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Preparation of organosolv lignin-stabilized nano zero-valent iron and its application as granular electrode in the tertiary treatment of pulp and paper wastewater

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Abstract

Organosolv lignin was used as stabilizer to synthesize Bentonite-Lignin nano zero-valent iron (BL-nZVI). Then FTIR, XRD, SEM and TEM were carried out to characterize this new material. Results proved that organosolv lignin can effectively prevent the aggregation of nano zero-valent iron particles. BL-nZVI was applied as particle electrodes and formed a three-dimensional (3D) electrode system with ruthenium/iridium coated titanium plates and acted as tertiary treatment process to dispose the pulp and paper secondary wastewater. The removal efficiency of the chemical oxygen demand (COD) and color of the effluent were selected as indicators to check the performance of the system. It was found that the removal efficiency of COD and color depended on the current density, electrolysis time, distance of electrode plates, initial pH value and particle electrode dosage. The optimal parameters of each factor were also determined by a series of single factor experiments. Under the optimum conditions, removal efficiency of COD and color can reach 87.6% and 93.1% respectively. Possible mechanism of the 3D electrode system with BL-nZVI particle electrodes for treatment of pulp and paper wastewater was also proposed.

Keywords Organosolv-lignin \cdot nano zero-valent iron \cdot Three-dimensional electrode system \cdot pulp and paper wastewater

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1. Introduction

Pulp and paper wastewater which contains large amounts of toxic organics originated from materials (such as tannins, resin acids) or produced during the processes of manufacturing (such as chlorinated organic compounds) [1], is one of the hardly remediated industrial wastewater. In general, pulp and paper mill wastewater all require the secondary treatment which is comprised of physical process and biochemical process. Nevertheless, the COD and color indexes of wastewater are still certainly high even after secondary treatment which fail to meet the emission standard (GB3544-2008). As a result, extended treatment of the secondary wastewater to improve wastewater discharge quality is completely critical for pulp and paper enterprises.

Three-dimensional (3D) electrode system as a promising depth treatment process has been attracting much attention recently. Compared with conventional 2D system, 3D system has a much larger interfacial electrode surface area and higher mass-transfer efficiency by placing a certain amount of particle electrodes into the 3D reactor to form charged microelectrodes [2]. In the past decades, the preparation of particle electrode has become a hotpot. Chen et al prepared graphene aerogel particle electrodes [3,4], Jung et al prepared modified activated carbon particle electrodes [5,6,7,8] and Sun et al used Ti-Sn/ γ -Al₂O₃ as particle electrodes in a three-dimensional reactor [9]. All of these particle electrodes have the common characteristics of high conductivity and large specific surface area. In our previous researches we had described the application of cetyl trimethyl ammonium bromide modified bentonite which was used as particle electrodes in 3D system for the treatment of pulp and paper wastewater and achieved satisfied results [10,11].

As a fairly strong electron donator, nano zero-valent iron (nZVI) has been widely applied to disposal various types of wastewater for removing organic and inorganic contaminants [12]. Furthermore, nZVI has the great potential of becoming an ideal particle electrode due to its high conductivity and large specific surface area. But to the point of our knowledge, there was still no report about this until the present day. In our recent researches, nZVI particles were synthesized and acted as particle electrodes to treat wastewater; they exhibited good performance and also showed some shortcomings. As is known, bare nZVI particles are inclined to react promptly with its surrounding medium (e.g., dissolved oxygen, or water) or aggregate fleetly into micro scale flocs, this reduced its reactivity and dispersity in solution and confined its field application. To overcome these defects, we synthesized bentonite supported nano zero-valent iron to improve its performance and achieved some enhanced results [13]. To further improve its performance, some new measures must be exploited.

Lignin, as the abundant and eco-friendly terrestrial biopolymer in the ecosphere, has caused great attention by the researchers because of its extraordinary properties such as high carbon content, high thermostability, antioxidant activity and favorable stiffness [14,15,16]. In this research, organosolv lignin was used as stabilizer to synthesize Bentonite-Lignin nano zero-valent iron (BL-nZVI), in which bentonite was used as the core skeleton to accommodate the lignin stabilized nZVI. BL-nZVI was applied as particle electrodes in the 3D system to deal with secondary treatment wastewater of pulp and paper mill. Meanwhile, single factor experiments were conducted to determine the optimal conditions of the 3D system and possible mechanisms of wastewater treatment in the 3D system were also proposed.

