Effect of montmorillonite-loaded nano zero-valent iron-activated persulfate on the degradation of ACE and THX

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Abstract. To investigate the degradation characteristics and mechanism of acetamiprid and thiamethoxam under the system of montmorillonite-loaded nano zero-valent iron activated persulfate, a novel nanocomposite material M-nZVI was prepared by liquid phase reduction method using montmorillonite as raw material. The effect of the nanocomposite material on the degradation of acetamiprid and thiamethoxam in water by the activation of persulfate was investigated. The results showed that the degradation of acetamiprid and thiamethoxam by single nano zero-valent iron activated persulfate was only 43% and 49%, indicating that the nano zero-valent iron has the deficiencies of being easy to oxidize and easy to be agglomerated, which led to a significant reduction of its reactivity. However, the ability to activate persulfate was greatly enhanced after the nano-zero-valent iron was modified by montmorillonite, and the degradation of acetamiprid and thiamethoxam by the modified material could reach 100% within 60 min, and the material was stable, and the degradation rate could still reach 100% after 90 days of storage. Therefore, the modified nano zero-valent iron-activated persulfate technology is promising for the remediation of neonicotinoid pesticides, but the modification method should be adjusted accordingly for different pollutants, and in-depth explorations should be carried out subsequently.

Keywords: Montmorillonite; Nano-zero-valent iron; ACE; THX; Modification.

1. Introduction

Neonicotinoid pesticides (NEOs) were discovered in the late 1980s as the fourth major class of insecticides after organophosphorus insecticides (OPs), pyrethroids (PYRs), and carbamates (CBs). It is one of the major discoveries in the field of agrochemistry in recent decades and is of landmark significance [1]. Neonicotinoid pesticides have unique advantages such as high efficiency, low toxicity, high broad-spectrum insecticidal activity, high adaptability, and low susceptibility to cross-resistance in the field of agriculture [2, 3], which makes them the fastest-growing class of insecticides in the domestic and international markets [4], with a high market share and soon aroused widespread interest among researchers, neonicotinoid pesticides have become the boom in the development of pesticides nowadays, and the neonicotinoid pesticides, amidoflagellate (ACE) and thiamethoxam (THX) are the most widely used neonicotinoid pesticides [5]. The use of neonicotinoid pesticides has greatly reduced the number of vector insects and crop morbidity in agriculture and forestry and produced great economic benefits. However, with the gradual increase in the number of years and the number of neonicotinoid pesticides put into use, more and more studies have exposed the ecological health hazards they pose to non-target organisms [6-8]. For example, a large number of field and semi-field experimental studies have shown that exposure to neonicotinoids causes a decrease in navigational homing accuracy, foraging efficiency, immunity, queen reproduction, and development in honey bee populations [9, 10], which ultimately results in a significant decrease in honey bee populations and induces colony collapse syndrome in honey bees [11]. Therefore, neonicotinoid residues in the environment should receive sufficient attention, and it is imperative to find an efficient, safe, and fast method to remove neonicotinoid pesticide residues.

Activated persulfate oxidation is a very promising process for advanced oxidation. The process involves the activation of persulfate (PDS) or peroxomonosulfate (PMS) by thermal activation, alkali activation, UV activation, and transition metal ions, resulting in the generation of $SO4^{\bullet-}$ radicals [12, 13]. It is well known that $SO4^{\bullet-}$ radicals have longer lifetimes in water and higher oxidation compared

