

Application Potential of Layered Double Hydroxides for The Treatment of Persistent Organic Pollutants

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Abstract: Layered double hydroxides (LDHs) is a widely used emerging material. With its adjustable composition, other ions or materials can be incorporated on the surface or in the layer to synthesize modified materials with stronger ability to capture target pollutants. Persistent organic pollutants (POPs) exist in air, water and soil for a long time, which not only affect the ecosystem and ecological balance, but also endanger human health. Therefore, it is of great significance to study the application potential of LDHs in the treatment of POPs. The removal mechanism of persistent organic pollutants by LDHs includes adsorption and activated persulfate oxidation. The factors affecting the removal of POPs by LDHs include the characteristics of LDHs itself (including the inherent characteristics of composition, structure, morphology, etc.), coexisting substrates, temperature, etc.

Keywords: Layered double hydroxides (LDHs), Persistent organic pollutants (POPs), Modified LDHs, Removal mechanism.

1. Introduction

The industrial revolution has changed human life, but also brought some potential hazards. One of the hazards is the production of a large number of chemical pollutants. These pollutants include organic matter, inorganic matter, persistent organic pollutants and heavy metals. Some of these chemicals, known as persistent organic pollutants (POPs), can exist in the environment for a long time due to their semi-volatility[1].

Typical POPs include pesticides, industrial chemicals such as polychlorinated biphenyls (PCBs), perfluorinated compounds (PFCs), bromides, and industrial by-products such as dioxins and furans. Persistent organic pollutants not only affect our ecosystems and ecological balance, but also endanger human health[2]. Most persistent organic pollutants exist in the air, water and soil for a long time, and are easily ingested by organisms at the bottom of the food chain[3]. And many persistent organic pollutants are fat-soluble substances, which are easily accumulated in adipose tissue and transmitted to the human body through the food chain. Moreover, POPs can also be transferred to the fetus through the pregnancy process. Bjrvang R D[4] measured the concentrations of 9 organochlorine pesticides (OCPs), 10 polychlorinated biphenyl (PCB) congeners and polybrominated diphenyl ether (PBDE) congeners in serum, placenta and fetal tissues (adipose tissue, liver, heart, lung and brain) of 20 stillbirth pregnant women (36-41 weeks of gestation). The results showed that all 22 persistent organic pollutants were detected in all fetal adipose tissue samples. Therefore, it is imperative to study an environmentally friendly and simple method for removing POPs.

The existing methods for the treatment of POPs include adsorption, advanced oxidation, bioremediation and physicochemical-biological combination. Among them, the use of layered double hydroxides (LDHs) to remove persistent organic pollutants has received extensive attention. Under the background of 'double carbon', how to treat pollutants with high efficiency and low carbon has become an important issue. LDHs have simple preparation and

adjustable composition and structure, which can effectively deal with a variety of POPs.

The purpose of this paper is to summarize the properties and synthesis of LDHs, the mechanism of removing POPs in the environment and the factors affecting the removal effect. The application potential of LDHs in the treatment of persistent organic pollutants was pointed out.

2. The Properties and Synthesis of Layered Double Hydroxides (LDHs)

2.1. Properties of LDHs

LDHs (Layered Double Hydroxide) is a general term for hydrotalcite and hydrotalcite-like compounds. The general expression is $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]_x^+(A_{x/n}^{n-}) \cdot y\text{H}_2\text{O}$ [5]. x represents the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$, n is the valence state of interlayer anions, and y is the number of interlayer water molecules. LDHs are composed of multiple MO_6 octahedra closely arranged to form a laminate. The interlayer anions and water molecules are sandwiched between the two layers, and the interlayer anions are connected by non-covalent bonds. Part of the divalent metal cation M^{2+} is replaced by the trivalent metal cation M^{3+} , and the excess positive charge is neutralized by the interlayer anion, and the whole is electrically neutral[6].

The physical and chemical properties of LDHs are very similar to those of clay materials, and they are called 'anionic clay' because of their anion exchange properties. The main properties of LDHs include: 1) Acid-base bifunctionality: LDHs are usually alkaline because the laminate contains abundant hydroxyl groups. Its alkalinity depends on the type of metal ions. LDHs are also acidic due to trivalent metal hydroxides and interlayer anions; 2) Interlayer ion exchangeability: The structural characteristics of LDHs enable the exchange of interlayer ion energy with higher valence anions; 3) Thermal stability: Due to the strong covalent bond and electrostatic interaction, it shows thermal stability in a certain temperature range. Taking Mg-Al-LDH as an example, when it is higher than 200°C in the air, it will cause structural changes; 4) Memory effect: Under certain

conditions, when the oxide obtained by the thermal decomposition of hydrotalcite is immersed in a solution containing anions, its layer structure will be reconstructed and LDHs will be produced again.

