Research progress of heterogeneous Fenton catalyst for organic wastewater treatment

Xin Zhang¹, Qiaosheng Zhang¹,², Tao Yang¹,², Yanfang Li¹,², Jinling Li³, Tao Yu¹, Chengtun Qu³,*

¹ The National Engineering Laboratory for Exploration and Development of Low Permeability Oil & Gas Fields, China
² Xi’an Changqing Science and Technology Engineering Co. LTD, China
³ College of Chemistry and Chemical Engineering, Xi’an Shiyou University, Shaanxi Oil and Gas Pollution Control and Reservoir Protection Key Laboratory, Xi’an 710065, China

*Corresponding author e-mail: Wangshuangct@yeah.net

Abstract. The catalytic degradation of organic wastewater by heterogeneous Fenton has attracted much attention in recent years. Compared with homogeneous Fenton, heterogeneous Fenton reaction has the advantages of wide pH range, low dissolved iron content after reaction, easy magnetic separation and good reusability. This paper mainly introduces the research progress of heterogeneous supported Fenton catalyst in the treatment of organic wastewater in recent years. In this paper, the degradation performance and recyclability of organic wastewater by catalysts are discussed, and the development direction of catalysts in the future is prospected.

1. Introduction

The rapid development of the industrial field will inevitably lead to different degrees of environmental pollution. The organic wastewater produced by petrochemical, printing and dye industries is difficult to degrade and the treatment cost is high, which has become a major challenge in the field of industrial water treatment. Traditional wastewater treatment methods such as physical adsorption method [1], electrochemical method [2] and biodegradation method [3] can’t be effective treatment of organic wastewater.

2. Research status of Fenton reaction

As an advanced oxidation technology, Fenton method takes iron and its oxides as catalyst, reacts with H₂O₂ to produce highly oxidizing •OH (second only to fluorine), which can degrade organic pollutants, the reaction mechanism is as follows:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+$$ (1)
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + •OH$$ (2)
$$HO_2^- + H_2O_2 \rightarrow O_2 + H_2O + OH^-$$ (3)
$$Fe^{3+} + OH^- \rightarrow Fe^{3+} + OH^-$$ (4)
$$RH + OH\cdot \rightarrow R\cdot + H_2O$$  \hspace{1cm} (5)

$$R\cdot + Fe^{3+} \rightarrow R^+ + Fe^{2+}$$  \hspace{1cm} (6)

$$R^+ + O_2 \rightarrow ROO^+ \rightarrow CO_2 + H_2O$$  \hspace{1cm} (7)

However, the traditional homogeneous Fenton reaction has the following disadvantages: (1) the reaction is highly limited by the pH value, and it needs to be conducted under the acidic condition of pH=3.0. The reaction solution should be acidified before degradation, and the pH value should be adjusted to neutral after degradation [4]; (2) The iron content in the solution increases after the reaction, and the iron sludge is easy to cause secondary pollution [5]; (3) The catalyst has low recyclability. These shortcomings limit the development of homogeneous Fenton catalysis, so heterogeneous Fenton catalysis appeared.

Heterogeneous Fenton catalysis is that iron and its oxides are loaded on functional carriers, and Fenton reaction occurs at the solid-liquid interface to degrade organic wastewater. The specific steps are as follows: the reactants diffuse to the surface of the catalyst to form complexes; the reactants adsorbed on the active site undergo electron transfer catalytic degradation of pollutants, product desorption and regeneration of active sites of catalyst reaction [6]. Heterogeneous Fenton reaction broadens the application range of pH which can degrade organic wastewater under the condition of near neutral or even alkaline; the amount of iron ions in the solution was low after the reaction; the catalyst has stable performance, easy separation and good recyclability. In this paper, the degradation performance and cycling usability of various heterogeneous supported Fenton catalysts for organic wastewater are mainly introduced.