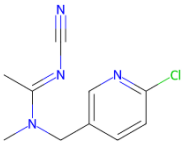
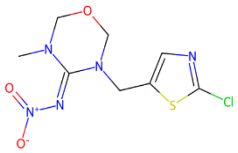
to •OH radicals (2.7 V in acid solutions and 1.8 V in neutral solutions) reduction potential (2.5-3.1 V) [14]. In addition, most PDS/PMS activators are relatively unaffected by changes in pH [15]. nZVI, although it is well able to activate persulfate for the degradation of neonicotinoid pesticides, there are still many drawbacks of nZVI that need to be addressed in time. For example, nZVI itself is easily oxidized in air and forms a passivation layer with a certain thickness, reducing its catalytic activity. At the same time, hydroxides and metal carbonates, etc. are formed during the degradation of pollutants, which reduces the degradation efficiency of pollutants. In addition to the formation of passivation film, the aggregation of nZVI is also a major drawback that significantly reduces its effective surface area, which will be particularly worrisome when using excessive amounts of nZVI [16]. Since biochar and inorganic minerals are abundant in the environment and are good carriers of nZVI, researchers have conducted many studies in this field. Wu et al. synthesized organo-montmorillonite-loaded nano-zero-valent iron (nZVI/OMt) composites by liquid-phase reduction and carried out experiments on the degradation of sulfamodimethoxydiazide (SMZ) degradation by activation of the peroxynitrite in nZVI/OMt composites, and experimental The results showed that sulfadimethoxine (SMZ) could be removed up to 97% at the original pH=6.8, nZVI/OMt composite dosage of 1.5 mM, and PDS concentration of 4 mM, and this phenomenon is a good indication of the better stability of nano-zero-valent iron after loading with inorganic minerals and the better activation of persulfate [17]. This work provides a promising technological approach to convert inorganic minerals into highly efficient and low-cost nano-catalysts to activate persulfate for the degradation of difficult-to-degrade neonicotinoid pesticides in aqueous environments.

2. Material and method

2.1 Material

M-nZVI used in this study were synthesized in the laboratory and the made nanocomposites were ground into a black powder state, sieved through 100 mesh sieve, and stored in brown bottles for use in subsequent experiments. The detailed physicochemical properties of two typical neonicotinoid pesticides, acetamiprid (analytically pure grade) and thiamethoxam (analytically pure grade), selected for this experiment are shown in Table 1. The solvents used to configure the solutions in the experiment were deionized water (>18.2MΩ·cm).

Table 1 Physicochemical properties of acetamiprid and thiamethoxam

Compound	Molecular	Molecular weight (g/mol)	Water solubility (mg/L)	Molecular structure
Acetamiprid	$C_{10}H_{11}ClN_4$	222.67	4200	
Thiamethoxam	$C_8H_{10}ClN_5O_3S$	291.71	4100	

2.2 Preparation of zero-valent iron nanocomposites

In this experiment, inorganic mineral-loaded nano zero-valent iron composites (X-nZVI) were prepared by the liquid phase reduction method [18, 19]. 1.12 g of montmorillonite through a 100 mesh sieve was added into a 500 ml three-necked flask with 200 ml of ultrapure water for thorough mixing. The pH was adjusted to 4 using H_2SO_4 (pH is a key factor in the preparation of nanozero-

valent iron, and nanozero-valent iron begins to precipitate in the aqueous solution in the form of iron oxides and ferric hydroxides as the pH value approaches neutrality). Subsequently, 2.780 g of FeSO4·7H2O was added to the suspension and subjected to ultrasonication for 30 min (ultrasonication was used to disperse the iron sulfate agglomerates and to improve the adsorption of iron sulfate on the surface of the montmorillonite), and the mixture was subsequently stirred vigorously under nitrogen for 30 min. Afterward, 200 ml of 0.188 M $NaBH_4$ was added into the suspension drop by drop at 2 drops/s with a molar ratio of $NaBH_4$ to NaOH of 8:1. After the addition of NaBH4, the suspension was continued to be stirred at room temperature for 30 min, and the whole process was carried out in an environment of N_2, to avoid the oxidation of nZVI. Finally, the solid complex material was washed twice with ethanol and once with ultrapure water to remove residual chlorides and borohydrides, vacuum dried for 24 h, and removed for spare use. The newly prepared materials were M-nZVI composites with a montmorillonite-to-iron mass ratio of 2:1. For comparison, pure phase nZVI particles were synthesized similarly without the addition of zeolite.

