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Recent developments in synthesis of attapulgite composite materials for refractory organic wastewater treatment: a review

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Attapulgite clay, due to its unique crystalline hydrated magnesium–aluminium silicate composition and layer-chain structure, possesses exceptional adsorption and catalytic properties, which enable it or its composites to be utilized as adsorbents and catalysts for wastewater treatment. But the drawbacks of attapulgite are also very obvious, such as relatively low specific surface area (compared to traditional adsorbents such as activated carbon and activated alumina), easy aggregation, and difficulty in dispersion. In order to fully utilize and improve the performance of attapulgite, researchers have conducted extensive research on its modification, but few specialized works have comprehensively evaluated the synthesis, applications and challenges for attapulgite-based composite materials in refractory organic wastewater treatments. This paper provides a comprehensive review of controllable preparation strategies, characterization methods and mechanisms of attapulgite-based composite materials, as well as the research progress of these materials in refractory organic wastewater treatment. Based on this review, constructive recommendations, such as deep mechanism analysis from molecular level multi-functional attapulgite-based material developments, and using biodegradable materials in attapulgite-based composites, were proposed.

1 Introduction

Organic pollution, particularly refractory organic pollution, poses a significant global environmental challenge due to its profound toxicity to living organisms and humans. Refractory organic pollutants (ROPs) comprise a diverse range of highly toxic compounds, including halogenated organics, surfactants, nitro compounds, heterocyclic compounds, phenolic compounds, and polycyclic aromatic hydrocarbons. These compounds are notoriously resistant to microbial degradation, often undergoing slow and incomplete decomposition. Many ROPs exert harmful effects on human health and the environment, with some even possessing carcinogenic properties.

The primary sources of wastewater contaminated with refractory organics stem from various chemical industries such

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Table 1 Types and hazards of refractory organic substances

Refractory organics	Sources	Harmful effects	References
Polycyclic aromatic hydrocarbons compounds (PAHs), such as naphthalene, anthracene, phenanthrene, pyrene, *etc.*	Wood and coal burning, petrol and diesel combustion, industrial discharge, vehicular emission, *etc.*	Carcinogenic, teratogenic, mutagenic and toxic	1–5
Heterocyclic compounds, such as furan, pyrrole, thiophene, *etc.*	Domestic sewage treatment plants and some chemical engineering industries such as textile, dyestuff, pharmaceutical and chemical productions	Stable in nature, easy to bioaccumulate, mutagenic and carcinogenic	6–8
Organic cyanides, such as acetonitrile, propionitrile, acrylonitrile, *etc.*	Coking, electroplating and pharmaceutical industries	Highly toxic. Short-term exposure to cyanide could cause shortness of breath and neurological diseases, and prolonged exposure would lead to nerve damage and even death	9–11
Synthetic detergents, such as sodium alkylbenzene sulfonate, sodium fatty alcohol sulfate, *etc.*	Laundry wastewater originated from households, industries and hospitals	Foaming thus affects biological treatment effect and has solubilization effect on polycyclic aromatic hydrocarbons	12 and 13
Polychlorinated biphenyls (PCBs), from PCB3 to PCB10	Preparation of capacitors and transformers, oil for chemical engineering	Entering the human body through the food chain, causing acute poisoning and carcinogenesis to the human body	14 and 15
Plasticizers, such as phthalates, aliphatic dicarboxylic esters, fatty acid esters, *etc.*	Plastic products	It is stable and has inhibitory effect on human central nervous system	16
Synthetic pesticides, such as organochlorine pesticides, organophosphorus pesticides, *etc.*	Agricultural fields and non-agricultural settings such as households, industries, sport fields and other urban green areas	Toxic and carcinogenic to humans	17 and 18
Synthetic dyes, such as methylene blue, orange II, methyl violet, *etc.*	Textile industry	High chroma, toxic and carcinogenic	19 and 20

as coking, pharmaceuticals (encompassing traditional Chinese medicine), petrochemicals/oil, textiles/printing and dyeing, and paint manufacturing. Table 1 provides a comprehensive overview of common refractory organics, detailing their sources and associated hazards. This type of wastewater typically exhibits a complex mixture of refractory organics and salts, characterized by high concentrations and poor biodegradability.

The pervasive threat posed by refractory organic compounds to human health and ecological systems underscores the critical importance of addressing their pollution control. As such, the exploration of effective strategies for alleviating refractory organic pollution has emerged as a vital research focus within the environmental protection domain.

In recent decades, significant research efforts have been devoted to developing treatments for refractory organic pollutants.[21,22] A range of techniques has been explored for their removal, including adsorption,[23,24] biological treatment processes,[25–27] membrane separation,[28,29] catalysis,[30,31] and advanced oxidation processes.[32,33]

Notably, catalytic oxidation processes have made considerable progress in treating refractory organics. These processes encompass photocatalytic oxidation,[23] catalytic wet air oxidation,[31] electro-catalysis,[21,34,35] Fenton catalysis,[36–40] semiconductor catalysis, and heterogeneous catalysis.[35,41–43] Among these, heterogeneous catalysis has emerged as a particularly promising approach due to its ability to generate hydroxyl radicals ($^{\bullet}OH$) and holes with strong oxidizing power. These radicals can effectively decompose toxic, harmful, and non-biodegradable macromolecular organic compounds into non-toxic, biodegradable small molecular organic substances.

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Heterogeneous catalysis offers advantages such as a wide pH range, no secondary pollution, and good reusability.[44–46]

Heterogeneous catalysts can be broadly categorized into bulk catalysts and supported catalysts. Catalytic reactions primarily occur on the surface of these catalysts. Supported catalysts are particularly advantageous due to their high surface area and abundance of active sites, which enhance their catalytic efficiency compared to bulk catalysts.[47] Supported catalysts typically utilize porous materials as supports, including carbon,[48,49] graphene and its derivatives,[50,51] oxides such as ZnO, SiO_2, Bi_2O_3,[52–54] and clays.[55,56] The active components, which can be metals or metal oxides, are deposited onto the surface of these supports to form the catalysts.

2 Attapulgite

Clays, including montmorillonite, kaolin, bentonite, and attapulgite, have found application as natural, economical supports for heterogeneous catalysis in wastewater treatment.[57–60] Among these, attapulgite clay distinguishes itself with its distinctive crystalline hydrated magnesium–aluminium silicate composition and its unique layer-chain structural arrangement. It exhibits exceptional dispersibility, high-temperature resistance, salt resistance, and strong adsorption capabilities, alongside good plasticity and cohesion.[61,62] These attributes make it a versatile material for use as an adsorbent or catalyst support in the removal of hazardous substances.[57–59]

Structurally, attapulgite belongs to the monoclinic system and features an acicular, slender hollow tubular structure reminiscent of amphibole asbestos. Its ideal molecular formula is $Mg_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$, and a diagram of its crystal structure is presented in Fig. 1. This structure consists of eight Si–O tetrahedrons arranged in 2 : 1 layers that extend along the *C*-axis, and cations like Mg^{2+} and Al^{3+} are filled in coordination octahedra formed by –O– and –OH, that is, two layers of silicon-oxygen tetrahedrons sandwich a layer of magnesium (or aluminium)- oxygen octahedron, creating pores parallel to the *C*-axis between the $[Si_4O_{10}]$ zones. These pores, with cross-sectional radii ranging from 0.37 to 0.64 nm, are occupied by water molecules. Some of this water is zeolite water aligned with the fiber axis, while the rest is crystalline water coordinated with magnesium ions.[63,64]

Attapulgite's distinctive structure, characterized by a high specific surface area and an unbalanced charge surface due to its crystalline morphology and abundant internal channels, endows it with remarkable properties such as excellent adsorption, catalytic activity, heat resistance, and rheological behavior. These qualities have led to its widespread application across various domains,[65–70] as illustrated in Fig. 1.

