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Research Article

Application of Metal Oxides Prepared Based on Ferroelectric-Based Photoelectric Conversion Materials in the Thermal Degradation of Polybrominated Diphenyl Ethers

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In today's environment where the society attaches great importance to environmental pollution, there has been a certain amount of research at home and abroad to explore the solutions to pollution of the large amount of polluting and persistent harmful substances that remain in nature. And most people think that it is necessary to solve the problem of pollution in two ways. (1) Energy: without discussing other energy sources, we will only discuss the main oil of today's energy. The treatment and use of this energy will cause pollution to a certain degree, and it has been overexploited. The exploration of new energy sources and increasing the use of natural energy such as wind and solar energy are the main research directions today. (2) Degradation of existing pollutants: nowadays, due to the rapid development of various industries, attention to environmental pollution has reached a point that cannot be ignored. As a kind of brominated flame retardant, polybrominated diphenyl ethers are widely used because of their low price and stable chemical properties, mostly in electronic appliances, building materials, textiles, furniture, and other products. But the substance is extremely harmful. This article focuses on the degradation treatment of tetrabromodiphenyl ether, which is one of the polybrominated diphenyl ethers that are long-lasting and difficult to be degraded in the environment. It has become an emerging persistent organic pollutant due to its toxicity, persistence, and bioaccumulation. Based on the reduction and debromination of zero-valent iron, the effect of debromination of tetrabromodiphenyl ether is explored under the coupling effect of the nanosized iron powder with the smaller particles of zero-valent iron and vitamin B_{12}. The experimental results in this paper show that when the dosage of nanoiron powder is between $0.0\,g/L$ and $0.15\,g/L$, according to the degradation diagram, the reaction rate is continuously strengthened with the increase of nanoiron powder. When the dosage of nanoiron powder is $0.15\,g/L$-$1.0\,g/L$, the effect will be weakened with the increase of the concentration. Therefore, an increase in the concentration of nanoiron powder will promote the progress of the debromination reaction. But when it reaches a certain level, the reaction rate will gradually decrease until it stops.

1. Introduction

The current state of environmental pollution cannot be underestimated. Through the diffusion of the food chain in nature, the atmosphere, and the air, pollutants are permeated around people, which have affected people's daily life, and even the weather has undergone abnormal changes due to its influence. The intensification of the greenhouse effect will have serious consequences. Now, the era is devel-

oping rapidly. With the advancement of related scientific research results of computer network portable technology, the process of electrical appliance industrialization has accelerated and expanded. Nowadays, a large number of electronic devices are updated every year, resulting in a large amount of electronic waste. Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in industrial production and they are widely used in plastic flame-retardant parts in electronic appliances. By analyzing the

physical and chemical properties, exposure pathways, and pollution levels of PBDEs, this article summarizes the main pathways of photodegradation and aerobic and anaerobic microbial degradation. This article makes a corresponding risk assessment for its carcinogenic properties and compares the risk of impact in various environments. Through the risk comparison between adults and children, this article explores the catalytic debromination effect of metal oxides under sunlight. Metals and vitamin B_{12} have catalytic reduction effects and are highly efficient in the field of degrading organic matter. Therefore, this article proposes the debromination reaction of tetrabromodiphenyl by metal combined with vitamin B_{12} and conducts corresponding experiments on the effects of various metals.

Polybrominated diphenyl ethers are a type of global organic pollutants that are widespread in the environment. Because of its good flame retardancy, it is often used as an additive flame retardant and widely used in various products. In the process of production and use, it can be released from the product and enter the ecosystem through various channels. But it has high bioaccumulation effect and high carcinogenicity. It has a great impact on the environment, and children are more affected by its toxicity than adults. It can be seen that the research on the degradation direction of polybrominated diphenyl ethers is of inevitable significance. Now, a large amount of electronic waste is generated every year. The flame-retardant plastics of electronic waste release highly toxic by-products during their disposal, and related research has attracted the attention of many scholars. The original treatment of e-waste may release a large amount of organic pollutants into the environment, but its scale and mechanism still need to be fully resolved. Li et al. have carried out heat treatment and open burning of typical electronic waste, namely, plastics and printed circuit boards. The emission factor of the sum of 39 polybrominated diphenyl ethers ($\sum\_(39)$PBDE) in the heat treatment is $817 - 1.60 \times 10 \sim (5)$ng g $\sim (-1)$ and undetected $-9.14 \times 10 \sim (4)$ ng g $\sim (-1)$. In open burning, airborne particulate matter (87%) is the main carrier of PBDEs, followed by residual ash (13%) and gaseous components (0.3%). In the open fire heat treatment, they were 30%, 43%, and 27%, respectively. Evaporation and reabsorption may be the main emission mechanism of slightly brominated BDE, but severely brominated BDE is often related to particles produced by heating or combustion. The different size distributions of PBDEs in the emission source and nearby air indicate a remarkable reprocessing process in the atmospheric diffusion process [1]. The triglyceride of ricinoleic acid and the acid residue contain both hydroxyl and double bonds, which can be easily functionalized. Hydroxyl groups can be converted into phosphorous esters of different structures, and unsaturated groups can easily be added to bromine. Using spectroscopy and thermal methods, Howell and Ostrander fully characterize castor oil derivatives that contain phosphorus, bromine, or phosphorus and bromine. The thermal stability and degradation modes of these compounds have been evaluated by thermogravimetric analysis and infrared spectroscopy [2]. In terms of phosphorus-based flame retardants, Daniel and Howell use four phosphorus esters derived from industrially