2.3 Degradation experiments

The degradation experiments were all performed in 250mL conical flasks with at least two parallel samples set up for each set of experiments. The experimental methodology for the catalytic degradation of ACE and THX by inorganic mineral-loaded nano-zero-valent iron is briefly summarized as follows: the experiments were carried out in conical flasks containing 250 mL of either ACE or THX solution, the temperature was maintained at 25 ℃ unless otherwise stated, the flasks were fixed in an oscillating shaker, the M-nZVI composites and polysulfate required for the reaction were added, and the speed of the oscillator was set to 150 rpm. The initial reaction time was defined as the moment of addition of M-nZVI composite and persulfate, and 0.5 ml of the liquid in the conical flask was removed at specific time points (0 min, 5 min, 10 min, 15 min, 20 min, 30 min, and 60 min) and the reaction was immediately terminated by adding an equal volume of the liquid phase flask containing methanol, and the reaction was filtered through a 0.45μm filter tip and The filtrate was placed in a new liquid-phase flask, and the concentration of the remaining ACE or THX in the filtrate was measured by high-performance liquid chromatography, and the results were recorded, and the pH value of the solution in the conical flask was measured and recorded in time after the end of the reaction.

2.4 Stability and Regeneration Experiments

To investigate the stability of different inorganic minerals-nZVI, the X-nZVI composites were stored in air (25 ℃, 81% humidity) under the same reaction conditions for 15, 30, and 60 days, respectively, and comparative experiments were conducted with freshly prepared X-nZVI composites to investigate the influence of the stability of X-nZVI composites on the degradation effect of ACE and THX.

3. Results and discussion

3.1 Effect of M-nZVI composite stability on the degradation of ACE and THX

The external morphology of M and M-nZVI before and after loading of nano zero-valent iron is observed in Figure. 1. As seen in Figure. 1(a), M unloaded with nano-zero-valent iron has a layered structure consisting of irregular sheets stacked and the surface of each sheet is relatively flat. Figure 1 (b) shows the M-nZVI after loading nano zero-valent iron, and compared with the electron microscopy of M, the surface of which is grown with uniform-size particles, and most of the particles can exist independently, which indicates that M has a better-dispersing effect on the nano zero-valent iron, and it can reduce the tendency of the nanoparticles to agglomerate with each other.