In addition, the crystalline water in the structure of attapulgite is located on the surface of its channel, facilitating the formation of hydrogen bonds with the adsorbate entering the channel.[61,62] Consequently, the surface of attapulgite is rich in adsorption active sites, exhibiting a preference for the adsorption of polar molecules like water. Additionally, attapulgite clay boasts impressive thermal stability and mechanical properties, rendering it a versatile material commonly employed as a purifier, decolorizer, filter aid, and deodorant.[65–68,70]

Although the unique structure and properties of attapulgite give it potential application advantages, its drawbacks are also obvious: the specific surface area of attapulgite is still relatively low compared to other commonly used adsorbents (such as activated carbon, activated alumina, *etc.*), it is easy to agglomerate, not easy to disperse, has poor compatibility with other

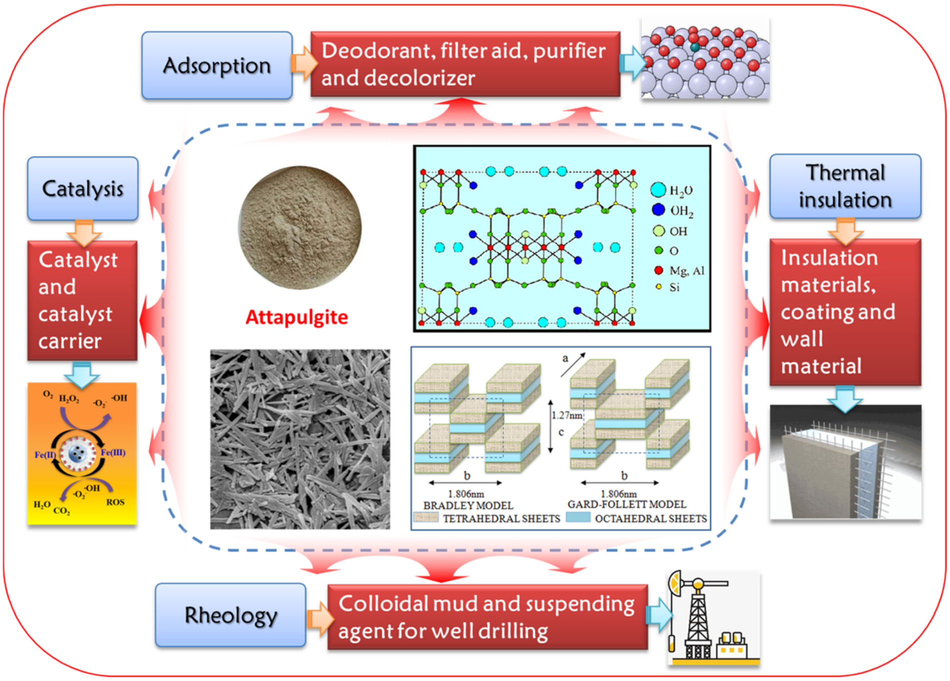

Fig. 1 The schematic diagrams of attapulgite crystal structure and its properties and usages.

substances, and the active substances are not easily uniformly loaded during the preparation of catalysts. To address the aforementioned issues, researchers have undertaken various modifications to attapulgite or have compounded it with other substances. These modifications aim to boost its specific surface area, enhance conductivity, and mitigate its aggregation tendencies. Additionally, the modifications enable uniform loading of active substances, increase the number of effective catalytic active sites, and ultimately improve the catalytic performance of the materials. Until now, there is a lack of comprehensive and multi-dimensional literature summarizing the latest progress in the application of modified attapulgite for the removal of refractory organics from water, particularly addressing the technical challenges and future research avenues. A systematic review of the latest achievements in attapulgite-based material development and mechanism exploration is crucial for guiding future research efforts and promoting the large-scale application of these materials for the removal of refractory organics from water. This review illuminates diverse types of attapulgite-based materials, detailing their preparation methodologies, characterizations, applications, and mechanisms, and it also highlights the associated challenges and recommendations of improvement in this field of research.

3 Modifications of attapulgite and their utilizations in treating refractory organics

To enhance the specific surface area, porosity, adsorption capacity, and catalytic performance of attapulgite, it is commonly modified or combined with various functional materials. The modification of attapulgite can be achieved through numerous techniques, which can be broadly categorized based on the type of modifier used: heat modification, acid/alkaline/salt modification, organic modification, carbon-based materials modification, and metals/metal oxides modification.

Heat and acid/alkaline/salt modification are straightforward methods, primarily aimed at increasing the specific surface area of attapulgite by removing water, melting impurities and facilitating ion exchange. Liu *et al.*[71] have conducted a relatively in-depth discussion on these modifications, and we will not elaborate those further. Instead, this paper will primarily explore the organic modification, carbon-based materials modification, and metals/metal oxides modification of attapulgite.

3.1 Organic modification of attapulgite

Organic modification involves the introduction of organic functional groups onto the surface of attapulgite, which can improve its compatibility with organic systems and enhance its adsorption properties. Organic modifiers commonly used for this purpose include surfactants, silane coupling agents, and polymers (Fig. 2). The are three typical ATP organic modification methods:

(1) Grafting: this method often uses surfactants as modifier to change the ATP's surface functional groups, improving its wettability, dispersibility, and compatibility with organic matrices. Grafting can be achieved through chemical reactions that create covalent bonds between the organic molecules and the ATP.

(2) Silane-coupling: silane coupling agents are used to modify the surface of ATP and change its hydrophobicity. These agents react with the hydroxyl groups on the ATP surface, forming siloxane bonds that introduce organic functional groups. This makes the ATP surface more hydrophobic, which can be beneficial for certain applications, such as the adsorption of organic compounds from aqueous solutions.

(3) Coating: coating involves the deposition of a thin layer of organic material onto the surface of ATP. This layer can be composed of polymers or other organic compounds and serves to change the surface structure of ATP. Coating can improve the mechanical properties, stability, and compatibility of ATP with organic media. It can also provide additional functional groups that can enhance the adsorption or catalytic properties of ATP.