obtained glucose derivative isosorbide as starting materials. After thermal degradation, the four esters showed different degradation curves. Phosphate esters provide better coke yields than phosphonates and phosphinates, the latter being more thermally stable. Fourier transform infrared spectroscopy and thermogravimetric analysis were used to monitor the thermal stability of the compound under constant temperature and variable time. Studies have shown that degradation is accompanied by the release of corresponding phosphoric acid [3]. By rationally manufacturing metal nanostructures to excite plasmon resonance, the efficiency of hot carrier excitation can be significantly improved. Ishii et al. have conducted in-depth research on these plasma-enhanced photoelectric and photothermal conversion from a basic and application-oriented perspective. Among them, it exclusively uses gold and silver. In contrast, this progress report covers nonmetallic materials that can be used for plasma-enhanced photoelectric and photothermal conversion [4]. After exploring and researching many modified anodic oxides, Chen et al. tried to summarize the latest developments in the rational design and modification of these oxides before, during, and after anodization. Each part completely solves the reasonable design strategy, aiming to improve the overall PEC performance [5]. Park et al. proposed and researched a transparent light-emitting diode (LED) panel with a 16×16 multicolor LED array for signage applications. As a transparent electrode, it can use established simulation models to manufacture and characterize three layers of oxide/metal/oxide (OMO) with various Al interlayer thicknesses. Using commercial ray tracing optics and SPICE simulation tools, Park et al. designed the LED panel and studied its optical and electrical characteristics. In addition, in order to solve the waveguide effect and voltage drop problems of the entire panel, they integrated additional optical structures and various OMO widths in the design. The results show that the OMO electrode interconnection and the proposed design consider the key aspects of implementing transparent LED digital signage applications [6]. Guo et al.'s research results show that low temperature is an important way to improve the stability of high-concentration precursor solutions in the sol-gel process. In addition, a stable precursor solution is used, followed by spin coating and sequential layer annealing. Then, a thick BLFO film is prepared on an indium tin oxide/glass substrate, which has a perovskite structure without impurity phases. In particular, it can obtain a high remanent polarization (P r) of 42.85 μC/cm^2. This may be related to lanthanum doping, preferred (110) orientation and relatively dense microstructure [7]. The scholars' research discussed above has certain auxiliary guidance for the research of this paper, but most of the abovementioned research processes require special professional techniques and a deep understanding of experimental supplies in order to further avoid the process harm. Its content is too complicated, and the experiment process is accompanied by certain dangers and the harmfulness of gases, so more attention should be paid to the experiment.

The innovations of this article are as follows: (1) It is proposed to use nanoscale iron powder for debromination
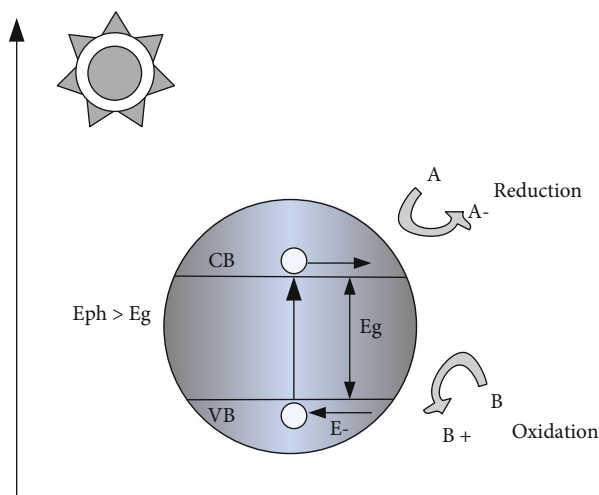
FIGURE 1: The basic principle of photocatalysis of metal oxide materials.

reaction; (2) after coupling vitamin B_{12} and iron powder, the tetrabromodiphenyl ether is debrominated, and the Good results; and (3) the degradation ability of various metals such as Al, Zn, Fe, and Sn on the reduction and debromination of tetrabromodiphenyl ether was discussed. And this article analyzes the effect of debromination with the addition of vitamin B_{12}.

2. Polybrominated Diphenyl Ethers Based on Metal Oxides

2.1. Application of Metal Oxides in the Catalytic Degradation of Pollutants Under Sunlight. Now, the world is facing the same dilemma, that is, the shortage of available energy and the increasingly serious environmental pollution. It has caused extreme weather in the global climate [8]. And the emission of greenhouse gases has caused global warming. People attach great importance to sustainable and pollution-free new energy sources in nature [9]. The first thing that comes to our mind is solar energy. As a daily visible and very important existence in nature, solar energy has naturally attracted people's attention. Solar cells, photocatalytic hydrogen production, and photocatalytic degradation of organic pollutants are all intuitive manifestations of people's utilization of solar energy [10]. Metal oxide semiconductor materials are used for photovoltaic power generation, hydrogen production, and catalytic decomposition [11]. Due to the different properties of metal elements, the oxides formed by them exhibit different properties and application characteristics, such as in a wide range of environmental pollution control, metal oxide materials can be used as catalysts and adsorbents to treat industrial toxic waste gas and environmental organic pollutants [12]. In semiconductor materials, when the energy is greater than the band gap, the surface can be irradiated with light energy to absorb the light energy. Electrons are excited from the valence band to the conduction band and become holes. Figure 1 shows its catalytic texture, which can improve catalytic efficiency.

For the research of metal semioxide semiconductor materials, there have been research directions for related content as early as before. It was discovered that titanium dioxide can catalyze the start of hydrogen production under the action of sunlight [13]. The photocatalysis of metal oxide semiconductor materials has been rapidly developed. Through the study of the photocatalytic reaction of a variety of metal oxide materials, it is found that the hyperactive metal oxides have a certain degree of restrictive conditions in the reaction effect of photocatalytic hydrogen production. From all researches on catalytic hydrogen production, it is found that not all metal oxide semiconductor materials can be used for catalytic hydrogen production. However, the application of this material in environmental protection has only begun to develop and prevail in the past ten years. Studies have found that titanium dioxide can catalyze the degradation of organic pollutants polychlorinated biphenols under ultraviolet light in the sun [14]. In the research of metal oxide materials in the past few years, it can be said that this material has become an important research object in the chemical field for the treatment of pollutants due to its high efficiency, less secondary pollution, low cost, and easy preparation [15].

2.2. Polybrominated Diphenyl Ethers Based on Metal Oxides. Polybrominated diphenyl ethers are abbreviated as PBDEs, which are brominated flame retardants [16]. PBDEs are aromatic compounds based on bromine-substituted hydrogen atoms in biphenyls. According to the position and number of bromine substitutions, there are 209 kinds of homologues. It has good flame retardant properties and stable performance. It is also widely used in electronics, electrical appliances, fabrics, building materials, petroleum, and other industries because of its low price and low impact on materials [17]. PBDEs have the characteristics of low vapor pressure and strong lipophilicity at room temperature, high boiling point, and low solubility in water. It has a fairly stable chemical structure [18], and its chemical structure is shown in Figure 2. It is difficult to degrade through physical, chemical, or biological means.