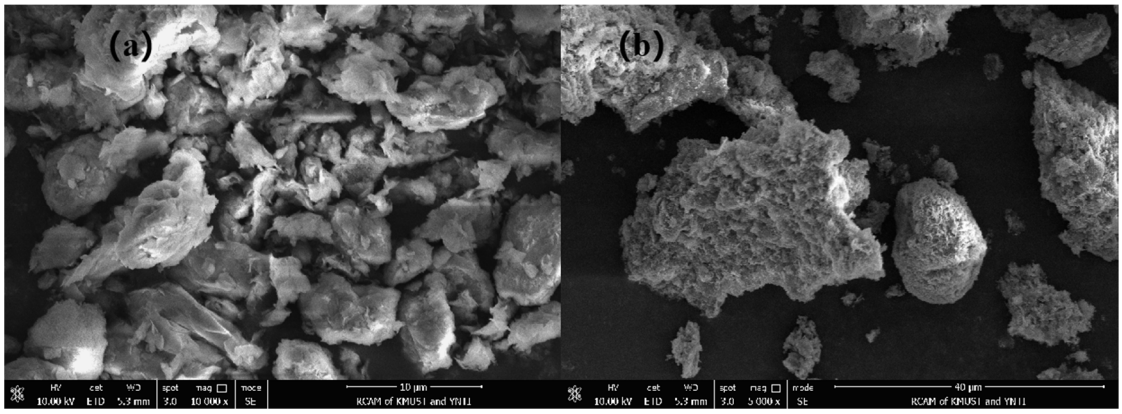


Figure 1. SEM images of M and M-nZVI: (a) M; (b) M-nZVI

To investigate the stability of M-nZVI, the loaded nano zero-valent iron after 15, 30, and 90 days of storage in air (25 ℃, 81% humidity) was compared with freshly prepared loaded nano zero-valent iron in a comparative experiment under the same reaction conditions, and the results are shown in Figure. 2. It can be seen that the degradation rate of M-nZVI on acetamiprid and thiamethoxam can still reach 100% within 1 h after storing the montmorillonite-loaded nano zero-valent iron for some time, indicating that M-nZVI has good stability, which may be because montmorillonite has a high cation exchange capacity and spacing of the layers, and has better dispersion and suspension in water, so that its loaded nano zero-valent iron has a better antioxidant property, and the specific reasons need to be further investigated.

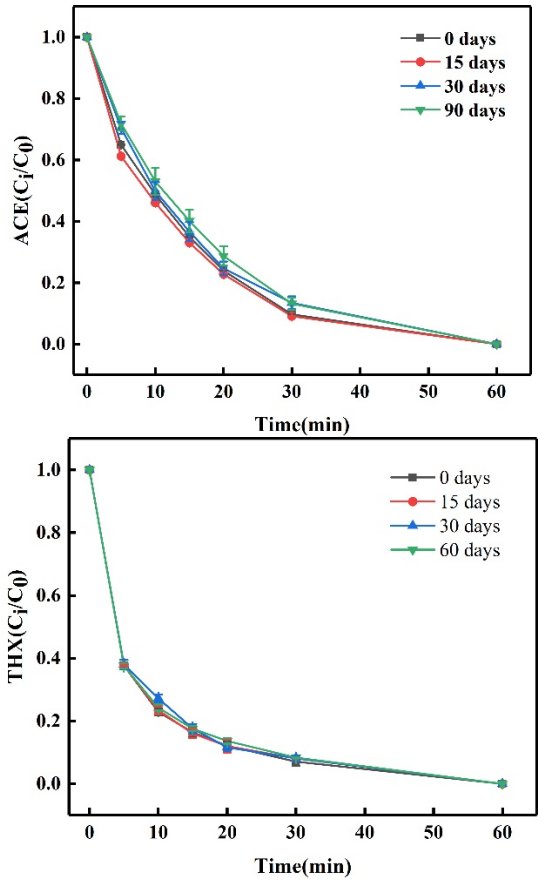


Figure 2. Stability of ACE and THX removal by M-nZVI

3.2 Effect of M-nZVI composites on the degradation of ACE and THX in different systems

To investigate the role of montmorillonite-loaded nano zero-valent iron composites in the activation of persulfate, the catalytic degradation effects of ACE and THX were investigated in the

M system, PDS system, nZVI system, nZVI/PDS system, M-nZVI system, and M-nZVI/PDS system, respectively.

Figure 3 shows the degradation of ACE and THX under M, PDS, nZVI, nZVI/PDS, M-nZVI, and M-nZVI/PDS systems, respectively. As can be seen from the figure, in the case of Montmorillonite only or nZVI only, the removal rate of ACE after 60 min of reaction was about 2% or 5%, and the removal rate of THX was about 3% or 7%, which was due to the adsorption of Montmorillonite or nZVI; in the case of PDS system, the removal rates of ACE and THX were about 2% or 5% after 60 min of reaction, which was due to the adsorption effect of Montmorillonite or nZVI; and the removal rates of ACE and THX were about 4% or 4% after 60 min of reaction. In the case of PDS system, the removal rate of ACE and THX after 60 min of reaction was about 3% and 2%, which was due to the weak decomposition ability of PDS itself in the absence of catalyst, and PDS could only decompose a very small amount of free radicals to react with ACE and THX, and only a very small amount of ACE and THX could be removed; when only catalyst M-nZVI was added to the ACE and THX solution, the removal rate of ACE and THX in 60 min was 9% and 7%, respectively. When only the catalyst M-nZVI was added to the ACE and THX solutions, the removal rates of ACE and THX were 9% and 10% respectively within 60 min, indicating that the M-nZVI composite material has a certain adsorption capacity for ACE and THX; when M-nZVI and PDS were added to ACE and THX solutions together, the degradation rate of ACE and THX was significantly enhanced, and a 100% removal rate could be achieved within 60 min, which demonstrated the excellent catalytic activity of PDS with M-nZVI, and suggested that M-nZVI could effectively activate the peroxidized ACE and THX. -nZVI can effectively activate persulfate to degrade ACE and THX. The results showed that neither PDS nor adsorbent could effectively remove ACE and THX when added alone and that the degradation of ACE and THX was mainly caused by the oxidation of free radicals generated by the M-nZVI/PDS system.