3.1.1 Grafting on attapulgite. Grafting is considered as a promising approach for ATP modification, because grafting process can provide functional groups which show helpful properties for up-taking cationic, anionic and neutral pollutants from aqueous media,[72] which can help attapulgite to have a better adsorption ability. Typically, functional groups grafting on attapulgite was prepared by graft copolymerization reactions and attapulgite was often modified with surfactants. Take NH_2-grafted attapulgite as an example, the common modifiers are amino-terminated surfactants, such as polyacrylamide (PAM),[73] octadecyl trimethyl ammonium chloride (OTAC),[70,73] octadecyl trimethylammonium bromide (OTAB) and dioctadecyl dimethylammonium bromide (DDAB).[74] NH_2-grafted attapulgites had higher adsorption capacity than before modification, and they were used to adsorb dyes,[75,76] phenol,[65,77] tannin[68] and obtain high removal percentages. Attapulgite was also functionalized by chloroacetic acid (CA) with –COOH functional groups, improving its adsorption properties for MB and got 99.8% removal ratio after modified.[78]

3.1.2 Modification of attapulgite with coupling agents. Attapulgite is rich in Si–OH polar groups and can be modified by coupling agents to change its surface property from hydrophilic to hydrophobic. Silane coupling agents and titanate coupling agents are usually used to modified ATP, and silane coupling agents are the earliest developed and most widely used type of coupling agents.[79] Silane coupling agents can improve the surface properties of attapulgite at a very small dosage, take 3-aminopropyltriethoxysilane (APTES)[75] as an example, its modification mechanisms are as follow: APTES first hydrolyzed then combined with ATP by hydrogen bond, the hydroxyl on ATP surface was replaced by silyl group and its surface changed from hydrophilic to lipophilic, which makes ATP adsorb some oil pollutants.

More researches on the modification of attapulgite by coupling agents are focused on the adsorption of heavy metals after modification, which will not be mentioned here.

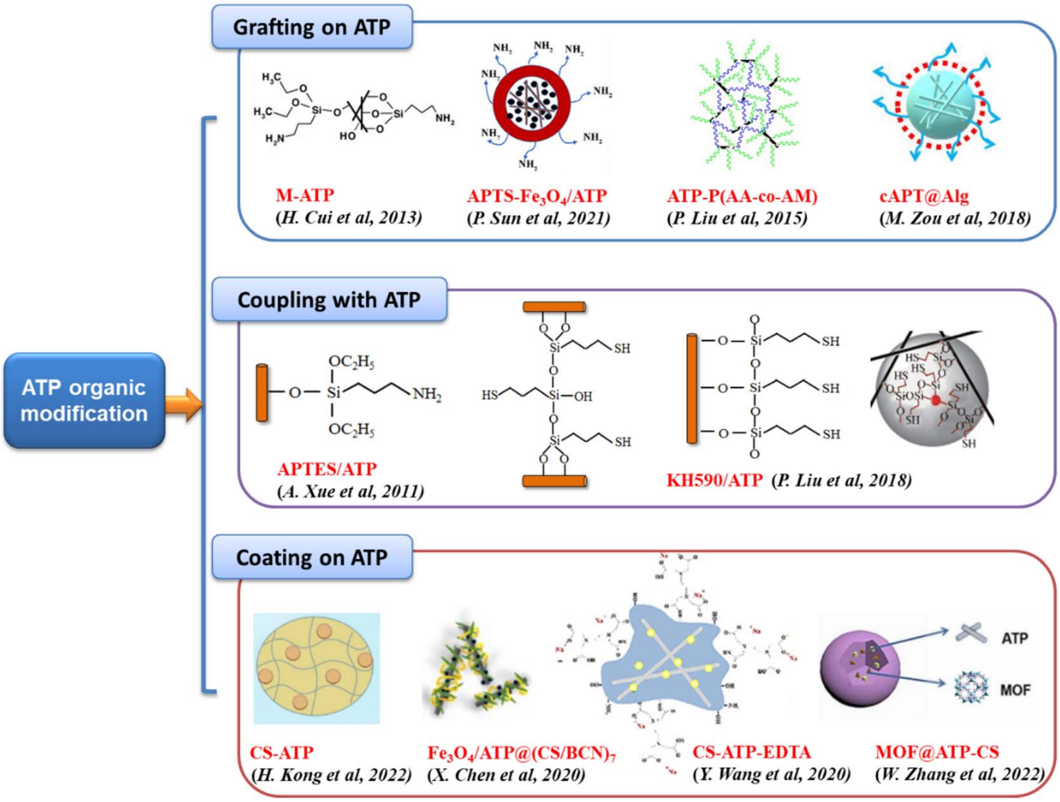

Fig. 2 ATP organic modification methods.[75,86–94] Copyright 2024, Elsevier.

3.1.3 Modification of attapulgite with polymers. Polymer compounds, such as chitosan, polyaniline and polyurethane, can be used to prepare various of adsorbents by coating on the surface of ATP with non-covalent bond. Chitosan itself can be used as adsorbent for dyes, organic pesticides, fats, heavy metals and other toxic substances in wastewater due to its active sites $-NH_2$ and –OH. Based on this, chitosan can be used to wrap ATP and promote adsorption capacity. Chitosan-coated attapulgite (CCATP) was prepared for removing the organic pollutant tannic acid (TA) from aqueous solution with maximum sorption capacity of 68 mg g^{-1}.[80] Chitosan functionalized attapulgite clay nanoparticle adsorbent (ATP@CCS) was fabricated by hydrothermal carbonization of chitosan at a mild temperature and applied for methylene blue (MB) removal from wastewater, and the calculated maximum adsorption capacity could be up to 215.73 mg g^{-1} at 318.15 K.[81] Sun *et al.*[82] fabricated a composite CPA composed of uniform purified attapulgite (PA) nanorods modified by chitosan under acetic acid conditions. Benefiting from the mesoporous structure of the PA nanorods and the carboxyl groups of chitosan, the prepared hybrid CPA exhibited a quick response (2 min for 80% removal ratio) and excellent adsorption capacity (the maximum adsorption capacity could reach 112.07 mg g^{-1}) towards HA.[82]

After coating attapulgite with polyaniline or polyurethane, nitrogen containing groups are introduced to the surface of attapulgite, which makes it have good adsorption effect on heavy metals and organic pollutants. Wang *et al.*[83] used polyaniline coated attapulgite to remove humic acid in water, and the adsorption effect of coated attapulgite was significantly higher than that of unmodified attapulgite, the maximum adsorption capacity can reach 61.35 mg g^{-1}. Dong *et al.*[84] prepared a series of polyurethane–attapulgite porous (HATT/PU) materials for the removal of MG dye from aqueous solutions, and at the optimum conditions, the porous material had the highest adsorption ratio of 99.51%.

3.1.4 Combination attapulgite with COFs. Jia *et al.*[85] reported a facile synthetic method of attapulgite@covalent organic frameworks (ATP/COFs). Covalent organic frameworks were synthesized from 1,3,5-triformylphloroglucinol and *p*-phenylenediamine, which were grafted onto attapulgite at room temperature, and the composite was synthesized. The extracting ratios of pyrethroids by ATP/COFs ranged from 71.2% to 88.7%. The removal ratios of methyl violet and tetracycline were still remained at 77.6% and 60.2% of the initial adsorption capacity after ten adsorption–regeneration cycles *via* a facile thermal regeneration strategy.