2. Materials and methods

2.1. Materials

Bentonite (sodium bentonite) was purchased from Xianye Technologies Co., Ltd. (Hebei, China). organosolv lignin was purchased from Shanfeng Chemical Co., Ltd. (Jiangsu, China). The other chemicals which were used were analytical grade reagents that had not been further purified, including iron (III) chloride hexahydrate (FeCl₃·6H₂O, Sinopharm Chemical Reagent Co., Ltd., China); sodium borohydride (NaBH₄, Shanghai Zhanyun Chemical Co., Ltd., China); acrylamide (AA) monomer (Tianjin Kemiou Chemical Reagents Co., Ltd., China); N, N'-methylenebisacrylamide (Bis–AA) (Tianjin Beifangtianyi Chemical Reagents Factory, China); N, N, N'. N'-tetramethyl ethylenediamine (TEMED) (Shanghai Zhanyun Chemical Co., Ltd., China); potassium peroxodisulfate (K₂S₂O₈, Tianjin Beifangtianyi Chemical Reagents Factory, China); hydrochloric acid (HCl, Laiyang Economic Development Zone Fine Chemical Plant, China); sodium hydroxide (NaOH, Sinopharm Chemical Reagent Co., Ltd., China); dichloromethane (CH₂Cl₂, Tianjin Guangcheng Chemical Reagents Co., Ltd., China); sodium chloride (NaCl, Sinopharm Chemical Reagent Co., Ltd., China). Sodium sulfite anhydrous (Na₂SO₄, Sinopharm Chemical Reagent Co., Ltd., China).

Pulp and paper wastewater provided by Tralin Paper Industry (Shandong, China) was from a secondary sedimentation tank. The characteristics of pulp and paper wastewater before and after treatment were shown in table 1.

Table 1

Characteristics of pulp and paper wastewater before and after treatment.

Characteristics	Color	Conductivity	COD	TOC	TDS	UV ₂₅₄
		$(\mu S \cdot cm^{-1})$	(mg/L)	(mg/L)	(g/L)	(cm^{-1})
Before treatment	Brown	4200	256	196.2	4.2	4.039
After treatment	Clarify	4400	32	14.32	0.16	0.310

2.2. Preparation of materials

In order to better illustrate the characteristics of such new material, bare nano zero-valent iron (bare nZVI) and Bentonite-supported nano zero-valent iron (B-nZVI) were prepared for comparison according to published literatures [17,18].

In this research, Bentonite-Lignin nano zero-valent iron (BL-nZVI) was synthesized using liquid phase reduction method according to Eq. (1). Firstly, 9.66 g ferric chloride hexahydrate (FeCl₃· $6H_2O$) were dissolved in 50 ml of distilled water and then transferred into a 500 ml of three-open neck flask reactor, one of the necks was equipped with a mechanical stirrer. Then 2.0 g of bentonite and 2.0 g of

lignin were added into the reactor and stirred for 30 min under nitrogen atmosphere, afterwards 100 mL of sodium borohydride solution (0.94 M) was added drop-wise (2 drops/s) into the reactor, using a dropping funnel, with vigorous stirring (500 rpm). Subsequently the mixture was stirred for another 10 min. Then 10 ml of aqueous solution containing 4 g acrylamide monomer and 20 ml of aqueous solution containing 0.2 g N, N'-methylenebisacrylamide were added into the reactor in sequence and stirred for 30 min. Finally, 10 ml of aqueous solution containing 0.5 g potassium peroxodisulfate and 100 μ L of N, N, N', N'-tetramethyl ethylenediamine were added into the suspension in turn and stirred for 1 h. All of the processes were carried out under N₂ atmosphere at room temperature. The products were filtered by vacuum filtration and rinsed three times promptly with absolute ethanol to prevent Fe⁰ nanoparticles from immediate oxidation. Products were dried at 60 °C using vacuum oven for night and stored in nitrogen atmosphere before use.

$$4Fe^{3+} + 3BH_4^{-} + 9H_2O \rightarrow 4Fe^{0} + 3H_2BO_3^{-} + 12H^{+} + 6H_2$$

2.3. Characterization

The conductivity of materials was measured by a 4-point probes resistivity measurement system (RTS-8, Guangzhou, China).