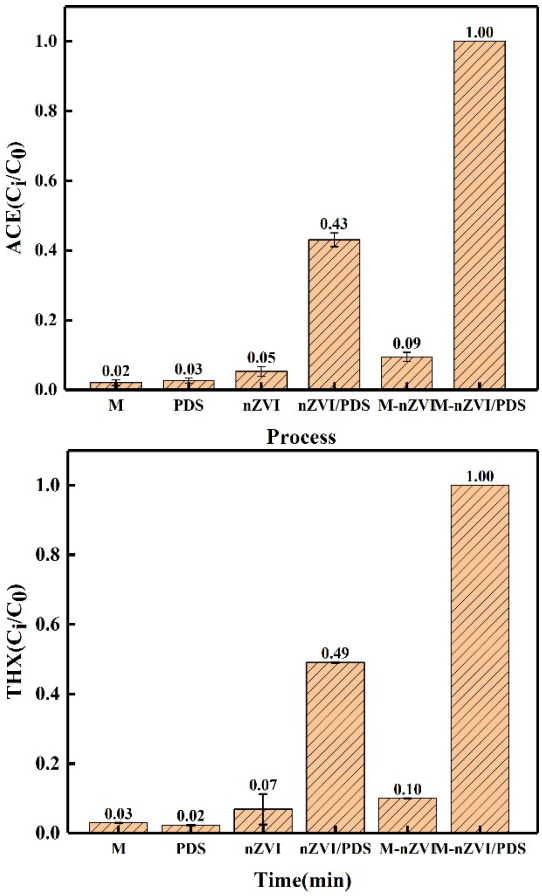


Figure 3. Effect of different systems to degrade ACE and THX

3.3 Degradation mechanism of ACE and THX by M-nZVI activated persulfate

Typically, $SO_4^{\bullet-}$ and •OH are the main reactive substances produced during the activation of persulfate by nZVI, and in this regard, free radical burst experiments were carried out to investigate which reactive substances in the M-nZVI/PDS system play a role in the ACE and THX degradation reactions.

In this experiment, methanol and tert-butanol were used as quenchers for $SO_4^{\bullet-}$ and •OH. Both methanol and tert-butanol are capable of reacting with $SO_4^{\bullet-}$ and •OH, with methanol reacting with both at comparable rates, both very rapidly, while tert-butanol reacts with •OH at a significantly higher rate than with $SO_4^{\bullet-}$, while the reaction rate of tert-butanol with •OH was significantly higher than that with $SO_4^{\bullet-}$. Therefore, after the addition of methanol and tert-butanol in the experiment, the degradation efficiency of ACE and THX can indirectly determine the free radicals present in the system, and thus determine the free radicals that play a major role in the reaction system. The experimental results are shown in Figures 4 and 5, respectively.