2.2. Preparation of LDHs

The structure of LDHs contains layered double hydroxides and intercalated anions. According to the different intercalation anion addition methods, LDHs can be divided into primary LDHs and modified LDHs. Among them, the primary LDHs are intercalated with inorganic anions (such as NO_3^- , Cl^- , CO_3^{2-}) in the synthetic mother liquor, and the modified LDHs introduce other metals or replace the interlayer anions with other anions in the laminate of the primary LDHs.

2.2.1. Synthesis of primary LDHs

The preparation methods of primary LDHs include co-precipitation method, hydrothermal method, sol-gel method and mechanical grinding method. Among them, the co-precipitation method is the most widely used[7].

1) Co-precipitation method: Co-precipitation method refers to the reaction of mixed metal ion solution and alkali solution, stirring until the precipitation reaction occurs, let the product aging for a period of time, and then filtering, cleaning, drying method.

2) Hydrothermal method: Hydrothermal method is to mix metal salts and urea in an autoclave. After mixing the chemical substances in the solution, they are loaded into the reactor, and the reaction is accelerated under high temperature and high pressure conditions. After cooling, the solution is filtered and dried.

3) Sol-gel method: Sol-gel method refers to the metal organic or inorganic compounds through solution, sol, gel and curing, and then by heat treatment and the formation of oxide or other compound solid method.

4) Induced hydrolysis method: Under certain temperature and pH conditions, the hydroxide solution containing MIII and the salt solution containing MII with the same pH were first prepared, and the two were mixed to induce the hydrolysis of MII to form LDHs precipitation.

5) Mechanical grinding method: the synthetic hydrotalcite raw material metal salt and alkali into high-energy ball mill for high-speed grinding, high-energy mechanical force induced physical and chemical and structural changes in the generation of LDHs method.

2.2.2. 2.2.2 Synthesis of modified LDHs

With the in-depth study of layered double hydroxides (LDHs), the advantages of low cost, non-toxicity and structure of LDHs make it widely used in flame retardant, medicine, sewage treatment and other fields. However, the traditional LDHs have low specific surface area, less functional groups, and easy leaching of metal ions to produce secondary pollution, and the adsorption and catalytic effects are not ideal. In order to achieve a more comprehensive demand, researchers are committed to improving the performance of LDHs by transition metal modification, surface modification, anion intercalation and other methods.

1) Transition metal modification

Transition metals are usually used as components of LDHs cation layers to activate persulfate. However, the ineffective redox from $\text{M}^{(n+1)+}$ to M^{n+} leads to a decrease in catalytic performance. By introducing another transition metal through

modification, there is electron transfer between different metals, which can accelerate the original cycle. Zhang[8]prepared transition metal modified Mg-Al-M hydrotalcite by means of hydrotalcite 's ' memory effect '. It is used to catalyze urea and phenol to synthesize salicylamide. The results showed that CHT-Mn had the best catalytic effect, and the synthesis rate was as high as 41.2 %. After repeated use for several times, the catalytic activity remained basically unchanged. It can be seen that the introduction of external metals can also improve the stability of heterogeneous catalysts.

2) Surface modification

Surface modification is a common method to change the surface function. Zhang[9]modified MgAl-LDH with anionic surfactants to prepare organic LDHs. The intercalation of anionic surfactants changed the surface properties of MgAl-LDH from hydrophilic to hydrophobic. Surfactants were not only embedded in the interlayer space, but also adsorbed on the outer surface of LDH particles. The interlayer space and outer surface of LDHs are modified by surfactants, which realizes the dual effects of electrostatic interaction and intermolecular interaction, and improves the adsorption of dyes. The experimental data show that the modified Mg-Al-LDHs can be used as a broad-spectrum adsorbent to remove anionic, non-ionic and cationic dyes.

