°C), the adsorption performance of NH_2 -SBA-15 ($0.6\text{--}1.7 \text{ mg g}^{-1}$) is about two to four times higher than SBA-15 ($0.1\text{--}0.85 \text{ mg g}^{-1}$). This result indicates that amine groups are the key to enhancing the adsorption capacity.

5. Doping Modification

Doping some elements or compounds on the surface of materials by physical or chemical methods thereby changes the properties or structural characteristics of the original matrix materials and expands their application range.

Wang et al. [75] studied the effect of hole doping on the selectivity of Nap toward single-wall carbon nanotubes. The results of the Nap adsorption experiment showed that the amounts of charge transfer of Nap to the four single-wall carbon nanotubes (SWNTs) ((10, 0), (6, 6), (8, 0), and (5, 5) SWNT, respectively) increase with rising hole doping, and the adsorption strengths of Nap on the four SWNTs also monotonically increase. Moreover, Nap adsorption on the (6, 6) SWNT was better than that of (10, 0) SWNT, and Nap adsorption on the (5, 5) SWNT was favorable than (8, 0) SWNT. However, when the hole concentration exceeds $8 \times 10^{-3} \text{ eV}$ per C atom, the (10, 0) SWNT with larger-sized exhibits stronger Nap adsorption than smaller-size (5, 5) SWNT.

Alfonso et al. [77] prepared chitosan-based beads doped with FeO and TiO_2 nanoparticles and studied their adsorption mechanism toward Nap in solution. The results show that the chitosan after FeO and TiO_2 nanoparticles modification (Ch-FeO/ TiO_2) have higher adsorption performance (33.1 mg g^{-1}) than the unmodified chitosan (un-Ch, 29.8 mg g^{-1}). The adsorption mechanism of Nap on un-Ch and Ch-FeO/ TiO_2 was studied by using the

intraparticle diffusion model. As can be seen from Figure 4, the main adsorption behavior of Nap is carried out from the liquid phase to the surface of the material based on film diffusion and particle diffusion, respectively. The adsorption curve in Figure 4 can be divided into three stages. In the first stage, the adsorbent adsorbed Nap rapidly because of the large number of active sites. The slow interparticle diffusion between the layers of the adsorbate occurs in the second stage. The third stage shows that with the decrease in the active sites in the adsorbent, the interparticle diffusion decreases until reached the adsorption equilibrium.

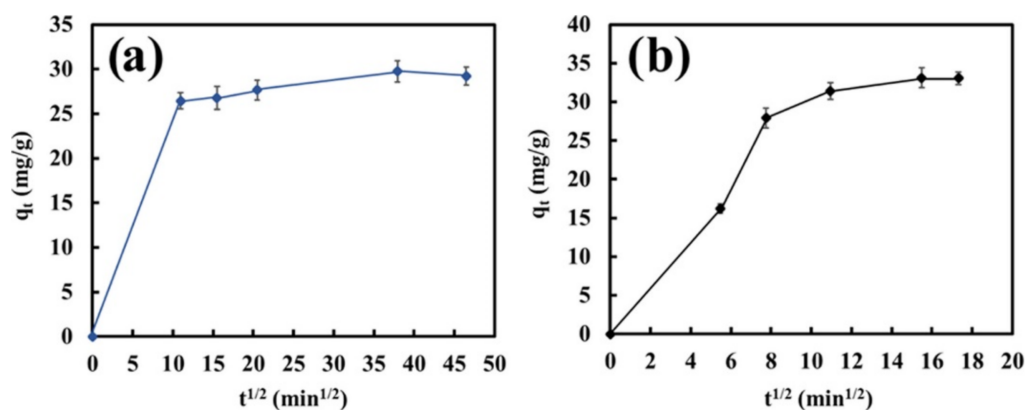


Figure 4. Description of the adsorption mechanism using the intraparticle diffusion model for (a) un-Ch and (b) Ch-FeO/TiO₂.

6. Microwave and Plasma Modification

6.1. Microwave Modification

The conventional chemical reagents mentioned above such as acid, metal, alkali, and halogen modify raw adsorbents to enhance the adsorbent adsorption capacity. However, this method still has some shortcomings, such as easily producing secondary chemical pollution, destroying the structure of the adsorbent, and being time-consuming. Therefore, many researchers study physical modification methods to modify adsorbents to improve their adsorption performance.

Heat modification is the most common means of physical modification. Compared with other heat modifications, microwave modification has the advantages of fast temperature rise, good surface functionalization, energy saving, and uniform heating temperature for adsorbents of different shapes and sizes [78]. The microwave energy is transferred to the material through the interaction between molecules, and the material can be heated uniformly and rapidly [79]. The temperature difference between the surface heat of the sample material and the internal heat of the material will lead to higher energy consumption and a longer activation time [80]. The intermolecular interactions promote the microwave energy transferred to the inner of the material, and the microwave energy is converted into heat energy through the ion conduction and dipole rotation, thus realizing a uniform and fast heating of the thick materials [81]. In addition, microwave modification may appear as new or unique microstructures on the surface of the materials and trigger many chemical reactions that cannot be achieved by conventional heating.