The flame retardant properties of PBDEs are gas phase flame retardant, and the specific mechanism is as follows. PBDEs are decomposed by heat to generate HBr, which can capture active free radicals that transfer combustion chain reactions [19]. It can produce bromine free radicals with lower activity, which can slow down or stop the combustion reaction. In addition, HBr is a high-density, low-flammability gas [20]. It can not only dilute the oxygen in the air but also cover the surface of the material. It can be isolated from the air to slow down combustion and spontaneous combustion [21]. However, if it is in a high temperature environment, it can release bromine atoms and burn it under certain conditions, which will generate more toxic PBDD/DFs.

Studies have shown that PBDEs are a variety of pollutants found in the environment and have been detected in a variety of environmental media such as water, air, soil, organisms, and humans [22]. Highly brominated diphenyl ether is soluble in water or volatilized in the air and
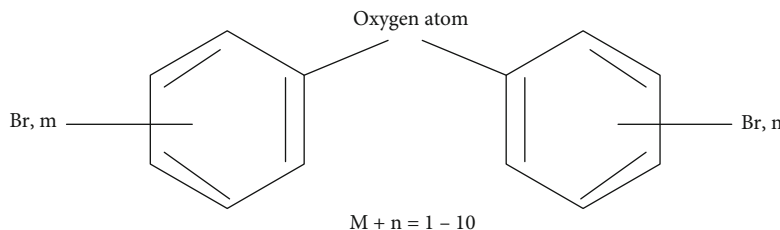
Figure 2: The chemical structure of polybrominated diphenyl ethers.

deposited on organisms. It is debrominated in the natural environment, decomposed into low-brominated diphenyl ether, and then passed through water, air, bioaccumulation, etc. The path propagates in the environment and finally constitutes the path [23]. The environmental behavior of PBDEs mainly includes the movement between pollution sources, environmental media, and the transformation and final fate during the movement [24]. Its impact on the environment is shown in Figure 3.

Because PBDEs are persistent in the environment, their increasing exposure routes bring great risks to human health [25].

3. Health Risks of Polybrominated Diphenyl Ether PBDEs Based on Optoelectronic Materials

Nowadays, people have a certain degree of awareness about the pollution of polybrominated diphenyl ethers, and the amount of exposure in the environment is increasing day by day, and the substance has a certain degree of carcinogenic risk. This ingredient is a serious hazard to human health, especially for children who are underdeveloped. This chapter evaluates the health risks posed by polybrominated diphenyl ethers and discusses the carcinogenic risks posed by them. Exposure refers to the exposure of the human body to one or more physical, chemical, or biological factors in time and space. There are two ways to expose. External exposure refers to the level of external environmental pollutants that the human body directly contacts; internal exposure refers to the actual exposure level of these pollutants in the body after being absorbed by the human body through various interfaces and other biological material samples to obtain the concentration of pollutants [26, 27].

3.1. Evaluation of PBDEs Exposure in Smoke. Respiratory inhalation is an important way to be affected by smoke pollution. Compared with other methods, breathing and inhalation of PBDEs is the main way of human exposure [28]. For the inhalation method, the risk assessment method affected by pollutants is adopted this time. The evaluation method calculates the concentration of pollutants contained in the flue gas in a specific scenario, and the calculation equation is as follows:

$$HRsingle = \frac{Rair \times inhC \times HEInh \times HF \times HD}{QHF \times BL}, \quad (1)$$

$$HRtotal = HRsingle \sum_{1-i}^{i=10} BDEs. \quad (2)$$

Among them, InhC represents the volume of air breathed by adults every day, and the related parameter value is 1.6E + 0.1. HEInh represents the absorption conversion factor of the lungs, and the value of this parameter is 7.5E + 0.5. HF represents the frequency of exposure, and the value is 2.5E + 0.2. HD represents the exposure period of an adult, and the parameter is 2.5E + 0.1. The value of the life cycle BL is 2.6E + 0.4. The concentration factor QHF of PM10 is 1.4E + 1.2. These values are combined with Equations (1) and (2), plus the required measurement values in the area, namely, the particle concentration *Rair* in the flue gas, the average monomer exposure concentration *Rai r*, and the total concentration HRtotal of lifetime exposure. The calculation results are shown in Table 1.

It can be seen from Table 1 that under different regeneration temperatures, the lifetime exposure concentration of PBDEs in the flue gas to adults is different [29, 30]. The general trend is that as the temperature increases, the exposure concentration continues to increase.

3.2. Risk Assessment Method. Health risk assessment includes noncarcinogenic risk assessment and carcinogenic risk assessment. The classification is based on whether the pollutants have carcinogenic properties. The formula for calculating the carcinogenic risk (CHF) of toxic compounds is

$$CHF = HC \times RUN. \quad (3)$$

In Equation (3), CHF represents the carcinogenic risk index of respiratory inhalation, and HC is the concentration of compound exposure and the carcinogenic risk RUN per unit of respiratory inhalation [31]. After referring to the toxicity of PCBs and the intake factors, the RUN value is calculated, and the following is calculated:

The carcinogenic risk of smoke also increases with the increase in temperature, which is consistent with the exposure level. The higher the level of exposure, the higher the risk of cancer. In the temperature range of 180-210°C, compared with the US EPA health risk standards, the carcinogenic risk of tribromo and nonabromodiphenyl ether is between 1.0E-03 and 1.0E-01. Its carcinogenic risk level is in a high position, and the carcinogenic risk values of other homologues are all higher than 1.0E-01, and its carcinogenic risk level is very high [32].
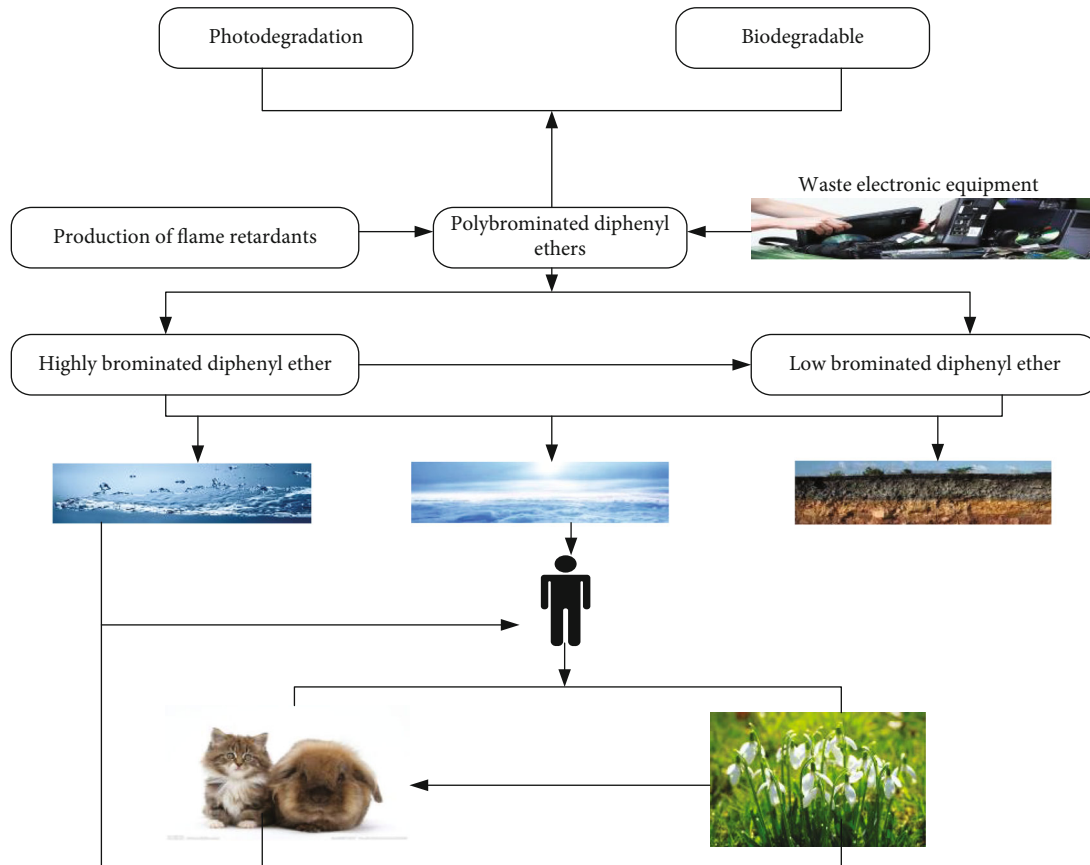
FIGURE 3: Environmental behavior characteristics of polybrominated diphenyl ethers.

TABLE 1: Respiratory exposure of PBDEs in flue gas at different temperatures.

Exposure level of each series	180-190°C	190-200°C	200-210°C
Tri	0.26	0.12	0.13
Tetra	0.26	0.18	0.2
Penta	0.34	0.32	0.25
Hexa	0.77	1.46	1.2
Hepta	1.65	2.17	3.16
Oeta	0.1	0.28	0.33
Nona	0.06	0.18	0.18
Deca	8.17	11.12	12.06
PBDEs	11.7	15.9	17.5

3.3. Exposure Risk Assessment Model. Exposure mainly refers to the process by which the human body is exposed to chemicals through different environments. It is closely related to the exposure time, way, and intensity. The selection of parameters is the basis for risk evaluation [33]. With reference to relevant literature, this section selects three models of breathing inhalation, skin contact, and hand-oral ingestion to analyze PBDE exposure. Among them, the hand-oral intake route is unique to children, and the details are as follows:

Model of breathing and inhalation method:

$$\text{Hinh} = \frac{R \times \text{IC} \times L}{\text{BW}}, \quad (4)$$

$$R = \frac{\text{MC} \times \text{BS}}{U \times Q}. \quad (5)$$

In Equations (4) and (5), Hinh represents the way of breathing and inhalation, R represents the release of PBDEs in the air, IC represents the inhalation rate, L represents the daily exposure time, and BW represents the quality of the inhaled population. The indoor volume U and the ventilation rate Q are related to each other. BS is the contact area. MC represents the daily release of indoor PBDEs.

Exposure model by skin contact:

$$\text{Hderm} = \frac{\text{MC}' \times \text{RA} \times L}{\text{BW}}. \quad (6)$$

Hderm is the amount of exposure by skin contact, and B is the probability of PBDEs migrating to the hands. RA represents the contact area of the skin.

Hand-oral intake model:

$$\text{Horal} = \frac{M \times \text{LH} \times \text{BS} \times \text{HF}}{\text{BW}}. \quad (7)$$

TABLE 2: Experimental reagents and material list.

Reagent materials	Chemical formula	Purity
Vitamin B_{12}	$C_{63}H_{88}O_{14}N_{14}PCO$	98%
Tetrabromodiphenyl ether	$C_{12}H_6C_{12}H_6Br_4O$	95%
Nano iron powder	Fe	99%
Methanol	CH_3OH	Chromatogram pure
Tetrahydrofuran	C_4H_8O	Analytically pure
Hydrochloric acid	HCl	Analytically pure
Sodium hydroxide	NaOH	Analytically pure
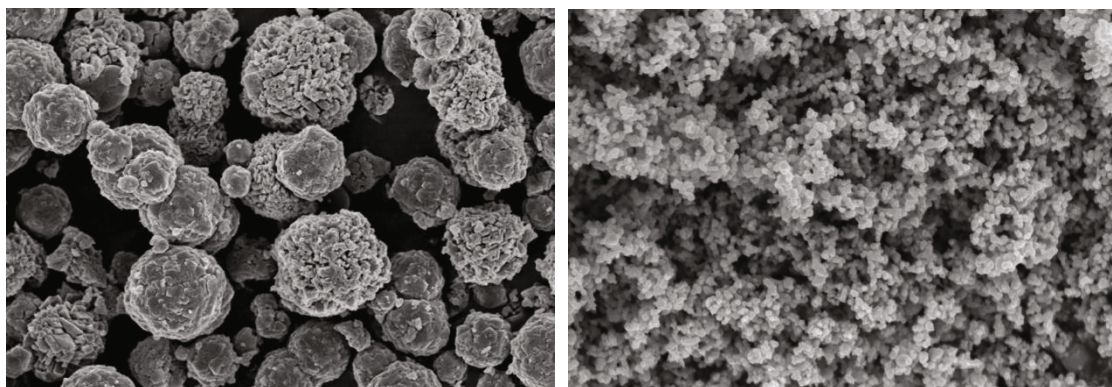
FIGURE 4: Scanning electron microscope image of reduced iron powder and nanoiron powder.