3. Performance study of heterogeneous Fenton catalyst

3.1. Nano zero valent iron and iron compounds

Compared with zero valent iron (ZVI), nano zero valent iron (NZVI) has the characteristics of small size, large specific surface area, strong reducibility, strong magnetism and fast reaction rate, so it is widely used in the field of wastewater treatment. Wang [6] et al. modified nano zero valent iron with hydroxyethyl cellulose (HEC) and hydroxypropyl cellulose (HPMC) and used it to degrade dye wastewater. The results showed that the decolorization rate decreased with the increase of initial pH value and dye concentration, but increased with the increase of iron dosage and reaction temperature. He [7] et al. prepared magnetic nano zero valent iron by liquid phase reduction method, which was used to treat dissolved oil wastewater and emulsified oil wastewater respectively. The results showed that when the catalyst was reused for 7 times, the removal rate was still 90.17%, and the removal rate was 88.7% when the catalysis was reused for 6 times.

Fe$_3$O$_4$ belongs to cubic crystal system with anti spinel structure, which can accommodate Fe$^{2+}$ and Fe$^{3+}$ at the same time. Fe$^{2+}$ occupies octahedral position and Fe$^{3+}$ occupies tetrahedral position. Redox reaction can take place in the same structure. Wang [8] et al. prepared Fe$_3$O$_4$ under the optimum experimental conditions, the degradation rate of phenol and COD can reach 98% and 76% respectively. When pH = 9 and degradation time is 120 min, the removal rate of phenol is 100%. After 8 cycles, the removal rate of COD is more than 60%.

3.2. Inorganic carriers

3.2.1. Clay minerals. The clay has small particle size (< 2μm), large specific surface area and rich pore structure. It has a layered structure composed of silicate structural units and alumina or aluminum hydroxide structural units, and has negative charges on the particles, showing superior ion exchange performance [9]. Clay minerals are widely distributed in nature, abundant in reserves, abundant in varieties, cheap and easy to obtain, and are widely used as catalyst carriers.

Kaolin has large specific surface area, excellent physical and chemical properties and mechanical properties, but the interlayer spacing is only 0.72nm, which makes it difficult to replace the lattice. Wang
Xuan [10] et al. modified kaolin by roasting and acid leaching, and prepared kaolin-Fe₂O₃/MnO₂ catalyst by coprecipitation method, so as to remove the surface organic matter and increase the specific surface area and dispersion. The decolorization rate of Rhodamine B (RhB) reached 99.12% after UV irradiation and 10mmol/L H₂O₂ were added, and the initial pH=3.0, and the reaction time was 30 min. Nanometer zero-valent iron (NZVI) can not directly degrade p-chlorophenol. To solve this problem, Bao Teng [11] et al. prepared zero-valent iron/rectorite nano-catalyst (NZVI/ rectorite) by reduction method to degrade p-chlorophenol. Compared with NZVI, NZVI loaded with rectorite had a higher mineralization rate, which reduced the agglomeration of particles and provided more active sites. After 4 times of recycling, the degradation rate of p-chlorophenol was still 100%. It can be seen that NZVI/ Reticite nanocomposites have great potential as catalysts for treating chlorophenol pollutants in aqueous solution. The octahedral structure of Fe₃O₄ can accommodate Fe²⁺ and Fe³⁺ at the same time, which promotes the reduction of Fe²⁺ in the same structure. However magnetic nano-Fe₃O₄ particles (MNPs) tend to agglomerate. For this problem, Wang Miaoting [12] et al. used co-precipitation method to load MNPs with particle size of 20nm onto diatomite surface. The degradation rate of Congo red (0.0308 min⁻¹) was 2.32 times of that of MNPs (0.0133 min⁻¹), and the removal rate of Congo red was 97.9% when the mass ratio of MNPs to diatomite was 1:2.

A large number of studies have shown that the modified clay is an ideal carrier for Fenton catalyst, and the degradation rate of organic wastewater can reach 97%~100%. However, the preparation time of the catalyst is long and accompanied with a certain amount of energy loss, which reduces the original cost advantage. Therefore, the preparation method should be improved. In addition, clay has a good ion-exchange performance and will expand in aqueous solution. These characteristics can be used to introduce cations with large particle size into clay pore channels, and then through treatment, the pillared clay with larger interlayer spacing and specific surface area can be obtained. At present, some researches have been done in this field, but the thermal stability of pillared clay is poor, and there are still deficiencies in practical industrial application.