3.2 Modification attapulgite by carbon-based materials

Carbon-based materials modification, typically involves the incorporation of carbonaceous materials like activated carbon or carbon nanotubes, which can significantly improve the porosity and adsorption capacity of attapulgite.

3.2.1 Combination attapulgite with carbon. Carbon is often used as an additive for attapulgite to enhance its specific surface area (Fig. 3 left). Tang *et al.*[95] developed a cost-effective attapulgite/carbon (APT/C) composite for wastewater treatment using waste hot-pot oil as a carbon precursor through a facile one-step calcination process. The optimal adsorption capacities reached 215.83 mg g^{-1}, and 256.48 mg g^{-1} for methyl violet and tetracycline, respectively. Furthermore, they[96] fabricated magnetic attapulgite/carbon supported NiFe layered double hydroxides (APT/C@NiFe-LDHs) based on the spent bleaching earth *via* a facile and green hydrothermal approach. The composites exhibited excellent adsorption capacities for methylene blue and chlortetracycline hydrochloride of 271.28 and 308.21 mg g^{-1}, respectively. Li *et al.*[97] used a novel low-cost clay–biochar (APB) composite with potato stem and natural attapulgite to enhance the removal efficiency of Norfloxacin (NOR) from aqueous solution. Batch sorption experiments indicated that NOR was adsorbed to the clay–biochar strongly with a maximum sorption capacity of 5.24 mg g^{-1}, which was about 1.68 times higher than the pristine biochar (PB).

3.2.2 Combination attapulgite with graphene oxide (GO). Graphene oxide (GO), as a graphene derivative, is a two-dimensional (2D) structure material. GO (or rGO) is often combined with metals, metal oxides, polymer materials as precursor or support carrier due to its special characters of easy to functionalize and high controllability, it can also provide large specific surface area to make the attached materials disperse uniformly and prevent agglomeration.[98,99] Recent researches on combination ATP with GO are about making composite membranes or catalysts. Cui *et al.*[100] successfully constructed a three-dimensional attapulgite (APT) layer with a sandwich-like structure through a gentle and widely applicable method, no need for any additional modification of the original membranes. This method employs ordinary material with underwater superoleophobicity towards the effective and fast separation of different oil-in-water emulsions and adsorption of organic dyes and heavy metal ions. Luo *et al.*[101] assembled an attapulgite (ATP) nanofibers/GO composite (ATP/GO) membrane by filtration of mixed aqueous colloidal suspensions of ATP and GO, which had a high water flux of 221.16 L m^{-2} h^{-1} bar^{-1}, 7.7 times higher than pure GO membrane. Wang *et al.*[102] successfully fabricated graphene oxide/attapulgite (GO/APT) composite membranes by the vacuum-assisted filtration for efficient dyes wastewater treatment. The water permeated flux was as high as 13.3 L m^{-2} h^{-1} of GO/APT membrane with preserving high rejection nearly to 100% for 7.5 mg per L Rh B wastewater under optimized conditions. Zhang *et al.*[103] prepared a novel rGO–ATP supported Fe_2O_3 catalyst for oxidation of ciprofloxacin and got over 80% removal ratio at optimal conditions.

3.2.3 Combination attapulgite with g-C_3N_4. g-C_3N_4 is a two-dimensional layered structure material similar to graphene. As a new non-metallic photocatalytic material, g-C_3N_4 has a wider absorption spectrum range and does not require ultraviolet light, it can play a photocatalytic role under ordinary visible light.[104,105] Liu *et al.*[106] synthesized attapulgite (APT) and C_3N_4 hybridized metal–organic frameworks (MOFs) *via* different strategies, and systematically studied its adsorption properties for alizarin yellow GG (AYGG). The result showed that APT/C_3N_4 had excellent adsorption capacity synthesized both by refluxing

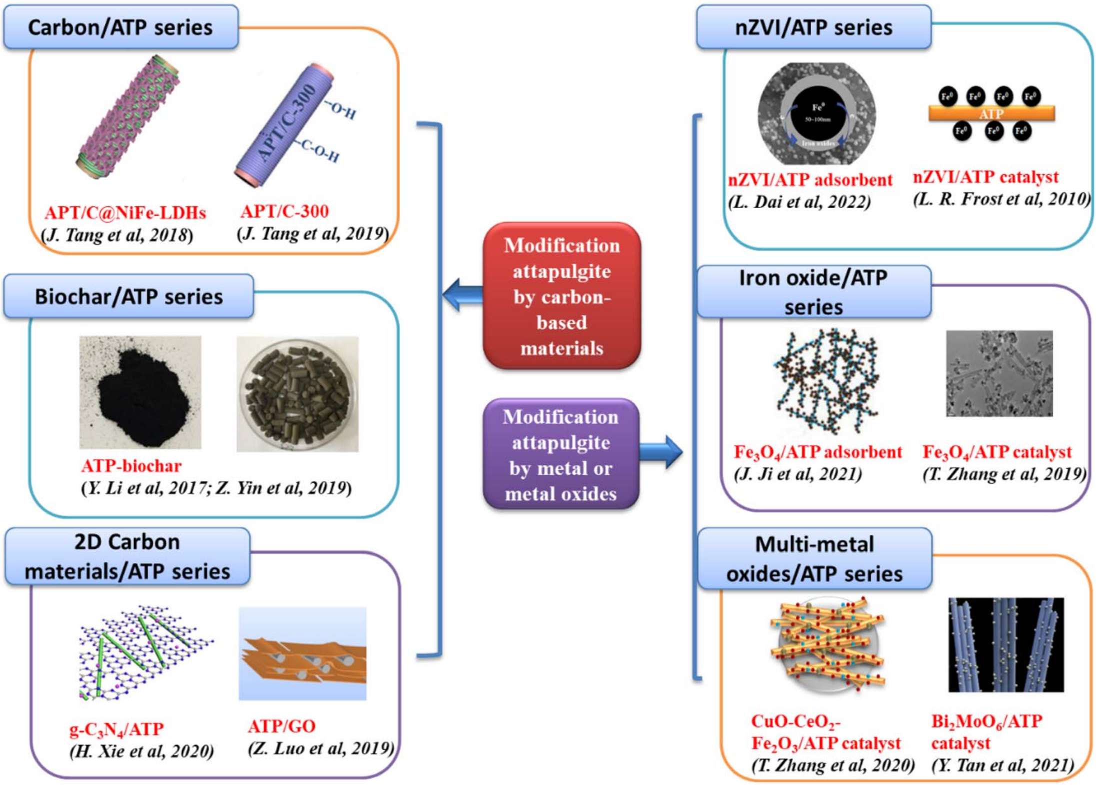

Fig. 3 ATP modification by carbon-based materials (left)[95–97,101,118,119] and by metal or metal oxides (right).[109,113–115,120,121] Copyright 2024, Elsevier.

method (366.0 mg g^{-1}) and by hydrothermal method (271.8 mg g^{-1}).