3) Calcination modification

The calcination method can also modify LDHs. The main principle is that the calcined LDHs increase many oxygen-containing functional groups, increase the specific surface area, and provide more active sites for adsorption. Huang[10] showed that the surface free energy of LDH film was reduced and some interlayer anions were removed by calcination, which improved the stability and permeability of LDH film. In addition, the performance of LDHs as adsorbent[11], photocatalyst[12] and steel corrosion inhibitor[13]was improved after calcination.

4) Anion intercalation modification

Benefiting from the high anion exchange capacity, anion intercalation is also one of the methods to improve the performance of hydrotalcite-like materials[14]. The intercalation of inorganic anions can usually be achieved directly by co-precipitation method. However, some organic anion intercalation reactions are not easy to be obtained directly by co-precipitation method. The precursor can be prepared by co-precipitation method, and then the interlayer anion exchange is carried out to obtain the ideal product[15]. Zhang[16] synthesized L-cysteine intercalated LDHs adsorbent by intercalation modification and used for the removal of heavy metals (Pb (II), Cu (II) and Cd (II)) in water. Through experiments and characterization, it was found that the interlayer of LDH was successfully inserted, and the functional groups of thiol (-SH), amino (-NH₂) and carboxyl (-COOH) were introduced, which provided a large number of adsorption sites for the removal of heavy metals.

5) Modification of composite materials

LDHs allow the incorporation of other materials on the surface or in the layer to form a composite material that can selectively capture the target pollutants, which can improve its performance to a certain extent. Periyasamy[17] synthesized chitosan / hydrotalcite composites by hydrothermal and in-situ precipitation methods for the treatment of chromium in farmland. The results showed that the adsorption effect of the composite on chromium was

higher than that of a single component, reaching 35.75 mg / g. HTLcs-SBA-15-x composites were synthesized by co-precipitation method using mesoporous material SBA-15 as carrier[18]. When the amount of hydrotalcite is 40wt %, the adsorption effect of CO₂ is better. The composite material not only has a complete mesoporous structure, but also has layered HTLcs in the pores, and the increase of specific surface area greatly improves the adsorption effect.

3. The Mechanism of LDHs Treatment of Pops

3.1. Adsorption mechanism

Adsorption treatment of small molecule pops is a simpler method. The adsorption mechanism of LDHs includes ion exchange, surface complexation, precipitation and electrostatic interaction. Generally, the adsorption process has three steps : external diffusion, intraparticle diffusion and chemical adsorption. Hu[19] studied the adsorption mechanism of perfluorooctanoic acid and found that when the initial concentration of perfluorooctanoic acid was low, intraparticle diffusion was the only factor restricting the adsorption rate. Increasing the initial concentration to a higher level, both external diffusion and intraparticle diffusion become steps that limit the adsorption rate. Others have found that the adsorption effect is related to the hydrophobicity of the adsorbed material[20].

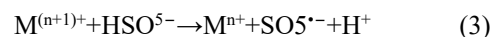
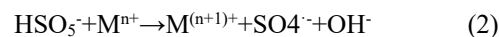
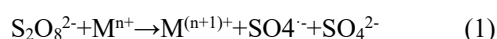
3.2. Oxidation mechanism of activated persulfate

Sulfate-based advanced oxidation processes (SR AOPs) have attracted much attention in the degradation of refractory organic pollutants. Oxidants with peroxy or peroxy groups, such as H₂O₂, peroxymonosulfate (PMS), peroxydisulfate (PS), etc., usually form free radicals under certain conditions, which are used to oxidize and degrade pollutants[21]. However, H₂O₂ as a free radical precursor has many disadvantages, such as short life, narrow working PH range and high cost. Persulfate AOPs have become a more popular pollutant removal method due to their advantages of strong oxidation, high free radical generation rate, diverse activation methods, and low reaction conditions. According to previous studies, there are free radical and non-free radical mechanisms for persulfate activation to eliminate pollutants.

3.2.1. Free radical mechanism

The free radicals in persulfate oxidation are mainly SO₄•⁻, •OH and •O₂⁻, and their production requires energy and electron transfer reactions to split persulfate bonds. LDHs / LDO and its composites can provide sufficient active sites to activate persulfate, promote the cleavage of peroxide bonds and the production of free radicals. The existence of active sites is usually related to transition metals and their oxides, surface hydroxyl, carbonyl (C = O), defect structure, and sp² hybrid carbon. In other words, the controllability of the composition of LDHs complexes can increase the active sites, thereby improving the activation ability. The activation mechanism of transition metals and their oxides and surface hydroxyl active sites is discussed below :

(1) The activation mechanism of transition metals and their oxides can be described as the following equation[22]:



In addition, the catalytic performance of single metal LDHs is low due to the accumulation of metal ions in high valence state. The synergistic effect between metal ions of multi-metal LDHs is helpful to solve this problem.