3.2.2. Carbon materials. When the size of magnetic materials is reduced to nanoscale, it will make them become a single domain structure and produce new magnetic properties. However, the surface free energy of nanoparticles is high, which is easy to agglomerate and reduce the catalytic activity. It also reacts with air dissolved in water to shorten the service life of the catalyst. In order to avoid these problems, carriers with higher specific surface area, such as activated carbon, graphene, carbon nanotubes and magnetic microspheres, can be used to prevent the agglomeration of nanoparticles and increase the reaction area and dispersion of iron oxides. The degradation effect of modified supported magnetic nano-catalyst on organic wastewater is shown in Table 1.

| Catalyst           | Target degradant | Reaction conditions                                                                 | Result                        | Catalyst cycling usability                                                                 |
|--------------------|------------------|-------------------------------------------------------------------------------------|------------------------------|-------------------------------------------------------------------------------------------|
| Fe₃O₄@PAC          | Aniline          | C₉₀=1.0 g/L, [H₂O₂]=0.27g/L, pH=3.0, 120min                                        | Aniline removal rate was 91.2%[13] | After 5 cycles, the aniline removal rate was 89.6%                                           |
| Fe₃O₄/AC           | Catechol         | C₉₀=0.9g/L, pH=3.0, 30min                                                          | Catechol removal rate was 98.2%[14] | After 6 cycles, catechol removal rate was reduced by 6%                                     |
| Fe₃O₄-GO           | Phenol           | C₉₀= 0.25 g/L, [H₂O₂] = 10 mmol/L, pH = 5.0, 120 min                              | Phenol removal rate was 98.8%[15] | After 5 cycles, phenol removal rate was 90.1%                                                |
| Fe₃O₄/3D GN        | Acid red B       | C₉₀= 1 g/L, [H₂O₂] = 0.67 mL/L, pH = 6.0, 30 min                                 | Acid red B removal rate was 95.64%[16] | –                                                                                           |
| Fe⁵-Fe₃O₄-RGO       |                  |                                                                                     |                              |                                                                                           |
| Catalyst                  | Methylene blue (MB) | Bisphenol A (BPA)                        | MB removal rate | After 5 cycles, MB removal rate was 68.8% | BPA removal rate | After 5 cycles, BPA removal rate was about 90% | After 10 cycles, MB removal rate was around 100% |
|---------------------------|---------------------|------------------------------------------|----------------|------------------------------------------|-----------------|-----------------------------------------------|-----------------------------------------------|
| Fe₃O₄/MWCNT MPCMS-500     | C_{cat} = 0.1 g/L, [H₂O₂] = 0.8mmol/L, pH = 3.0, 60 min | C_{cat} = 0.5 g/L, [H₂O₂] = 0.04 g/L, pH = 3.0, 360 min | MB removal rate was 98%[17] | After 5 cycles, MB removal rate was 68.8% | BPA removal rate was 97%[18] | After 5 cycles, BPA removal rate was about 90% | After 10 cycles, MB removal rate was around 100% |
| MB                        | C_{cat} = 2.0 g/L, [H₂O₂] = 4mmol/L, pH = 3.12, 25 min | MB removal rate was 100%[19] | After 5 cycles, BPA removal rate was about 90% | After 10 cycles, MB removal rate was around 100% |

It can be seen from Table 1 that the magnetic nano-catalyst loaded with carbon material can achieve a degradation rate of over 95%. Compared with the conventional homogeneous Fenton reaction, the pH range of catalyst was widened to 3.0–9.0. Due to the high saturation magnetization of magnetic nano-catalyst with particle size less than 20nm, the magnetic nano catalyst can be easily separated from the reaction medium under the external magnetic field, and can be dispersed in the solution after removing the external magnetic field. It shows good regeneration. In addition, carbon material mechanical strength is not high, which is easy to be destroyed by external forces. Therefore, it can be modified from the above two aspects to prepare better catalyst.