The Fourier transform infrared spectroscopy (FTIR) analyses of BL-nZVI, bentonite and organosolv lignin were studied using FTIR spectrophotometer (Inter-spec 2020, spectrolab, UK). KBr disk containing 1% (w/w) specimens was prepared for determination.

The X-ray diffraction (XRD) patterns of B-nZVI, BL-nZVI, used BL-nZVI and bare nZVI samples were determined using X-ray diffraction (D8-Advance, Bruker AXS Co. Ltd, German). The scan range was $10-70^{\circ} 2\theta$ with a scan speed of 5° min⁻¹.

The surface morphologies of bare nZVI, B-nZVI, BL-nZVI and used BL-nZVI were obtained by Scanning electron microscope apparatus (SEM) (Quanta 200, FEI, USA), and X-ray element analysis was conducted to characterize the distribution of nano zero-valent iron in BL-nZVI.

The nanoscale morphologies of organosolv lignin stabilized nZVI and bare nZVI were obtained by Transmission electron microscopy apparatus (TEM) (JEM 2100, JEOL, Japan).

2.4. Electrochemical apparatus

The model of three-dimensional (3D) electrode system was shown in Fig. 1, The 3D system equipped with an electrolytic reaction tank with the size of 100×50×60 mm and an electric stirrer. Ruthenium/iridium coated titanium plates (70×50×3 mm) were selected as the cathode and anode and paralleled to each other. And fresh prepared BL-nZVI particles were used as the particle electrodes. As for the two-dimensional (2D) electrode system, the only difference compared with the 3D system was the absence of particle electrodes. The ruthenium/iridium coated titanium plates should be washed with 10% of hydrochloric acid solution to remove the impurity layer before and after each electrolysis process.



Anode
 Cathode
 Particle electrodes
 Electric stirrer
 Electrolytic reaction tank
 Slide bar
 Scaleplate
 D.C. power

Fig. 1 Experimental apparatus of 3D electrode system.

2.5. Electrochemical process

In the process of the whole experiment, the volume of pulp and paper wastewater fed into the electrolytic reactor was 100 ml for each run. Then single factor experiments were conducted in 3D system, current density, electrolysis time, distance of electrode plates, initial pH value and particle electrode dosage were chosen as parameters. They were ranged between 10-50 mA/cm², 10-60 min, 2-6 cm, 2.0-8.0, and 0.05-0.4 g respectively.

To further investigate the mechanism of 3D system and demonstrate its superiority, experiments of 2D system, nZVI alone, BL-nZVI alone without applying current were conducted as comparison of 3D system respectively. The treated wastewater was filtered by 0.4 µm of membrane for COD and color removal detection.

2.6. Characterization of pulp and paper wastewater

The species and content of organic pollutants of pulp and paper wastewater were explored by gas chromatograph-mass spectrometer (GC-MS-QP2010, SHIMADZU). The pH value was detected using PHS-3C digital pH meter. The concentration of hydrogen peroxide was measured by an iodometric method in which starch solution was used as an indicator and sodium thiosulfate standard solution was used for titration. In this experiment, COD and color were used as the main indicators of the wastewater. In order to further demonstrate the changes of wastewater before and after treatment, TOC, TDS and UV₂₅₄ were also measured. The results can be seen in Table 1. UV₂₅₄ was measured by UV spectrophotometer (UV-2550, SHIMADZU). TOC was measured by Total organic carbon analyzer (TOC-L CPH, SHIMADZU). Chemical oxygen demand (COD) was obtained through oxidation with K₂Cr₂O₇ under acidic conditions and titrate analysis with (NH₄)₂Fe(SO₄)₂ aqueous solution according to national criterion of PR China (GB11914-89). And the color removal was obtained by the method of dilution multiple (GB11903-1989). The removal efficiency was determined using initial and final value of COD and color according to Eq. (2).