3.3 Loading metal or metal oxides on attapulgite

Metals/metal oxides (zero valent iron, Cu, Co, Fe_2O_3, Fe_3O_4, CuO, CeO_2 *et al.*) modification involves the deposition or incorporation of metal particles or metal oxides onto the surface of attapulgite. This modification can introduce new catalytic active sites, thereby enhancing the catalytic performance of attapulgite for various reactions. The specific metals or metal oxides used for modification depend on the desired catalytic application (Fig. 3 right).

3.3.1 Loading zero-valent iron (nZVI) on attapulgite. Nanoscale zero-valent iron (nZVI) technology is widely applied to treating numerous organic and inorganic pollutants because of its strong reducibility and high reaction activity.[107] However it is easy to be oxidized and agglomerate in water, in order to overcome these shortcomings, attapulgite is used as a support on which nZVI can be loaded and uniformly dispersed. For examples, Frost *et al.*[108] used attapulgite loaded nZVI to remove methylene blue from water, and the loaded adsorbent has higher adsorption capacity than before. A nanocomposite of nZVI/ATP[109] with nanoscale zero-valent iron (nZVI) directly supported on attapulgite (ATP) was synthesized for activating peroxymonosulfate (PMS) to generate reactive free radicals for oxidation of quinclorac. The removal efficiency of quinclorac was 97.36% in an hour using 0.5 g per L nZVI/ATP and 10 mM PMS.

3.3.2 Loading Fe oxides on attapulgite. As active components, Fe oxides are better than nZVI due to the fact that they are not easy to lose and have broad environmental adaptability. In these cases, metal salts were usually used as precursors, such as nitrates, carbonates, sulfates and chlorides. Fe_2O_3/ATP was often used due to easy preparation and high catalytic efficiency.[110] Fe_3O_4 normally worked as the carrier of magnetic material[111] and it can also be applied with ATP to facilitate the removal of cyanobacteria and heavy metals.[112]

Zhang *et al.*[113] prepared the Fe_3O_4/ATP catalyst by impregnation method, and nano-Fe_3O_4 particles were coated evenly onto the surface of ATP. Fe_3O_4/ATP was used as the catalyst to decolorize methylene blue (MB), and more than 99% MB decolorization were achieved under the optimum conditions.

3.3.3 Loading multi-metal oxides on attapulgite. Multiple metal oxide combinations can take an effect of synergistic oxidation. Zhang *et al.*[114] prepared multi-metal oxides loaded catalysts (CuO–Fe_2O_3/ATP, CeO_2–Fe_2O_3/ATP and CuO–CeO_2–Fe_2O_3/ATP) by impregnation method with CuO, CeO_2 or Fe_2O_3 directly coated on ATP surface for the degradation of MB. Under the optimum conditions, the as-synthesized three catalysts all showed more than 99% degradation efficiency of MB. Various metal oxides can also be loaded onto ATP in the form of alloys. Tan *et al.*[115] designed and prepared Bi_2MoO_6/attapulgite photocatalyst for the removal of tetracycline and formaldehyde, and got 1.7 times of removal ratio higher than pure Bi_2MoO_6. For endowing attapulgite-based catalysts with photocatalytic ability, TiO_2 is often used as one of the active materials. An environmentally friendly photocatalyst was synthesized by introducing BiOCl–TiO_2 hybrid oxide onto the surface of attapulgite (ATT) (denoted as ATT–BiOCl–TiO_2)[116] and used for the decomposition of methyl orange (MO). It was found that 100 mg per L MO was totally decomposed under the UV light within 70 min and 92.57% of MO was decomposed under the visible light within 120 min by using ATT–BiOCl–TiO_2 as photocatalyst. Magnetically separable attapulgite–TiO_2–Fe_xO_y composites also prepared for photodegradation of methyl orange under visible light radiation and got the highest methyl orange degradation ratio of 94.13% and COD removal of 90.91%.[117]

3.3.4 Compound modification of attapulgite. In some cases, researchers hope to achieve multi functions of attapulgite simultaneously, especially the excellent adsorption and catalytic performance, therefore attapulgite is often modified by compound methods. Attapulgite is often firstly modified by organics then coated with metals or metal oxides, as shown in Fig. 4. The surface modification of attapulgite by organics can change the surface functional groups, hydrophobicity and pore structure of attapulgite, and loading active components on ATP can make it have high catalytic performance. Zhang *et al.*[122] prepared catalyst Fe/OATP for HA–Na degradation. Fe/OATP is a heterogeneous catalyst synthesized by loading active substances—nanoscale zero valent iron—on the surface of organo-attapulgite in which ATP was modified by octadecyl trimethyl ammonium chloride (OATC), as seen in Fig. 4 (example 1). The removal ratio of HA–Na by Fe/OATP can reach more than 97% under the optimum conditions. Chen *et al.*[123] successfully fabricated polypyrrole/attapulgite-supported nanoscale zero-valent iron (nZVI–Ppy/ATP) composites by chemical oxidative polymerization and liquid-phase reduction method (Fig. 4 example 2), and employed it to extract Naphthol Green B (NGB) from aqueous solution. The results showed that 99.59% of NGB was removed using nZVI–Ppy/ATP after 25 min. Fe_3O_4/attapulgite/polyvinylalcohol composites[124] were successfully prepared by the method of coprecipitation. The composites had the ability of treating methyl orange effectively in neutral condition. When the dosage of H_2O_2 was 15 mL and the laying time was 24 h, the efficiency of treatment was 99.99%. Other porous supports are often combined with ATP to improve specific surface area, porosity and catalytic performance of ATP. Li *et al.*[125] prepared a novel ATP/$Ce_{1-x}Zr_xO_2$ nanocomposite by a facile homogeneous deposition method. The catalytic activity of ATP/$Ce_{1-x}Zr_xO_2$ was investigated by oxidizing methylene blue with O_3, and a maximum degradation ratio (99%) of methylene blue is achieved. Single-atom Cu-supported attapulgite/polymer carbon nitride (PCN/ATP) photocatalyst was successfully synthesized and its degradation rate toward methylene blue dye was 7.7 times higher than that of PCN (Fig. 4 example 3) (Table 2).[126]

4 Characterizations of attapulgite composite materials

The morphology and structure properties of attapulgite-based composite materials play a crucial role in their adsorption

Table 2 The summary of different modified attapulgite

Modification methods		Modifiers	Targets	Applications	Ref.
Organic modification	Grafting	PAM, OTAC, OTAB, DDAB, CA	To change the surface functional groups of ATP	Adsorption of dyes, phenol and tannin	65, 68, 73, 74 and 78
	Silane-coupling	APTES	To change the hydrophobicity of ATP surface	Adsorption of oil pollutants	75 and 79
	Coating	Chitosan, polyaniline, polyurethane	To change surface structure of ATP	Adsorption of dyes, organic pesticides, fats, and other toxic substances in wastewater	80–84
Modification ATP by carbon-based materials	3D-C	Carbon, biochar	To enhance specific surface area of ATP	Adsorption of dyes and antibiotics	95–97
	2D-C	GO	To enhance specific surface area and conductivity of ATP	Removal of dyes	98–103
		g-C_3N_4	To enhance specific surface area and photocatalysis ability of ATP	Removal of dyes	104–106
Loading metal or metal oxides on ATP	Fe	nZVI	To improve reducibility and high reaction activity of ATP	Adsorption and catalytic reduction of dyes and organic pesticides	107–109
	Fe oxides	Fe_2O_3, Fe_3O_4	To improve catalytic ability of ATP	Catalytic reduction of dyes and other organics	110–113
	Multi-metal oxides	CuO–Fe_2O_3, CeO_2–Fe_2O_3, BiOCl–TiO_2	To achieve an effect of synergistic oxidation	Catalytic reduction of dyes and antibiotics	114–117
Compound modification of attapulgite		Organics and metals or metal oxides	To achieve multi functions of ATP simultaneously	Catalytic reduction of dyes, antibiotics and HA–Na	122–126

and catalytic efficiency, making them directly relevant to their performance. Characterization techniques such as BET, SEM, TEM, FT-IR, XRD, and XPS are commonly used to analyze attapulgite and attapulgite-based catalysts. These techniques provide valuable insights into the surface area, pore structure, elemental composition, phase purity, surface functional groups, and other properties that influence their performance.