3.2.3. Mesoporous silica. In 1992, researchers from Mobil company of the United States prepared MCM-41 with ordered pore structure, large specific surface area and pore volume [20]. In 1998, Zhao et al. synthesized SBA-15 with better hydrothermal stability [21]. Mesoporous silica has been widely used in the field of catalysis due to its easy availability of raw materials and mature synthesis methods.

MCM-41 has a large specific surface area and highly ordered hexagonal structure, which can promote the mass transfer of reactants to the active center. However, the direct catalysis of organic wastewater by MCM-41 is limited by the following two aspects: (1) replacing silicon skeleton with Al, Fe, Mn, Ti, Cu and other metals; (2) introduce heteroatoms into the pore wall or surface, and then adding organic groups on the surface to realize functionalization. Tian Zhiming [22] et al. prepared Fe-MCM-41 catalyst by impregnation method with MCM-41 as support. The average pore size of Fe-MCM-41 catalyst was 1.88 nm, slightly smaller than that of MCM-41 (2.00 nm). Under the conditions of pH = 3.0, 30 mmol/L H₂O₂, 20 mmol/L methyl orange and 2 g/L catalyst, the degradation rate of methyl orange was 96.82%. However, during the calcination of the samples, the surface of the nanoparticles was slightly agglomerated due to polycondensation. Therefore, it is necessary to modify the nanoparticles during the preparation of the catalyst. A variety of oxidation states exist in Mn ions, which are easy to take place electronic transition. However, Fe and Mn are loaded on inorganic support at the same time and are seldom used for heterogeneous Fenton reaction.

The SBA-15 with hexagonal mesoporous structure has a specific surface area of 600 ~ 1000 m²/g and pore wall thickness of 3 ~ 9nm. The use of SBA-15 with ordered porosity as the carrier is conducive to the diffusion of metal nanoparticles to the active site, thus increasing the catalytic activity of the catalyst. Hu Longxing [23] et al. prepared Fe / SBA-15 catalyst by impregnation method can broaden the applicable range of pH to 3.0 ~ 9.0, and the RhB removal rate can reach 93% when pH = 5.4, which is the result of the synergistic effect of Fe / SBA-15 catalyst and H₂O₂. Compared with the calcination regeneration method, the operation of Fe / SBA-15 catalyst by soaking in H₂O₂ is simple, economic and feasible. After 6 cycles, the RhB degradation rate in each run is above 80%, especially the iron content is less than 0.1mg/L. It can be seen that the modified mesoporous silica solves the shortcomings of uneven distribution of active sites and great diffusion resistance of Fenton catalyst, and significantly improves the catalytic activity.

3.2.4. Zeolite and molecular sieves. Molecular sieve is a kind of inorganic porous material with cage or channel shape. Molecular sieves with different pore sizes can be obtained according to different molecular ratios of SiO₂ and Al₂O₃. Due to its abundant pore channels, good chemical and thermal
stability, high adsorption capacity and selectivity, it plays a good role in catalytic degradation of organic pollutants.

In order to ensure the specific surface area of materials, and rapidly degrade organic wastewater, Liu Hui [24] et al. modified the zeolite by NaOH, NaCl and HCl, and selected the NaOH modified zeolite with stable state and the largest iron loading capacity. Under the optimal reaction conditions: pH = 5.33, catalyst dosage 2.40 g/L, H2O2 dosage 5.93 mmol/L, reaction 30min, MB removal rate reached 98.52%. After 5 cycles, the degradation rate of MB is still above 90%, which shows that the catalyst has good regeneration. Chen Jiajin [25] et al. found that different SiO2 / Al2O3 molar ratio will lead to different forms of Fe in Fe-ZSM-15. When the molar ratio of SiO2 / Al2O3 is 100, the catalytic performance of Fe-ZSM-15 is the best, and the degradation rate of methyl orange reached 97.4%. Polyaniline (PANI) as a conductive polymer, has a lower reduction potential (0.70-0.75 V) than Fe3+/Fe2+ (0.77 V), and has potential reducibility to Fe3+.