Removal efficiency
$$(\%) = \frac{(V_i - V_f) \times 100}{V_i}$$
 (2)

Where V_i is the initial value of COD or color, V_f is the final value of COD or color after treatment. The Total Dissolved Solid (TDS) was determined by weighing method and obtained according to Eq. (3).

$$C = \frac{(W_1 - W_2) \times 1000 \times 1000}{V}$$
(3)

Where *C* is the total dissolved solids of the wastewater (mg/L), W_1 is the total mass of evaporating dish and TDS (g), W_2 is the mass of free evaporating dish (g), *V* is the volume of the wastewater (mL).

2.7. GC-MS detection of wastewater before and after treatment

Firstly, three samples of wastewater (each sample volume was 50 mL) were prepared for the detection, one was adjusted to less than 2.0 with H_2SO_4 (the ratio with deionized water was 1:1) and the other was adjusted to more than 12.0 with NaOH (10%), standing for a few minutes and filtering. Then, dichloromethane (50 mL) and salting-out agent NaCl (0.2 g) were added into all samples to extract (4 min) and stew (6 min) the samples for stratification. The extraction process repeated twice and then the organic phases were collected and merged. Concentrated the organic phase by rotary evaporation until its volume was less than 5 ml, 2.0 g anhydrous Na₂SO₄ was added to dehydrate. Similarly, the treated wastewater was also extracted using the same process.

The type of the chromatographic column was DB-5. The chromatographic test conditions were high purity helium and CV mode for 0.086 MPa; the temperature of the injection port was 250° C, the sample size was 1 µL and the split radio was 30:1; the heating procedure was initial temperature of 40° C with residence time of 5 min, and heated up to 180° C with 10° C/min and keeping for 5 min, then heated up to 280° C with 5° C/min. The mass spectrometer conditions were 1.2 kV electron bombardment voltage, 70 eV EI source electron bombardment energy, 30-550 amu mass scan range and 3 min solvent delay.

3. Results and Discussion

3.1. Characterization

3.1.1. Characterization - Conductivity

Table 2 showed the conductivity of activated carbon, bentonite, B-nZVI and BL-nZVI at room temperature. It can be seen that the conductivity of BL-nZVI was better than other materials. Thus, BL-nZVI has a better potential to be used as particle electrode in the 3D electrode system for the treatment of wastewater.

Conductivity of several materia	als.				
Samples	Activated Carbon	Na-bent	B-nZVI	BL-nZVI	_
Conductivity(10 ⁻³ S/cm)	12.5	0.3	15.9	16.2	

Table 2

3.1.2. Characterization - FTIR

FTIR spectra for BL-nZVI, Lignin and Bentonite were scanned in the wavelength range of 4000-400 cm⁻¹ (Fig. 2), where Fig. 2(a), Fig. 2(b) and Fig. 2(c) refer to BL-nZVI, Lignin and Bentonite, respectively. In Fig. 2(a) adsorption bands at 1030 cm⁻¹, 522 cm⁻¹ and 466 cm⁻¹ corresponding to the Si-O vibration of montmorillonite from bentonite were observed, which can also be discovered in Fig. 3c. In addition, all samples showed a wider adsorption band at 3250-3550 cm⁻¹, corresponding to the vibration of hydroxyl groups in aliphatic and phenolic structures. Adsorption bands at 2940 cm⁻¹ and 2842 cm⁻¹ corresponded to the C-H stretching vibration in methyl and methylene of side chains and in aromatic methoxyl groups [19]. Aromatic skeleton vibrations at 1595, 1507 and 1426 cm⁻¹ were discovered in BL-nZVI (Fig. 2(a)) and Lignin (Fig. 2(b)), which demonstrated that the lignin had been successfully applied to the synthesis of BL-nZVI. But the band intensities of BL-nZVI at 1507 cm⁻¹ showed obvious decrease which may be due to the reducing action of sodium borohydride. Adsorption bands at 1662 and 1220 cm⁻¹ corresponding to the stretching vibration of conjugated carbonyl in BL-nZVI (Fig. 2(a)) were much weaker than that in lignin (Fig. 2(b)), this may be resulted from the hydrogen reduction of C=O [20]. However the reduction of carbonyl groups could increase the reactivity of lignin.