(2) Surface hydroxyl groups

The surface hydroxyl group reacts with persulfate to cleave the O-O bond to generate free radicals.

3.2.2. Non-free radical mechanism

It was found that some SR AOPs did not play a role in the removal of pollutants through SO₄•⁻ and •OH, mainly non-radical mechanisms such as singlet oxygen, mediated electron transfer and direct oxidation.

(1) Singlet oxygen

Studies have shown that there are usually two ways to produce ¹O₂. One is produced by the self-decay of PMS, and the other is produced by photochemical processes. The self-decay process is usually inefficient and cannot be used as the main way[23]. In addition, carbonaceous materials can catalyze persulfate to produce ¹O₂, and some carbon materials composite hydrotalcite can produce ¹O₂ through this way, thereby removing target pollutants.

(2) Mediated electron transfer

Under this mechanism, the catalyst usually acts as an electron transfer conductor to promote the transfer of electrons from pollutants to persulfate[24]. These catalysts usually have good electrical conductivity and can form charge transfer complexes with persulfate for organic oxidation.

4. Factors Affecting the Treatment Effect

4.1. Characteristics of hydrotalcite itself

The characteristics of hydrotalcite itself include composition (metal ions, interlayer anions, functional materials), structure, morphology and other inherent characteristics. These characteristics determine the density of active sites that play a role, which in turn affects the removal efficiency of pollutants. The morphology of LDHs produced by different synthesis methods is different.

Huang[25] synthesized Zn / Al-LDHs by ion exchange method, reconstruction method and one-pot method, and the morphology showed characteristic sheet, layered and irregular plate structure, respectively. The methyl orange adsorption test was carried out on the hydrotalcite prepared by three synthesis methods. The results showed that the one-pot method had the largest adsorption capacity. The magnetic material mixed with hydrotalcite can improve its reusability. For example, Wang[26] doped Fe₂O₃ magnetic material to synthesize magnetic flower-like hydrotalcite-like materials. By testing its reusability, it was found that after 5 cycles of adsorption, the fluoride removal performance of the adsorbent was still maintained at 80.93 % of the fresh adsorbent. The removal effect of LDHs pollutants doped with magnetic materials is significantly improved.

4.2. Coexisting substrates

In polluted water bodies, in addition to the target pollutants to be removed, there are usually some coexisting substrates. These coexisting substrates mainly include inorganic anions and natural organic matter (NOM). Inorganic anions (such as NO_3^- , HCO_3^- , Cl^- , PO_4^{3-}) often exist in water even at low concentrations. They can reduce catalyst performance and affect pollutant degradation by buffering solution pH, capturing ROS, and neutralizing electrostatic bonds between reactants.

Xiao[27] pointed out that anions such as Cl^- , HCO_3^- and HPO_4^{2-} inhibited MNZ degradation. There are two reasons for this phenomenon: one is the consumption of free radicals ($\cdot\text{OH}$ and $\text{SO}_4\cdot^-$) by these coexisting ions, and the other is that they increase the pH of the solution. Xu[28] prepared nano-zero-valent iron-loaded peanut shell biochar to degrade emerging pollutants PPCPs in water, and investigated the effect of inorganic anions on the degradation system. It was found that inorganic anions inhibited the degradation of tetracycline, and the inhibition intensity of inorganic anions on TC removal was $\text{HCO}_3^- > \text{Cl}^- > \text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{NO}_3^-$. NOM is a complex organic chemical substance that naturally exists in all water bodies. The content and characteristics of NOM in different water sources are very different. However, it can be determined that NOM interacts with ROS, thereby reducing the removal rate of target pollutants.

4.3. Temperature

According to the principle of thermodynamics, the increase of temperature can improve the reaction kinetics[29]. In the adsorption process, as the temperature increases, the entropy value in the system increases, the chance of collision between LDHs and target pollutant molecules increases, and the utilization rate of adsorption sites also increases. When exploring the effect of temperature on the adsorption of tetracycline, it was found that the adsorption curve with temperature as the abscissa and the adsorption amount as the ordinate showed a trend of increasing first and then stabilizing[30].