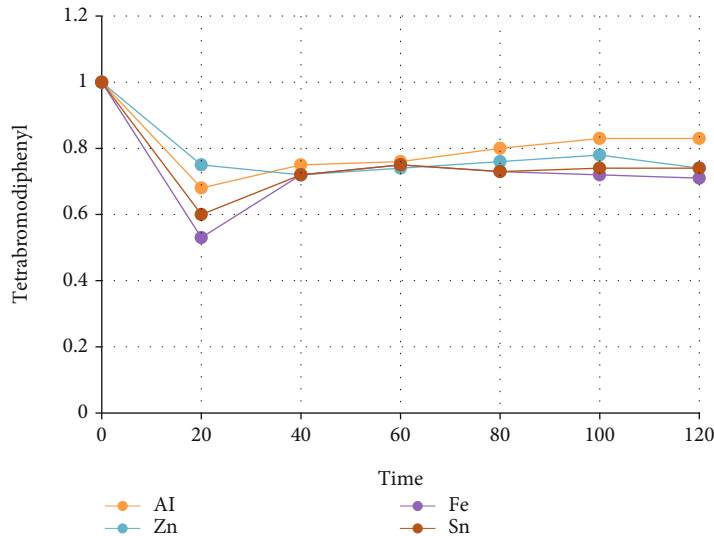
FIGURE 5: Degradation effects of different metals.

Horal represents the exposure by hand-oral ingestion, and LH is the transfer probability of PBDEs per exposure. HF represents the probability of contact.

As polybrominated diphenyl ethers are widely used as flame retardants in a variety of consumer products, the per capita annual exposure continues to rise. Moreover, bioaccumulation and environmental persistence may increase the risk of human carcinogenesis. Therefore, the following models can be used to assess its potential nonchemical carcinogenic risk:

$$EP = \frac{Hinh + Hderm + Horal}{CfD}. \qquad (8)$$

Among them, the risk of nonchemical carcinogenesis is represented by EP, and the noncarcinogenic reference dose of pollutants is CfD.
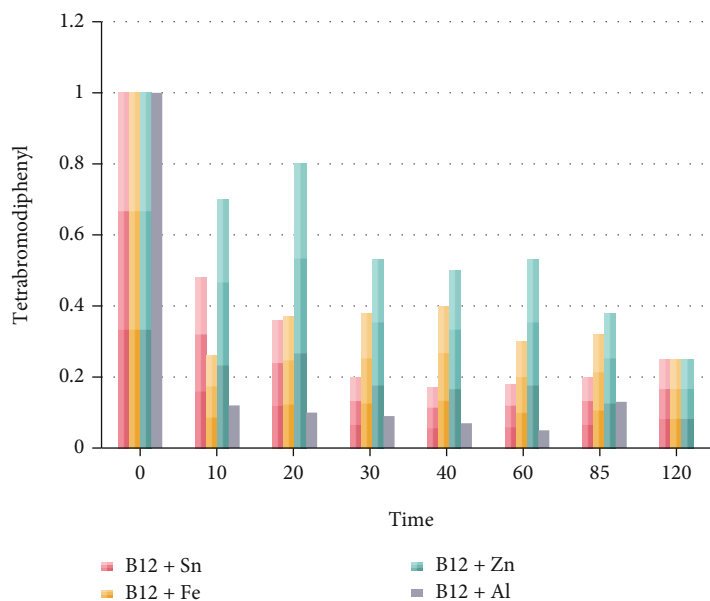
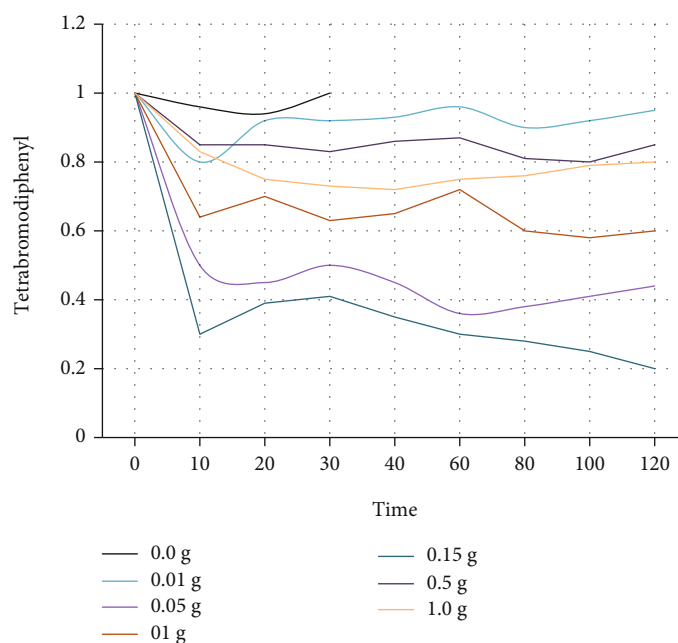FIGURE 6: Different metals coordinate the debromination effect of B_{12}.

FIGURE 7: The effect of increasing nanometer iron powder on debromination.

3.4. Degradation of PBDEs.

Biodegradation: it refers to the reduction of harmful substances by microorganisms in the natural environment [34]. Microbial degradation can be divided into two types: (1) aerobic degradation, which is mainly through the isolation and cultivation of a certain strain that has high degradability for PBDEs, and (2) anaerobic degradation, which refers to the use of the extracted anaerobic bacterial populations to debromine and degrade PBDEs through the cultivated bacterial species, because PBDEs will undergo debromination and degradation reactions to varying degrees in an anaerobic environment.