Fig. 2 FTIR spectra of samples. (a) BL-nZVI; (b) Lignin; (c) Bentonite.

3.1.3. Characterization - XRD

The XRD patterns of bare nZVI, BL-nZVI, B-nZVI and used BL-nZVI (after ten runs) are shown in Fig. 3. For the bare nZVI (Fig. 3(a)), the apparent reflection at $2\theta = 44.9^{\circ}$ was found corresponding to the formation of zero valent iron. In Fig. 3(b), the diffraction intensity at $2\theta = 44.9^{\circ}$ in BL-nZVI was

much stronger than that of B-nZVI, which indicated that the amount of nZVI particles in BL-nZVI was larger than that in B-nZVI (Fig. 3(c)). In addition, the formation of Fe₃O₄/ λ -Fe₂O₃ which corresponding to the peak at 20 of 36.5° was detected, which could be explained by the core-shell structure derived from the oxidation of nZVI [21]. However, for nZVI, the shell structure which served on a sorbent of reactants played a crucial role to remove pollutants from wastewater [22]. The diffraction intensity at 20 = 36.5° in BL-nZVI was weaker than that in B-nZVI, suggested that the addition of organosolv lignin inhibited the oxidation of nZVI. In Fig. 3(d), used BL-nZVI showed a weaker diffraction intensity at 20 of 44.9° and a stronger diffraction intensity at 20 of 36.5° compared with the unused BL-nZVI. This indicated that nZVI particles in used BL-nZVI were oxidized. The diffraction peak at 20 of 20° corresponding to the silica of bentonite. In conclusion, the nZVI particles with core-shell structure had been successfully synthesized and dispersed in BL-nZVI.



Fig. 3 XRD patterns of samples. (a) bare nZVI; (b) BL-nZVI; (c) B-nZVI; (d) used BL-nZVI.

3.1.4. Characterization - SEM.

Typical SEM images of bare nZVI, B-nZVI, BL-nZVI and used BL-nZVI (after ten runs) had been obtained in Fig. 4 to characterize the surface morphology of prepared materials. Obvious aggregation of no-supported nZVI could be seen in Fig. 4(a) which was due to the van der waals force and magnetic effect of nZVI particles [23]. The diameter distribution of bare nZVI agglomerates was shown in Fig. 4(b), it can be seen that the diameter of the agglomerates is mainly concentrated in 5-20 µm, which accounting for about 80.6% of the total particles. In Fig. 4(c), bentonite was used to support nZVI, however the aggregation phenomenon still occurred and the loading amount of nZVI on bentonite was also sparsely. In Fig. 4(d), BL-nZVI showed a uniform dispersion and a large loading amount of nZVI particles on the surface of bentonite because of the stabilizing effect of organosolv lignin. Lignin as an efficient stabilizer could prevent the aggregation of nZVI and keep the nZVI particles firmly on the surface of bentonite. Fig. 4(f) showed the result of X-ray element analysis of BL-nZVI, as can be seen, iron was uniformly dispersed on the surface of bentonite, this further proved the dispersive ability of organosolv lignin. In the image of used BL-nZVI (Fig. 4(e)), the amount of loaded nZVI on the surface



of bentonite decreased obviously, however there was no aggregation phenomenon occurred due to the stabilizing effect of lignin.

Fig. 4 SEM images of samples. (a) bare nZVI; (b) diameter distribution of bare nZVI; (c) B-nZVI; (d) BL-nZVI;
(e) used BL-nZVI; (f) X-ray element analysis of BL-nZVI.