Y type molecular sieve has large pore size and simple preparation. In order to degrade MB, Zhang [26] et al. prepared FeY-WG by wet gel crystallization method, FeY-IE by ion exchange method, FeY-HT by hydrothermal crystallization method. The FeY-WG has the highest load iron content, decolorization rate and regeneration. After 4 cycles, MB decoloring rate is over 90%, but the disadvantage is that pH value range is narrow and pH = 2.5 degradation rate is only 62.9%. Broadening the pH range of the catalyst is a concern for the future. Although zeolite molecular sieve has shape selectivity, the pore size can be adjusted according to the molecular size, but it will affect the diffusion rate of molecules in the channel, so it is necessary to modify its structure to prepare better catalysts.

3.3. Organic carriers

3.3.1. Metal organic skeletons. MOFs (metal organic frameworks) is composed of metal ions and organic ligands, with large specific surface area, adjustable size and high porosity. Its coordination unsaturated center and functional ligands can be used as active sites to improve catalytic activity. These characteristics make MOFs show great development potential in the catalytic field.

In order to solve the shortcomings of traditional iron-based MOFs, such as high dispersibility and difficult separation from solution, He [27] et al. prepared hollow core / shell structure from iron metal organic framework by mechanochemical method. Fe3+/Fe2+ could be accelerated when the raw material mass ratio was Fe/Pd=100:1 and the degradation performance of phenol with core/shell Fe-Pd @C catalyst was improved. After 4 cycles, the degradation rate of phenol was 75%. In addition, the catalyst has high saturation magnetization and is easy to be recovered under the action of magnetic field. The low iron content in the reaction solution can avoid the pollution caused by iron sludge. Due to the diversity of metal ions and organic ligands forming MOFs materials, efficient Fenton catalysts can be designed. In addition, solving the problem of easy decomposition of MOFs materials in water is the focus of current research.

3.3.2. Ion exchange resins. The heterogeneous Fenton catalyst supported on ion exchange resin is easy to separate and can broaden the application range of pH value of Fenton reaction. Li [28] et al. prepared heterogeneous Fenton catalyst by using macroporous chelating styrene cation exchange resin (D401) and perfluorosulfonic acid membrane (N-117) to prepare heterogeneous Fenton catalyst. Compared with the two catalysts, both catalysts can degrade phenol quickly, and the degradation rate can reach 100%. In addition, the degradation rate of phenol can be kept unchanged when the catalyst is stored in low oxygen water, which provides a good idea for the preservation of catalyst. The N-117 supported Fe3+ catalyst prepared by Sun [29] et al. can effectively catalyze heterogeneous Fenton reaction. Under the optimal experimental conditions, the degradation rate of p-chlorophenol can reach 95.6%, and the amount of iron dissolved after the reaction is low, and the applicable range of pH is widened to weak alkaline.
4. Summary and prospect

Up to now, heterogeneous Fenton catalysts have been widely used in the treatment of refractory organic wastewater due to its high catalytic activity, wide pH range and good stability, but there is still much room for improvement in practical industrial application. Therefore, heterogeneous Fenton catalyst should be further developed in the following aspects:

1) Catalyst activity. Catalysts will be deactivated after repeated use. At present, there are many measures to improve the reactivity of catalysts, such as reducing the size of catalysts to nanometer; using transition metals such as Cu, Co, Mn, Cr and Ce etc. for isomorphic substitution; modifying inorganic matter or organic matter on the surface of catalyst; loading the catalytic particles on the carrier with high specific surface area; adding ultraviolet light and ultrasonic during the catalytic process and so on. However, how to apply it to the improvement of catalyst activity is still worth studying.

2) The amount of iron dissolved in the solution after reaction. The European Union stipulates that the concentration of iron ions in water should not exceed 2mg/L, while the Fenton reaction contains the ion reaction, which will inevitably cause iron ions to leave the carrier and immerse in the solution, resulting in iron sludge pollution. Therefore, reducing the amount of iron dissolved in catalytic reaction is a difficult problem to be solved in the future.

3) Develop new catalysts. At present, there are still some shortcomings in catalysts, but at the same time, it provides us with room for improvement. The materials can be modified according to their characteristics to prepare better catalysts.

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