Photodegradation Method: it refers to the photolysis reaction of most harmful substances in the natural environment under the action of absorbed sunlight [35]. As an important way to transform PBDEs, PBDEs are degraded by absorbing the ultraviolet band in sunlight.

Zero-valent Iron Degradation: it is a relatively popular degradation method in recent years. It is mainly a degradation method of debromination of PBDEs through zero-valent metals [36].

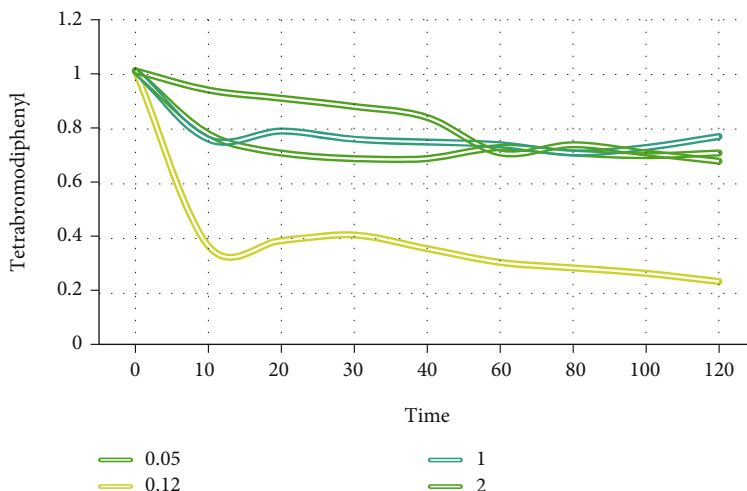Hydrothermal Reaction Treatment: it is a common treatment method in daily life. For example, tetrabromobisphenol

FIGURE 8: The effect of increasing B_{12} on debromination under the same quality of iron powder.
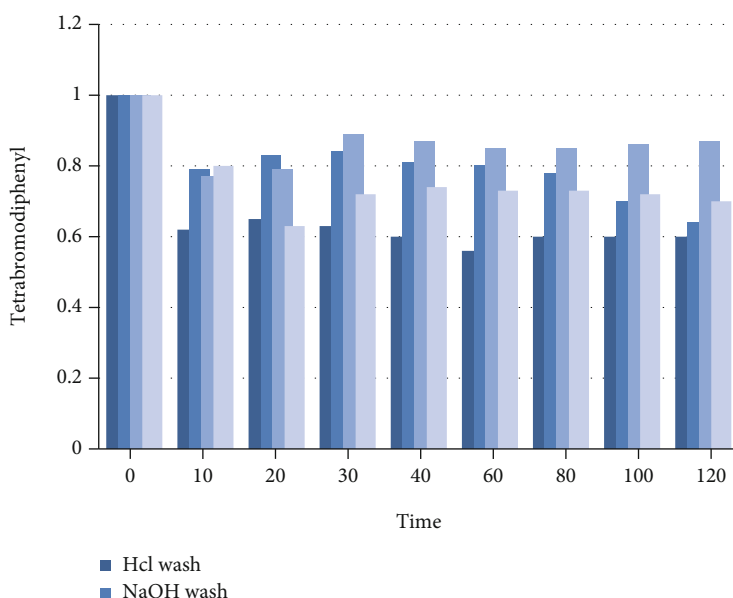

FIGURE 9: The effect of pretreatment on debromination.

reacts in high temperature subcritical water for a period of time, and the debromination reaction occurs [37] .

Composite Degradation Technology: based on the stable and long-lasting characteristics of PBDEs, a single degradation method cannot completely produce a good degradation effect on PBDEs. Therefore, the fusion application of multiple degradation methods can achieve a relatively good effect on its degradation [38].

3.5. Metal-Based Oxide Debromination Experiment. This experiment uses vitamins and zero-valent metal particles to decompose low-concentration halogenated organic matter in the soil and other systems to achieve actual therapeutic effects. The zero-valent iron reduction/debromination method has been developed in recent years. Because iron is a very active metal, and its chemical properties are also

very active, it is more and more popular. Facts have proved that it has greater electronegativity and redox characteristics. It can reduce a variety of pollutants. There are several other advantages of zero-valent iron in the treatment of pollutants. Due to its electrochemical properties, it has a certain role, such as in microelectrolysis. In addition, due to its porous material properties, it has the effect of adsorbing organic pollutants in a specific pH range. Compared with zero-valent iron powder, nanoiron powder has finer particles. This experiment uses metal materials, which decompose tetrabromodiphenyl ether under the combined action of vitamin B_{12}. Then, by observing the effect of each addition of zero-valent iron on the experimental effect, the experiment discussed the decomposition effect of various metals and the possibility of decomposition in the scene of fusion with vitamin B_{12}.
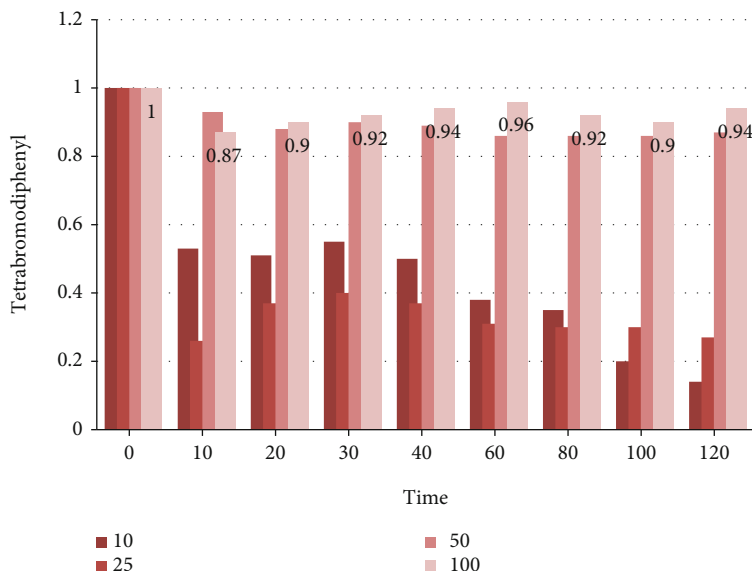
FIGURE 10: The effect of initial concentration on the debromination effect of tetrabromodiphenyl ether.