3.1.5. Characterization - TEM

TEM was conducted to characterize the nanoscale morphology and distribution of organosolv lignin stabilized nZVI and bare nZVI. However, due to the limitation of the TEM instrument, the morphology of bentonite was not given. As shown in Fig. 5(a), unstabilized bare nZVI particles aggregated as a necklace-like chain, which was beneficial to maintain the thermodynamically stable state [24,25]. Compared with the bare nZVI, organosolv lignin stabilized nZVI has a clear spherical appearance and no aggregation phenomenon occurred as shown in Fig. 5(b). Furthermore, an obvious oxidation layer can be discovered in bare nZVI, however it was non-significant in organosolv lignin stabilized nZVI. This was due to the coating layer of organosolv lignin as shown in Fig. 5(b), which could effectively

prevent the oxidation of nZVI particles. In conclusion, nZVI particles in BL-nZVI have a favorable dispersion and antioxidant capacity due to the addition of organosolv lignin. And the possible formation mechanism of BL-nZVI was proposed in Fig. 8.



Fig. 5 TEM figures of samples. (a) bare nZVI; (b) organosolv lignin stabilized nZVI.

3.2. Determination of optimum conditions in 3D system

In this part, we did a series of single factor experiments to determine the optimum conditions in 3D electrode system. The COD and color removal efficiencies were selected as indicators.

3.2.1. Effect of current density

The electrolysis time of each batch of experiments was 50 min. And the electrolysis process was conducted under initial pH, 4 cm of plates distance, 0.05g BL-nZVI and using electric stirrer. The range of current density was from 10 to 50 mA/cm². The results of COD and color removal efficiency were shown in Fig. 6(a). As the current density increased, the removal efficiencies of COD and color increased. This was due to the increase of current density increased the transfer rate of electron, thus enhanced the reduction and oxidation of organic pollutants on the surface of electrode plates. However, the increase trend was no longer distinctly when the current density exceeded 40 mA/cm². This was because the amount of hydrogen and oxygen bubbles produced during the electrolysis of water increased with the increase of current density, which could inhibit the contact opportunity of pollutants with the electrode plates. However, the bubbles generated from the electrolysis of wastewater can help to the uplift of insoluble matters generated from the electrolysis process. Taking into energy consumption and removal efficiencies of COD and color, the optimal current density should be 40 mA/cm². The removal efficiencies of COD and color, were 60.2% and 67.4%, respectively, and the energy consumption was 10kWh/m³ after 50 min.

3.2.2. Effect of electrolysis time

The range of electrolysis time was 10-50 min. The electrolysis process was conducted at initial pH, 40 mA/cm² of current density, 4 cm of plates distance, 0.05 g BL-nZVI and using electric stirrer. As

can be seen from Fig. 6(b), the removal efficiencies of COD and color increased with the prolongation of electrolysis time before 50 min. However, there was no obvious change when the electrolysis time exceeded 50 min. With the evolve of electrolysis time, the decrease of pollutants concentration result in the decrease of contact efficiency of pollutants with particle electrodes and electrode plates. When the concentration decreased to a certain level, the removal efficiency will take on a mild trend. Furthermore, in the electrolysis process, the generation of recalcitrant intermediate products resulted from the incomplete oxidation of organic pollutants may be another reason.

In consideration of operating cost and electrolysis efficiency, the optimum electrolysis time should be 50 min, and the COD and color removal efficiencies were 60.3% and 66.5%, respectively.



Fig. 6 Single factor experiments. (a) Effect of current density; (b) Effect of electrolysis time; (c) Effect of plates distance; (d) Effect of wastewater initial pH; (e) Effect of BL-nZVI dosage; (f) Effect of batch run times.

3.2.3. Effect of plates distance

The electrolysis experiment was conducted under the condition of 40 mA/cm², 50 min of electrolysis time, initial pH, 0.05 g BL-nZVI and using electric stirrer. The distance of the plates distance was ranged from 2 to 6 cm.

As shown in Fig. 6(c), the higher removal efficiencies of COD and color were resulted from the distance of 4-6 cm. However, the trend showed a rapid decline when the distance was less than 4 cm. This was due to that insoluble matters generated from the electrolysis would suspended between the two electrode plates, therefore blocking the flow of pulp and paper wastewater and reducing the effective contact of pollutants with particle electrodes and electrode plates. So the removal of COD and color showed a rapid decline. In addition, increasing the distance between the electrode plates will increase the operating voltage, thereby increasing the energy consumption. Thus the optimal distance of electrode plates should be 4 cm. The removal efficiencies of COD and color were 59.5% and 66.1%, respectively.