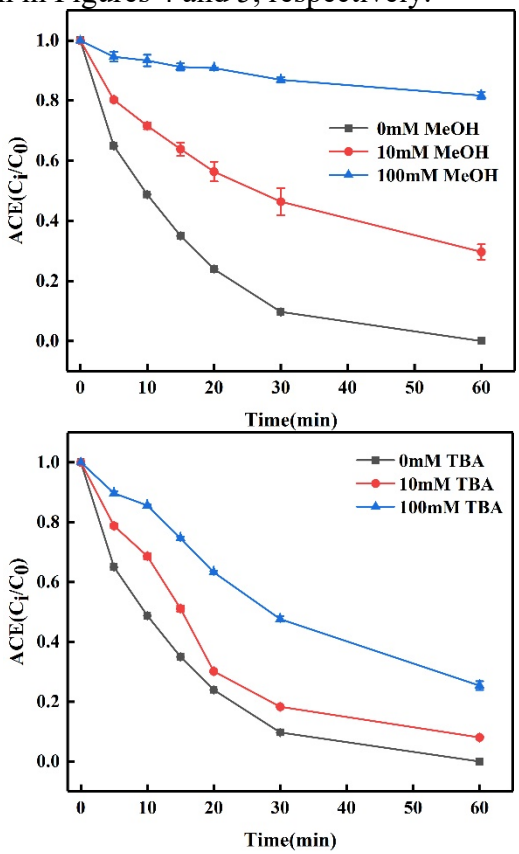
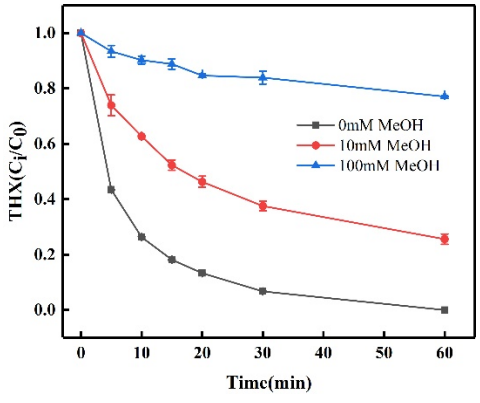


Figure 4. Effect of different concentrations of methanol and tert-butanol on the removal of ACE



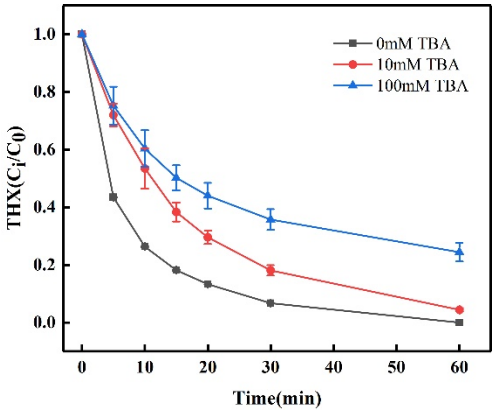


Figure 5. Effect of different concentrations of methanol and tert-butanol on the removal of THX

As can be seen from Figs. 4 and 5, the degradation of ACE and THX was significantly reduced after the addition of the two free radical quenchers, methanol, and tert-butanol, to the reaction solution. The inhibition effect on the degradation of ACE and THX was more obvious with the increase in the concentration of the quenchers in the solution. The stronger inhibition effect of methanol than tert-butanol on ACE and THX in solution at the same concentration of added quencher was caused by the different reaction rates of the two quenchers with $SO_4^{\bullet-}$ and •OH.

4. Conclusion

In this thesis, montmorillonite-loaded nano zero-valent iron composites (M-nZVI) were prepared and characterized using acetamiprid and thiamethoxam (ACE and THX) as the target pollutants, the catalytic degradation of ACE and THX by M-nZVI composites coupled with peroxodisulfate system (M-nZVI/PDS) was investigated and the mechanism of catalytic degradation of ACE and THX by the system was analyzed, with the following conclusions:

(1) The M-nZVI composites were successfully prepared by liquid-phase reduction, and the SEM images of the M-nZVI materials showed that the nano-zero-valent iron (nZVI) was uniformly dispersed and attached to the montmorillonite surface.

(2) By comparing the degradation effects of different systems on ACE and THX, it was found that the M-nZVI/PDS system degraded ACE and THX significantly better than the nZVI, M-nZVI, and nZVI/PDS systems.

(3) Free radical quenching experiments using methanol and tert-butanol in the M-nZVI/PDS system show that the free radical that plays a major role in the M-nZVI/PDS system is $SO_4^{\bullet-}$.

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