3.6. Reagents Needed for Experiment.

The main experimental materials are shown in Table 2.

3.7. Sample Analysis Method for Degradation Experiment.

The total amount of the reaction solution for the decomposition and debromination experiment is 30 mL. The experiment was carried out in a 50 mL three-necked flask, adding 500 mg/L of tetrabromodiphenyl ether stock solution and an initial concentration of 10 mg/L of tetrabromodiphenyl ether. Brominated diphenyl ether reaction liquid is a mixed solution of methanol and water. It is added with different amounts of vitamin B_{12} and nanoiron powder. It uses sodium hydroxide or hydrochloric acid to adjust the pH. The rotation speed is controlled to 220 rpm under protective gas and light-proof conditions. All reactions are completed under normal temperature and pressure.

3.8. Scanning Electron Microscopy (Sem) Analysis of Nanometer Iron Powder.

The scanning electron micrographs of iron powder and nanoiron powder are shown in Figure 4, respectively.

As shown in Figure 4(a), the particles of reduced iron powder are relatively coarse. The scanning electron micrograph of the nanoiron powder is shown in Figure 4(b). In contrast, the nanoiron powder has a much smaller particle size and the diameter is in the nanometer range. The study found that nanoiron powder is more reactive than ordinary iron powder and iron filings, and it has a larger specific surface area due to the nanosize effect. With strong reactivity and excellent adsorption performance, it has been widely studied and applied.

4. Result Analysis

4.1. The Influence of Different Metals on the Debromination Effect of Tetrabromodiphenyl Ether.

The results of degradation effect of different metals Al, Zn, Fe, and Sn are shown in Figure 5.

The decomposition rates of metals Al, Zn, Fe, and Sn are 16.64%, 24.20%, 29.04%, and 27.44%, respectively. Its low decomposition efficiency is mainly due to the high reduction of active metals, which can reduce many pollutants. It also has specific electrochemical and adsorption characteristics, electrolysis, and adsorption of pollutants. Therefore, the main catalytic reaction without a catalyst leads to less decomposition of pollutants. Secondly, in the larger metal particles and partial oxidation of their surface, etc., tetrabromodiphenyl ether is likely to deteriorate. The results show that the decomposition effect is Fe>Sn>Zn>Al. This may be related to the nature of the metal itself. The slow decomposition rate of aluminum is mainly due to the formation of a dense oxide film in the environment, which hinders the reaction.

4.2. The Effect of Different Metals and Vitamin B_{12} on the Debromination Effect of Tetrabromodiphenyl Ether.

Coupling Al, Zn, Fe, and Sn with B_{12} to degrade, the experiment takes a certain quality of metal B_{12}. The experimental results are shown in Figure 6.

As shown in Figure 6, the decomposition rates of metals and vitamins after coupling are 84.57%, 82.41%, 82.81%, and 98.89%. From the point of view of the increase of time, the decomposition rate shows an obvious decreasing trend with the passage of time, but the decomposition rate of several metals maintains a stable state at the end, respectively. The results show that the coupling of the ball-milled aluminum powder with B_{12} can efficiently and quickly decompose tetrabromodiphenyl ether. The reason for the impact may be that the ball mill restored the aluminum reduction ability. It destroys the oxide layer on the surface and makes the reaction more thorough.

4.3. 4.2 The Influence of the Dosage of Main Reactants on Debromination.

The dosage of nanometer iron powder affects the debromination effect. For the reaction system, when the dosage of B_{12} is 0.1 mM, the degradation diagram
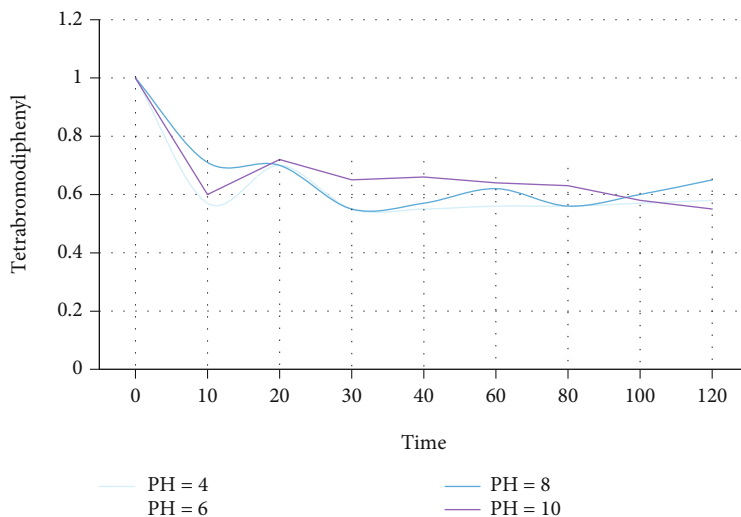
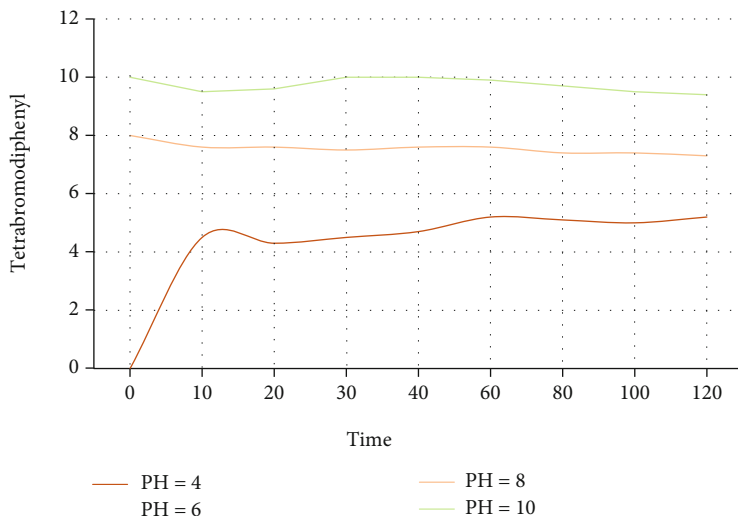FIGURE 11: The effect of pH on the debromination effect.

FIGURE 12: pH changes during the process.

of the dosage of nanometer iron powder on the debromination effect is shown in Figure 7.