SEM (Scanning Electron Microscope) tests are essential for observing the morphology of attapulgite and its composites. These tests allow for a close examination of the rod-shaped crystals of attapulgite as well as any new morphologies

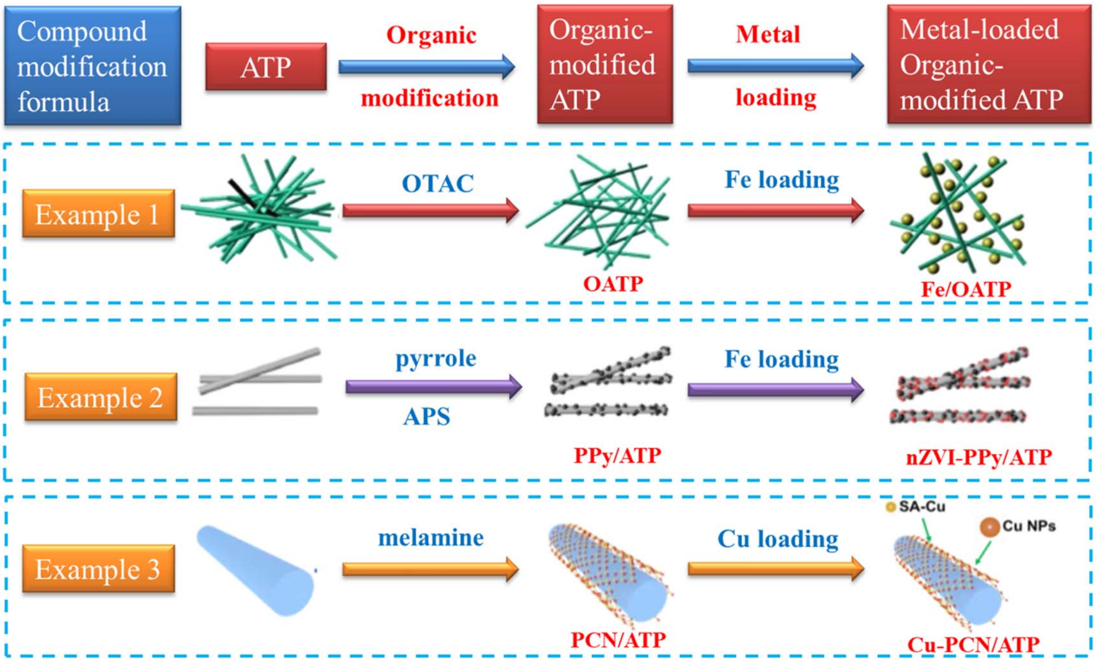

Fig. 4 Compound modification processes of ATP.[122,124,126] Copyright 2024, Elsevier.

introduced by other materials. The SEM technique also provides valuable insights into the loading situation of activated materials, such as metals and metal oxides, within the composite, as shown in Fig. 5a.

FTIR (Fourier Transform Infrared) tests are applied to characterize the molecular structure and chemical bonds of attapulgite composites. As a silico-aluminate mineral, attapulgite exhibits infrared spectral characteristic peaks that provide insights into its structure. The prominent peaks observed around 3500 cm^{-1} primarily correspond to the –O–H stretching vibration. Specifically, the absorption peak located at 3550 cm^{-1} represents the stretching vibration of crystalline water within attapulgite, while the peak at 3480 cm^{-1} signifies the stretching vibration of surface water and zeolite water present in attapulgite. Furthermore, the peak situated around 1655 cm^{-1} is primarily attributed to the H–O–H bending vibration of water molecules. Lastly, the peak near 1250 cm^{-1} is primarily associated with the bonding region between Si and Al. On this basis, researchers should be able to observe whether there are new peaks appearing after combination with or loading on attapulgite, as shown in Fig. 5b.

XRD (X-ray Diffraction) tests are employed to identify the crystal structure of attapulgite composite materials. The characteristic diffraction peaks of attapulgite are located at 2θ = 8.35°, 13.77°, 19.82°, and 27.58°, respectively corresponding to (110), (200), (040), and (102) faces of attapulgite.[127] When attapulgite is combined with other substances, new peak positions and crystalline phases will appear, proving that there are indeed new substances combining with it, as shown in Fig. 5c.

XPS tests are used to analyze the elemental and chemical valence states as well as valence electron states on the surface of attapulgite composite materials. The main elements of attapulgite are O, Si, C, Al. After loading with active substances, some metal elements such as Fe, Cu, Ti, *etc.* (based on the loading substances) may be present. The valence states of these elements can be analyzed based on the binding energy (Fig. 5d).

BET tests are to determine the specific surface area of micropores of attapulgite and its composite materials. The specific surface area of attapulgite clay is about 110–130 $m^2\ g^{-1}$, after being combined with other substances or loaded with active substances, its specific surface area may increase or decrease. However, researches have shown that the catalytic activity of attapulgite material is not directly proportional to its size of specific surface area. Sometimes, when the specific surface area decreases, the catalytic activity actually increases (Fig. 5e).

In addition to above characterizations, there are other testing methods, such as Raman spectroscopy and thermogravimetry (Fig. 5f), that can be employed to characterize attapulgite-based composite materials. It's worth noting that