The modification of adsorbents by microwave irradiation has attracted extensive attention over recent years. Some researchers [5,82–85] use microwave irradiation to modify the adsorbent to improve the adsorption performance of PAHs. Microwave activation can improve the specific surface area, microporous volume, and total pore volume of the adsorbent, and improve the adsorption performance of Nap. However, it can also be found that although the pore structure of the adsorbent is improved after microwave activation, the adsorption rate of Nap by the adsorbent is decreased. Ge et al. [82,83] studied the effects of microwave irradiation, microwave-assisted nitric acid, and iron modification on the adsorption capacity of coal-based activated carbon for Nap. The results showed

that microwave radiation could effectively increase the specific surface area and pore volume of coal-based activated carbon and enhance the adsorption ability of Nap. The best effect was obtained when the microwave power was 500 W; at the same time, it also has a strong regeneration performance. When the microwave power was 500 W for 8 min with 20% nitric acid treatment for 16 h, the modified coal-based activated carbon with strong adsorption capacity is obtained. The micropore's specific surface area and the adsorption capacity increased by 51.0% (from 191.42 to 390.85 m² g^{−1}) and 25.84% (from 47.85 to 64.52 mg g^{−1}), respectively. The experiment of iron-modified coal-based activated carbon by microwave radiation showed that optimum effect is obtained at 0.05 M of Fe(NO₃)₃ when the microwave power was 300 W. At this time, the specific surface area of activated carbon increased greatly, and the adsorption capacity of Nap increased from 95.74 to 160.88 mg g^{−1}. Sun et al. [5] used a cationic surfactant to modify activated carbon through microwave heating, enhancing the adsorption capacity of Nap. The results showed that the specific surface area and mesopore volume of the modified activated carbon was significantly improved. In addition, after modification, the average pore size increased from 0.79 to 0.93 nm, and its adsorption performance was improved from 152.831 to 192.502 mg g^{−1}.

6.2. Plasma Modification

Nowadays, plasma treatment with the characteristics of solvent-free, rapid, non-toxic, energy saving, etc., is a green and environmentally friendly modification method to improve the adsorption capacity of the adsorbents. During the plasma discharge, a large number of active species, such as free radicals, electrons, and ions are produced, which act on the surface of the adsorbent to form new pores and react with chemical composition to form new functional groups [85–88]. In addition, NTP acts only on a nano-scale without damaging the matrix properties of the sorbent [89].

Figure 5a,b show the schematic diagrams of the plasma modification device. It can be seen that the plasma modification process does not need chemical reagents, and the device is simple. In our previous studies, Wang et al. [85] modified the macroporous resin XAD-2 by using the line-tube dielectric barrier discharge (DBD) plasma under air/oxygen conditions. The results showed that the adsorbents treated by oxygen plasma had good adsorbability of Nap. The results analyzed by FTIR and XPS show that plasma modification increases the amount of oxygen-containing functional groups (C=O and -COOH) on the surface of the adsorbent. In our other literature [86], we modified macroporous adsorption resin XAD-2 with plate-plate DBD plasma at atmospheric pressure to change the pore structure and active sites on the resin for Nap removal. The results showed that a new type of resin with a large amount of micro-mesoporous pore size was obtained after plasma treatment. The adsorption performance of the resin after plasma modification is rapidly improved, which is attributed to the increase of the porosity, the number of micro-mesoporous pore sizes, and the content of C=O functional groups.

Figure 6 shows the interaction between the plasma and the surface of the XAD-2 resin. The high-energy electrons and the active species in the plasma play a key role during the modification process. Firstly, the high-energy electrons in plasma have enough energy to break the common chemical bonds in the XAD-2, forming new chemical bonds on its surface. Secondly, many strong oxidizing active species in the plasma, especially O₃, OH, and O, react with the surface of the XAD-2. Part of the reaction produces CO₂ and H₂O separated from the resin itself and forming new pore channels on the surface; the other part forms a substance that has the functional groups of C=O and O-C=O on the surface. The change of surface chemical property and pore structure of XAD-2 is an important reason to improve the adsorption performance.

Nap in the environment. The adsorption capacity of the adsorbent is the key to this method. In response to current environmental challenges, the adsorption capacity and regeneration performance of modified adsorbents by different methods are enhanced. This work reviews the applications of different modification methods (such as oxidative acid and alkaline modification, halide modification, microwave modification, and plasma modification method) on zeolites, biosorbents, macroporous resin, and activated carbon materials. These methods can be divided into chemical and physical modification whether the chemical reagent was used. Chemical modification methods include oxidation acid, alkali, and the halide modification method, while physical modification methods include microwave irradiation and plasma treatment methods.

Oxidative acid and alkaline modification can add oxygen-containing groups and nitrogen-containing groups on the surface of the adsorbent by reacting with surface carbon-based substances, thereby greatly enhancing the adsorption ability of adsorbents. Through the halide modification process, more X-covalent bonds on the surface of adsorbents were generated, improving the adsorption performance of adsorbents. However, there are still some shortcomings of these wet modification methods, such as easily damaging the material substrate and causing secondary pollution, so it is necessary to develop economical, green, and efficient modification methods.

Microwave radiation can heat the material evenly and rapidly and enrich the surface pore structure of the material. However, the microwave radiation modification results in the loss of many chemical adsorption sites on the surface of the adsorbent, which reduced the adsorption capacity of Nap. Therefore, microwave radiation is often accompanied by chemical reagents. There are many active species in plasma, such as free radicals, electrons, and ions, which acts on the surface of the adsorbent to form new pores and react with chemical composition to form new functional groups (C=O, -COOH, etc.), thus improving the adsorption performance of Nap. Plasma treatment does not need the assistance of chemical reagents without damaging the matrix properties of the sorbent.

The presented case studies show that the enriched mesoporous, microporous, and C=O functional groups can greatly enhance the adsorption of Nap. In addition, increasing the porosity of the adsorbent can increase the number of adsorbent cycles.

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