3.2.4. Effect of initial pH

The electrolysis experiment was conducted at condition of 4 cm of plates distance and the current density of 40 mA/cm², 0.05 g BL-nZVI and using electric stirrer. The electrolysis time of each group experiment was 50 min. The initial pH was adjusted from 2.0 to 8.0, the results were shown in Fig. 6(d).

As shown in Fig. 6(d), the higher COD removal efficiency and decolorization rate resulted from an inferior pH value. During electrolysis process, hydrogen peroxide will be generated through the reduction of O_2 under acidic condition. Indirect Fenton reaction will take place between added Fe^0 and H_2O_2 and will generate hydroxyl radicals. Meanwhile part of the Fe³⁺ are reduced to Fe²⁺ on the cathode surface. The OH generated from Fenton reaction will combine with the organic pollutants and degraded most of them into harmless substances through oxidize reaction. Furthermore, in acidic condition, the CO₂ generated from the oxidation of organic pollutants could escape from the liquid phase into the air directly without the formation of CO_3^{2-} and HCO_3^{-} which could react more rapidly with OH radicals than organics, and the consumption of OH radicals has a negative impact on the removal of COD and color. However, when the pH was less than 4.0, the COD and color removal efficiency showed a slight drop which can be attributed to that the saturated hydrogen ions provided a proton for H_2O_2 to form hydroxonium ions (H_3O^+ , Eq. (4)) and the $\cdot OH$ radicals can also react with H^+ (Eq. (5)) [26], which could restrict the generation of \cdot OH radicals thus reducing the removal efficiency of COD and color. Therefore, pH = 4.0 was chosen as the optimal parameter and the concentration of hydrogen peroxide in the wastewater was approximately 0.76 mmol/L with electrolysis treatment for 50 min.

$$\mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{H}^{+} \to \mathrm{H}_{3}\mathrm{O}_{2}^{+} \tag{4}$$

$$OH + H^+ + e^- \to H_2O$$
(5)

3.2.5 Effect of particle electrode dosage

The dosage of BL-nZVI particles was adjusted from 0.05 to 0.4 g. The electrolysis process was conducted at current density = 40 mA/cm^2 , electrolysis time = 50 min, plates distance = 4 cm, pH = 4.0 and using electric stirrer. The results were shown in Fig. 6(e).

Obviously, the increasing trend of COD and color removal efficiency was noticeable when the dosage of BL-nZVI was less than 0.2 g, however a downward trend occurred when the dosage of BL-nZVI exceeded 0.2 g. The maximum removal efficiencies of COD and color were 87.6% and 93.1%, respectively.

The reason for this phenomenon was summarized as follows: the contact frequency between organic pollutants and particle electrodes increased with the increase of BL-nZVI particle dosage, thus enhanced the opportunity of adsorption and reduction. Meanwhile, the increased dosage can also promote the Fenton reaction. However, when the dosage of granulated electrodes exceeded 0.2 g, the number of suspended particles which acted as particle electrodes was no longer change obviously. This could be attributed to two reasons. Firstly, the BL-nZVI particles aggregated with increasing the dosage hence total surface area of the adsorbent decreased and diffusion path length of organic pollutants increased. Secondly, since the concentration of pollutants was low, the increase of BL-nZVI dosage resulted in unsaturation adsorption sites, and a lot of nZVI particles were oxidized to Fe₂O₃ and Fe₃O₄, so the equilibrium adsorption and reduction capacity of BL-nZVI decreased when the dosage reached a certain level. Thus, the optimal dosage of BL-nZVI is 0.2 g (2.0 g/L).

In conclusion, the optimal conditions of 3D electrode system were as follows: 40 mA/cm² of current density, 50 min of electrolysis time, 4 cm of plates distance, initial pH = 4.0 and 0.2 g (2.0 g/L) BL-nZVI. The maximum removal efficiencies of COD and color were 87.6% and 93.1%, respectively.