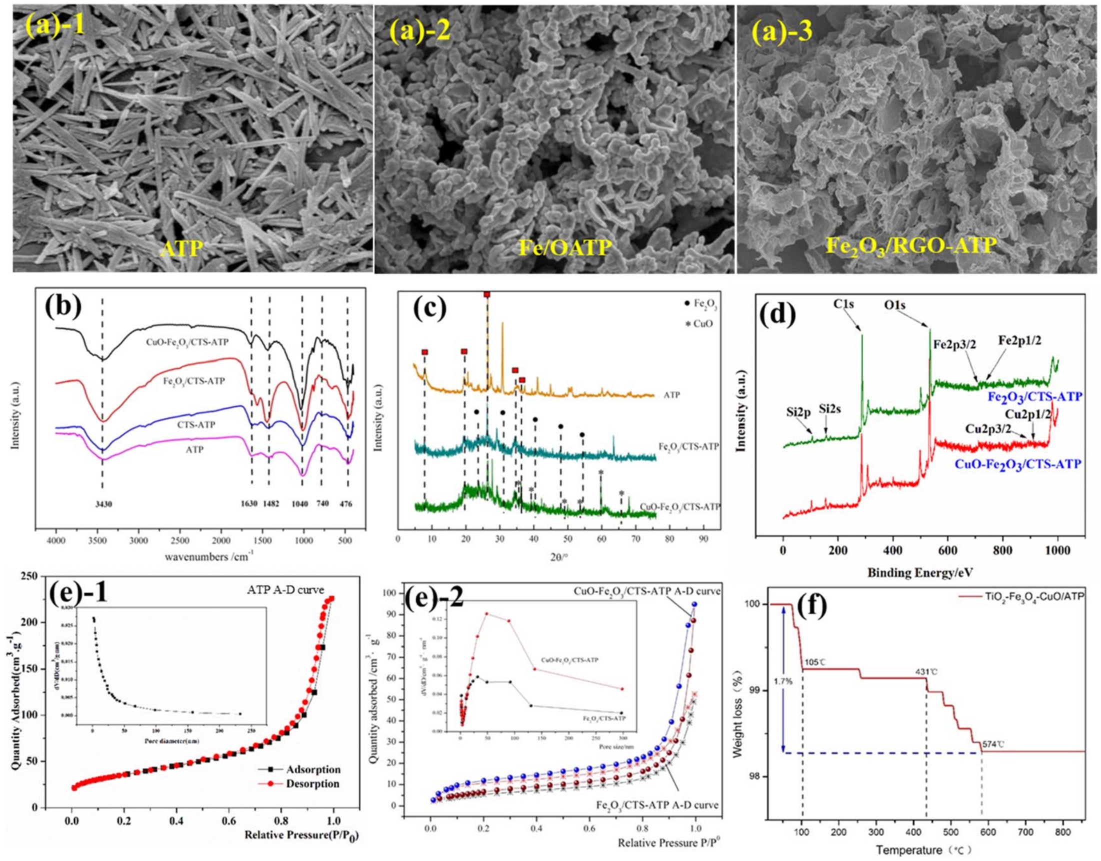

Fig. 5 Characterizations of attapulgite composite materials (a) SEM graphs (b) FT-IR curves, (c) XRD curves, (d) XPS, (e) BET A–D curves and (f) TG curve.[103,114,122,128] Copyright 2024, MDPI.

these tests are not discrete, but rather, they complement one another, offering a more comprehensive and accurate representation of the material's properties. By integrating these various testing methods, a more comprehensive understanding of the nature and performance of attapulgite-based composite materials can be achieved, ultimately aiding in their optimal application.

5 The mechanism of attapulgite composite materials removing contaminants from water

5.1 Adsorption mechanisms

The possible adsorption mechanisms of the refractory organics by attapulgite-based absorbents are based on the following properties: (i) the micropores, mesopores, and macropores structure of ATP or ATP-based composites, which facilitates the free diffusion of pollutants and guarantees mass transport to the internal structure; (ii) after introduction of organics to ATP,[74–79] the surface functional groups, surface structure and the hydrophobicity of ATP had been changed, fully increased the exposed active sites (–NH$_3$, oxygen-containing groups *etc.*) and negative charges, which made it favorable for encountering and capturing cationic molecules *via* hydrogen bonds and electrostatic interaction;[81] (iii) combined ATP with carbon series materials (GO, g-C$_3$N$_4$)[95–106] or Fe series materials (nZVI)[107–109] to enhance specific surface area and conductivity, and these substances on ATP maybe have chemical reactions with the adsorbates,[107,109] reach the goal of refractory organics removal; (iv) the crystalline water in the structure of attapulgite is located on the surface of its channel, which is easy to form hydrogen bonds with the adsorbate entering the channel;[95–97] (v) some ATP based catalysts (such as APT/C@NiFe-LDHs[96]) with primarily p–p stacking could act as electron acceptors and be conducive to adsorbing the cationic pollutants with unsaturated double bond or conjugate structure, and cation–π bonding[95] can be formed between cation and π – rich electronic structure by electrostatic attraction and polarization. All these above examples reveal that π–π interaction, hydrophobic effect, cation–π bonding, chemical complexation, hydrogen bond and electrostatic attraction are mainly involved in the adsorption process. The diagram of adsorption mechanisms by attapulgite-based absorbents can be seen in Fig. 6.

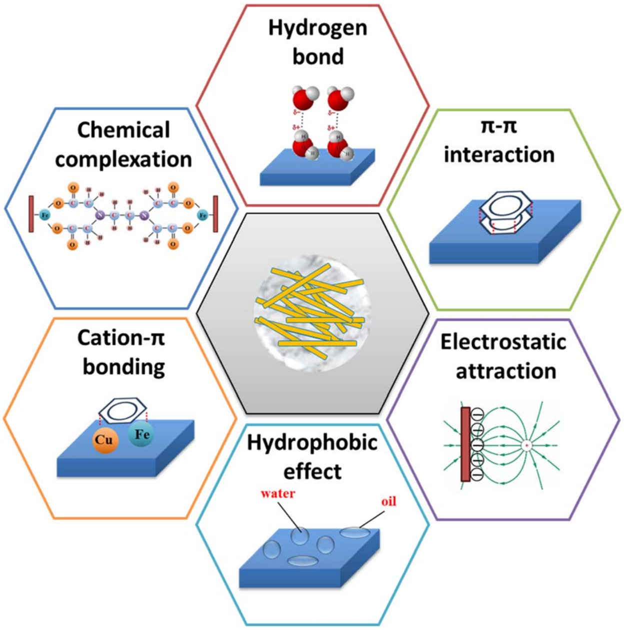

Fig. 6 The diagram of adsorption mechanisms by attapulgite-based absorbents.

5.2 Catalysis mechanisms

According to the different active components, the catalytic mechanisms of attapulgite-based catalysts for refractory organics can be divided into three types: heterogeneous Fenton process, photocatalysis and electric catalysis.

5.2.1 ATP-based heterogeneous Fenton catalysts. In general, iron or iron oxides (active components) were loaded on ATP or ATP composites, and the active components can catalyze and decompose the adsorbed hydrogen peroxide (or peroxysulfate) into $^{\bullet}$OH (or $^{\bullet}$SO$_4{}^-$) which have strong oxidation and can oxidize and mineralize most of the organic compounds[129,130] (Fig. 7). Attapulgite-based heterogeneous catalysts can catalyze and oxide organic pollutants effectively within a wide pH range, which is beneficial for *in situ* remediations of polluted groundwater and soil and can be reused for further runs. Heterogeneous Fenton-like reaction is a surface-controlled reaction that depends on the catalyst surface area, H$_2$O$_2$ (or peroxysulfate) concentration, the reaction temperature, and solution pH and ionic strength.[41,131]

5.2.2 ATP-based photocatalysts. An ideal photocatalyst is envisioned to exhibit exceptional performance characteristics, encompassing a suitable band edge potential, narrow band gap energy, enhanced charge separation, improved charge transportation, and minimized recombination.[132,133] To achieve this, attapulgite-based photocatalytic materials undergo modifications through alterations in their chemical compositions, achieved by methods such as doping,[134] composite formation,[135] metal sensitization, and molecule functionalizations.[136] Additionally, modifications are made to their physical structures, encompassing adjustments in size, shape, and surface morphology.