For the activated persulfate oxidation system, high temperature may lead to the thermal activation of PMS or PDS, thereby increasing the removal rate. However, high temperature may bring some negative effects, such as the damage of the carrier medium and the decomposition of the catalyst, resulting in an increase in metal leaching rate and a decrease in reusability. Therefore, combining the properties of the carrier and the catalyst, moderately increasing the degradation temperature is helpful to improve the reaction efficiency.

5. Summary

As an 'anionic clay', layered double hydroxides can be used to synthesize new modified materials that can selectively capture target pollutants through some modification methods such as anion intercalation, insertion of transition metals and addition of composite materials. Studies have shown that the removal mechanism of persistent organic pollutants by LDHs includes adsorption and activation of persulfate oxidation. For small molecule POPs, adsorption method is generally used to remove them. For macromolecular POPs that are difficult to remove completely, LDHs are usually used as activators to activate persulfate and remove pollutants. Among them, the catalytic activation persulfate oxidation

system includes free radical pathway and non-free radical pathway. At the same time, the characteristics of LDHs (including composition, structure, morphology and other inherent characteristics), coexisting substrates, temperature and other factors affect the effect of LDHs on the removal of persistent organic pollutants. In summary, LDHs have great prospects in removing POPs in the environment due to their low-carbon preparation process, wide operating conditions, and strong pertinence.

References

- [1] Alharbi O M L , Basheer A A , Khattab R A ,et al.Health and environmental effects of persistent organic pollutants [J]. Journal of Molecular Liquids, Vol. 263(2018) p.442-453.
- [2] Ighalo J O , Yap P S , Iwuozor K O ,et al.Adsorption of persistent organic pollutants (POPs) from the aqueous environment by nano-adsorbents: A review[J].Environmental research, Vol. 212(2022) p. 113-123.
- [3] Amutova F , Delannoy M , Baubekova A ,et al.Transfer of persistent organic pollutants in food of animal origin - Meta-analysis of published data.[J].Chemosphere, Vol. 262(2021) p.1-15.
- [4] Bjrvang R D , Vinnars M T , Papadogiannakis N ,et al.Mixtures of persistent organic pollutants are found in vital organs of late gestation human fetuses[J].Chemosphere, Vol. 283(2021) p.1-12.
- [5] Pizzoferrato Roberto, Richetta Maria. Layered Double Hydroxides (LDHs)[J]. Crystals, Vol. 10(2020) No. 12.
- [6] Matusik Jakub. Special Issue: Layered Double Hydroxides (LDH) and LDH-Based Hybrid Composites[J]. Materials, Vol. 14(2021) No. 10.
- [7] Yang Z G, Yan H Y, Zhang LY, et al. Preparation and Application Study on Layered Double Hydroxides [J]. Chemical Education (English & Chinese), Vol. 38(2017) No. 20, p.6-8.
- [8] Zhang X L, Zhang T, Wei S W, et al. Green Synthesis of Salicylamide From Urea and Phenol Catalyzed by Transition Metal Modified Mg-Al Mixed Oxides [J]. Journal of Petroleum (Petroleum Processing), Vol. 38(2022) No.1, p. 55-64.
- [9] Zhang B, Dong Z H, Sun D J, Wu T, et al. Enhanced adsorption capacity of dyes by surfactant-modified layered double hydroxides from aqueous solution[J]. Journal of Industrial and Engineering Chemistry, Vol. 49(2017) p. 208-218.
- [10] Huang Q F .Calcination of layered double hydroxide membrane with enhanced nanofiltration performance [J]. Journal of Industrial and Engineering Chemistry, Vol. 89(2020) p. 368-374.
- [11] Daniel C, Dolores E, Francisco J, et al. Use of Raman Spectroscopy To Assess Nitrate Uptake By Calcined Ldh Phases [J]. News of Science, Vol. 38(2020).
- [12] Zhang G S, Hu L M, Zhao R B,. Microwave-assisted synthesis of ZnNiAl-layered double hydroxides with calcination treatment for enhanced PNP photo-degradation under visible-light irradiation[J]. Journal of Photochemistry & Photobiology, A: Chemistry, Vol. 356(2017).
- [13] Liu S H, Ouyang J Y, Ren J. Mechanism of calcination modification of phosphogypsum and its effect on the hydration properties of phosphogypsum-based supersulfated cement[J]. Construction and Building Materials, Vol. 243(2020).
- [14] Yang M, Liu S X, Nie Y M, et al. Preparation and Functional Modification of Hydrotalcite -like Compounds[J]. Package Engineering, Vol. 43(2022) No.11, p. 89-98.