As shown in Figure 7, the amount of nanoiron powder ranges from 0.0 g/L to 0.15 g/L. With the increase in the amount of nanoiron powder, the decomposition rate of tetrabromodiphenyl ether has a slope change. When the dosage of nanoiron powder is from 0.15 g/L to 1.0 g/L, the effect decreases as the concentration increases. This may be due to the increase in the concentration of nanoiron powder that can provide more reaction sites. If the concentration is too high, the hydrogen concentration generated by iron corrosion that covers the iron surface and interferes with the reaction will be too high. Therefore, increasing the concentration of nanoiron powder will accelerate the dehydrogenation reaction, but when it reaches a certain level, the reaction rate gradually decreases and stops.

The influence of the dosage of B_{12} on the debromination effect of tetrabromodiphenyl ether is shown in Figure 8. Under the dosage of 0.15 g/L nanoiron powder, this article

discusses the effect of vitamin B_{12} dosage on the degradation of tetrabromodiphenyl ether. In the range of 0.0 mM-0.1 mM, increasing the dose of vitamin B_{12} will accelerate the degradation efficiency. At concentrations between 0.1 and 2.0 mM, the degradation rate decreases as the concentration increases. When the amount of vitamin B_{12} is gradually increased to a certain amount, tetrabromodiphenyl ether is rapidly degraded within 120 minutes. This shows that increasing the vitamin B_{12} level within a certain range will significantly increase the rate of reaction degradation. Too high levels of vitamin B_{12} can interfere with electron transfer.

4.4. The Influence of Pretreatment Process on the Debromination Effect of Tetrabromodiphenyl Ether. When the reduced iron powder is subjected to various pretreatments and combined with B_{12}, the decomposition effect of the nanoiron powder is significantly higher than that of acid washing, alkaline washing, and methanol washing, as shown

in Figure 9. Alkaline washing refers to a high-strength lye solution prepared with sodium hydroxide and sodium carbonate or trisodium phosphate to soften, loosen, emulsify, and disperse deposits; pickling refers to the use of acid solution to remove oxide scale and rust on the surface of steel method. According to the degradation rate, the pretreatment methods are sorted into acid washing, alkaline washing, nanoiron powder, and methanol treatment processes. This is due to the large specific surface area and fine particles of the nanoiron powder, which can provide more reaction sites, which in turn can better provide electrons for the reaction. The results show that the effect of pickling is better than alkaline washing and methanol washing. Acid can remove the oxide film on the metal surface, clean the surface, and improve the debromination effect.

The initial concentration range of tetrabromodiphenyl ether is 10-100 mg/L. After 120 minutes of reaction, the result of measuring the effect on the dehydrogenation effect is shown in Figure 10. The degradation efficiency of tetrabromodiphenyl ether continued to decrease as the initial concentration increased. The removal rates after the reaction were 91.62%, 82.44%, 13.63%, and 5.39%, respectively. This is mainly because when the reaction concentration of tetrabromodiphenyl ether is low, nanoiron can provide a large effective surface area. So increasing the contact area ratio of the reaction will result in more active sites. So its dismantling is relatively complete. Therefore, if the pollutant concentration increases before the reaction, the tetrabromodiphenyl ether will eventually contact the nanoiron surface only after fierce competition. It can cover the surface when it is fully occupied, and only when it comes into contact with other molecules can it cause interference. Therefore, its debromination effect has been reduced.

4.5. The Influence of pH on the Debromination Effect of Tetrabromodiphenyl Ether. The initial pH of the system is 4.0 to 10.0, and the reaction is carried out under alkaline conditions. Figure 11 shows the effect of the initial pH of the system on the removal rate of tetrabromodiphenyl ether. The weakly acidic system environment is conducive to the dehydrogenation reaction. If the pH value changes during the reaction, the initial pH value of the system will become acidic, and the concentration of tetrabromodiphenyl ether will drop rapidly. The results show that the reaction is easier to proceed under acidic conditions, while the reaction is slower under alkaline conditions. The main reason is that the high hydrogen ion concentration enhances the cleaning ability of the metal, increases the corrosion rate, and at the same time promotes the production of reducing substances, thereby promoting the reaction, and vice versa. As the H+ concentration in the system increases, iron corrosion occurs rapidly, and its surface is blocked. This is not conducive to the progress of the reaction.

The change in pH value in Figure 12 shows a trend of small fluctuations during the reaction time, which is basically stable thereafter. With the initial increase of pH, the final degradation of tetrabromodiphenyl ether was 5.36, 7.08, 7.25, and 9.45. Under acidic conditions, the increase in pH may be due to the consumption of H+ or the produc-

tion of OH-. As the pH increases, the slowing down of degradation may be due to the fact that the reaction is basically stable. Iron dissolves in the aqueous medium and emits electrons to produce H2. These reactions increase the pH. Under acidic and neutral conditions, as an electron acceptor, H+ can compete with tetrabromodiphenyl ether for electrons.

5. Conclusions

This paper discusses that the environmental behavior of PBDEs is the basis for their pollution prevention and control, due to their far-reaching impact on social and economic development and human health. Therefore, it is urgent to develop a fast, efficient, and thorough polybrominated diphenyl ether degradation technology. In the experiment, we studied the catalytic reduction effect of tetrabromodiphenyl ether and influencing factors with nanoiron powder and vitamin B_{12}. The experiment investigated the effects of vitamin B_{12} dosage, iron dosage, pH value, pretreatment conditions, reaction concentration, pH change value, etc. on the decomposition rate of tetrabromodiphenyl ether. The optimal reaction conditions for the catalytic reduction of tetrabromodiphenyl ether with nanoiron powder and vitamin B_{12} are as follows: the amount of nanoiron powder is 0.15 g/L, the amount of vitamin B_{12} is 0.1 mM, and the initial pH value is 6.0 under pickling. It is the best reaction condition under all the listed conditions. The removal rate of 10 mg/L tetrabromodiphenyl ether after 120 minutes of reaction is as high as 91.62%. Compared with traditional zerovalent iron powder, nanoiron powder has stronger reducing power and higher surface activity. This means that it can provide more active centers for the reaction.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Acknowledgments

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