The fundamental principle underlying attapulgite-based photocatalysis is rooted in the theory of solid energy bands. When the light irradiation absorbed by the semiconductor components of catalysts (TiO$_2$, CdS, *etc.*) surpasses the width of the photon band gap, electron–hole pairs are generated as a result of the transition of electrons. This light irradiation prompts the excitation of electrons from the valence band (VB) to the conduction band (CB), simultaneously creating holes in the VB.[137,138] Subsequently, these electrons and holes, stimulated by the light radiation, migrate to the surface of the semiconductor particles through various interactions. Once there, they react with water or organic substances adsorbed on the surface of the semiconductor catalyst particles, thereby producing a photocatalytic effect.,[139,140] as shown in Fig. 7.

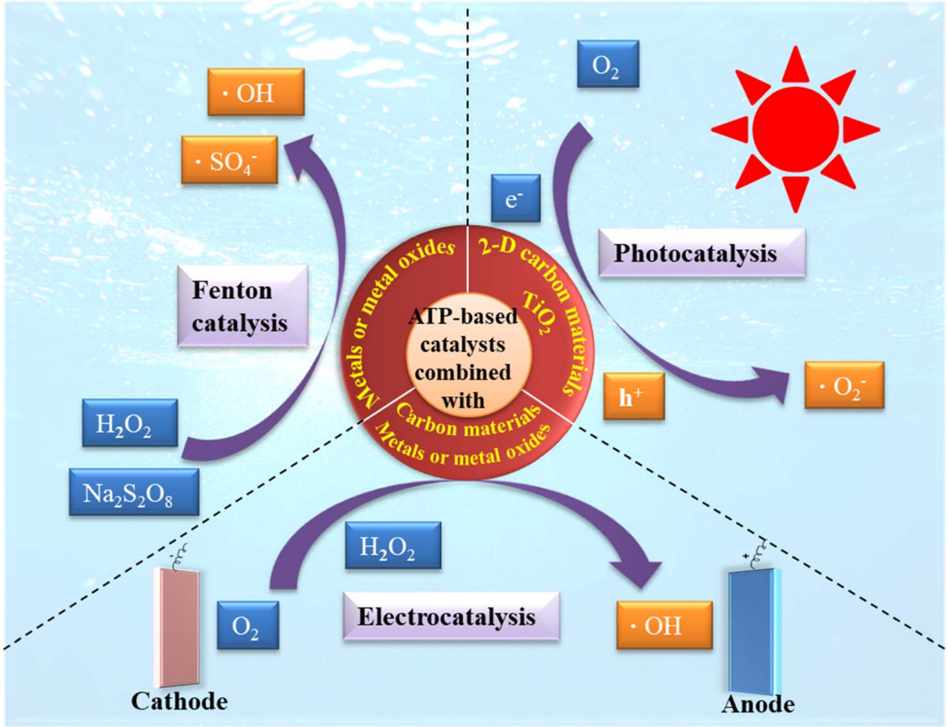

Fig. 7 Schematics of heterogeneous catalysis processes by ATP-based catalysts.

5.2.3 ATP-based electrocatalyst. ATP-based electrocatalysis process covers two steps: electrode reaction and catalysis. The electrode can be combined with or separated from the ATP-based catalyst. Firstly, H_2O_2 is formed from O_2 by anodic reaction at the anode; then H_2O_2 is decomposed into $^{\bullet}OH$ under the catalysis of iron containing ATP-based catalyst, which can degrade refractory organic compounds into CO_2.[35,141] Most of the electrocatalysis processes have the same mechanism (Fig. 7), they just used different electrodes and catalysts.

6 Future perspectives and attractions

Attapulgite indeed offer promising applications in the treatment of refractory organic wastewater due to its abundant reserves and low prices, easy modification and good compatibility, environmental friendliness, unique nanostructure and excellent performance. The attributes of attapulgite make it an attractive candidate for the development of novel composite materials for refractory organic wastewater treatment. With further research and optimization, attapulgite-based composites have the potential to become cost-effective and sustainable solutions for water pollution control.

It is necessary to further strengthen fundamental research, promote removal efficiency and solve the key problems restricting attapulgite applications. The researches of attapulgite composite materials will be carried out in the following aspects.

(1) Deeply explore the chemical and physical properties of attapulgite and attapulgite-based composite materials, as well as their reaction mechanisms in removing organic pollutants from the molecular level. Optimize the design and preparation of attapulgite composite materials through experimental and simulation methods to achieve higher removal efficiency and stability.

(2) The integration of attapulgite with other novel advanced materials could lead to the development of hybrid materials (such as aerogel materials, membrane materials, *etc.*) with multi-functional properties including filtration, adsorption and catalysis.

(3) Emphasizing the use of renewable and biodegradable modifiers in the synthesis of attapulgite composites could promote more sustainable wastewater treatment practices. Scaling up of attapulgite composites production and integrating them into commercial wastewater treatment systems could significantly contribute to environmental protection and sustainability.

7 Conclusion

Attapulgite exhibits a certain adsorption capacity and catalysis ability for organic pollutants in water due to its unique rod-shaped morphology and pore structure. However, the specific surface area and accumulation nature of natural attapulgite limit its widespread application in increasingly complex wastewater treatments. To overcome these limitations, attapulgite can be modified with organics, carbon series materials, and Fe series materials, significantly enhancing its adsorption and catalysis performance. These modified attapulgite-based materials effectively improve wastewater treatment efficiency, material recycling performance, and significantly reduce treatment costs. While surface modification maybe "sacrifice" the negative charge and pore of attapulgite composites, organic or inorganic modification of attapulgite exhibit good adsorption and catalysis performance due to the surface functional groups carried by the organics or inorganic materials.

At present, the main application problem of attapulgite composite materials is that adsorption and catalysis can only occur on the surface of them, and the internal of particle adsorbent/catalyst cannot be fully utilized. Therefore, attapulgite composite materials are usually made into powder or nano particles, which are not easy to recycle. Future research on attapulgite should not only focus on harnessing the unique properties of attapulgite and the synergistic effect of surface modification, but also focus on fully utilizing attapulgite composite materials both surface and inside, and at the same time they are easy to recycle. Promising attapulgite-based materials are those with multi-functional and stable performance that can be achieved by adjusting their morphology and structure.

Author contributions

Conceptualization, T. Z. and Y. W.; methodology, T. Z. and X. H.; validation, X. H. and J. Q.; formal analysis, T. Z.; investigation, J. Q. and Y. L.; resources, T. Z.; data curation, J. Z.; writing—original draft preparation, T. Z.; writing—review and editing, T. Z. and X. H.; visualization, T. Z.; supervision, Y. W.; project administration, T. Z.; funding acquisition, T. Z. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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