- [15] Zhang X: Study on Adsorption Performance and Mechanisms of Intercalated MgAl-Layered Double Hydroxide for Heavy Metals from Water (Master of Engineering, University of Jinan, China 2021). p.1-60.
- [16] Wang X R, Tang L P, Li Y, et al. The Photosensitization Based on Host-guest Interactions in a Layered Double Hydroxide [J]. *Imaging Science and Photochemistry*, Vol. 35(2017) No.3, p. 307-315.
- [17] Periyasamy, Soodamani, Gopalakannan, et al. Enhanced Chromium Sorption and Quick Separation of Magnetic Hydrotalcite Anchored Biopolymeric Composites Using the Hydrothermal Method [J]. *Journal of Chemical & Engineering Data the ACS Journal for Data*, Vol. 63(2018) No.5, p. 1286-1299.
- [18] Ji C, Wang Y, Zhao N. Synthesis of Cu-Al hydrotalcite-SBA-15 composites and CO₂ capture using the sorbent [J]. *Applied Surface Science*, Vol. 481(2019) p. 337-343.
- [19] Hu Z, Song X, Wei C, et al. Behavior and mechanisms for sorptive removal of perfluorooctane sulfonate by layered double hydroxides [J]. *Chemosphere*, Vol. 187(2017) No. 11, p. 196-205.
- [20] D Y C A B C, D A G, C W Z A B, et al. Mechanistic insights into fast adsorption of perfluoroalkyl substances on carbonate-layered double hydroxides [J]. *Journal of Hazardous Materials*, Vol. 408(2020) p. 1-8.
- [21] Yang R A, Lk A, Yz A, et al. Review on the synthesis and activity of iron-based catalyst in catalytic oxidation of refractory organic pollutants in wastewater [J]. *Journal of Cleaner Production*, Vol. 321(2021) p. 1-16.
- [22] C J W A B, B S W A. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants - ScienceDirect [J]. *Chemical Engineering Journal*, Vol. 334(2018) p. 1502-1517.
- [23] Ge L, Shao B, Liang Q, et al. Layered double hydroxide based materials applied in persulfate based advanced oxidation processes: Property, mechanism, application and perspectives [J]. Vol. 424(2021) p. 1-29.
- [24] Zhang T, Chen Y, Wang Y, et al. Efficient Peroxydisulfate Activation Process Not Relying on Sulfate Radical Generation for Water Pollutant Degradation [J]. *Environmental Science & Technology*, Vol. 48(2014) No. 11, p. 5868-5875.
- [25] Huang H H, Xia C F, Liang D R, et al. Comparative study of removing anionic contaminants by layered double hydroxides with different paths [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 624(2021) No. 1, p. 1-9.
- [26] Wang R, Wang D, Peng W. Removal of F⁻ from water by magnetic fluoriform magnesium zirconium hydrotalcite-like material doped with Fe₂O₃ and ZrO₂ [J]. *Desalination: The International Journal on the Science and Technology of Desalting and Water Purification*, 2022. Vol. 544(2022), p.2-14.
- [27] Xiao K, Liang F, Liang J, et al. Magnetic bimetallic Fe, Ce-embedded N-enriched porous biochar for peroxymonosulfate activation in metronidazole degradation: Applications, mechanism insight and toxicity evaluation. [J]. *Chemical Engineering Journal*, Vol. 433(2021), p.2-14.
- [28] Xu J: Study on the adsorption and degradation of emerging contaminant PPCPs in aqueous by iron-based peanut shell biochar composite functional materials. (Master of Engineering, Nanjing University, China 2019). p.1-125
- [29] Hori H, Nagaoka Y, Murayama M, et al. Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water. *Environmental Science & Technology*, Vol. 42(2008) No. 19, p. 7438-7443.
- [30] Hang Y R: Preparation of Modified Hydrotalcite and its Adsorption of Antibiotics in Water (Master of Engineering, North China University of Water Resources and Electric Power, China 2022). p.1-81.