3.2.6. Effect of run times

Reuse experiments were conducted to characterize the reusability of BL-nZVI in 3D system. And the result of run times was showed in Fig. 6(f).

With the increase of batch run times, the 3D system with BL-nZVI particle electrodes showed a decline in removal efficiencies of COD and color. This can be attributed to the consumption of particle electrodes. However, even after ten runs the system still maintain a high removal efficiency for COD and color removal which were 76.5% and 84.9%, respectively. The main reason for its excellent reusability is the formation of organosolv lignin coating layer which can prevent the oxidation of nZVI. On the other hand, organosolv lignin as an effective stabilizer can effectively prevent the aggregation of nZVI particles. This can significantly improve the performance of nZVI and extend its life in 3D electrode system.

3.2.7. Control experiments

The treatment of pulp and paper wastewater using 2D system, bare nZVI alone and BL-nZVI alone without current was also conducted.

When the current density was 40 mA/cm², electrolysis time was 50 min, plates distance was 4 cm, initial pH was 4.0, and using electric stirrer, the removal efficiencies of COD and color using 2D system were 51.5% and 54.7%, respectively. Under the conditions of pH = 4.0, 0.2 g particle dosage

and using electric stirrer, the removal efficiencies of COD and color using BL-nZVI alone without current were 20.1% and 19.3%, respectively. However, under the same condition, the removal efficiencies of COD and color using bare nZVI alone were only 11.2% and 14.3%, respectively.

Results indicated that the removal efficiencies of COD and color using 3D system were higher than the simple addition of 2D system and BL-nZVI alone, this further proved the positive effect of Fenton reaction in 3D system. Furthermore, the removal efficiency of COD and color using BL-nZVI alone was higher than that of bare nZVI alone, this was due to the better dispersibility of nZVI particles in BL-nZVI enhanced the contact opportunity between the particles and pollutants, thus increased the oxidation degradation effect of BL-nZVI.

3.3. Analysis of GC-MS

The results of GC-MS detection of pulp and paper wastewater extraction before and after treatment were shown in Fig. 7. Obviously, the species and contents of pollutants in treated wastewater have decreased significantly. Results exhibited the wastewater may contain the organic pollutants priority controlled by USEPA such as octodecane, tetradecane and hexadecanen [27]. Polycyclic aromatic hydrocarbons (PAHs such as naphthalene) were also found in the detected results. It could be concluded that the wastewater contains a variety of organic pollutants and some of them are severe poisonous. Fortunately, as shown in Fig. 7(c), most of the toxic and harmful substances were removed and the species and content of pollutants were also decreased evidently after the 3D system treatment. The products include trace amounts of octodecane, Fig. 7(b) showed the treated wastewater using 2D system, although the content of organic pollutants in the wastewater have been reduced, the treated wastewater still contains a certain amount of methyl biphenyl, octodecane and hexadecanen. This further proved that the 3D electrode system equipped with BL-nZVI particle electrodes was much efficient to degrade the organic pollutants in pulp and paper wastewater.



Fig. 7 The results of GC-MS detection of wastewater before and after treatment.



As shown in Fig. 8, the possible degradation mechanism of wastewater in the 3D system consists mainly of three parts: the electrolysis oxidation and reduction of pollutants on the surface of electrode plates, adsorption of organic pollutants onto BL-nZVI and reduced by nano zero-valent iron particles, and Fenton reaction occured at low pH value is another important reason for the degradation of organic compounds.

In the 3D electrode system, firstly, when BL-nZVI particles were added into the wastewater, because of its larger specific surface area and adsorption capacity, organic pollutants and their intermediates will be adsorbed on the surface of BL-nZVI particles. Then the nano zero-valent iron particles could be combined with organic matters and the reduction reaction taken place. Some unsaturated chromophoric groups such as C=C, C=O and benzene, will be reduced by nano scale zero-valent iron particles. Consequently the color of pulp and paper wastewater decreased. Finally, organic pollutants will be mineralized to be H_2O and CO_2 .



Fig. 8 Possible mechanism of degradation of pollutants in 3D electrode system.

BL-nZVI as an effective reducing agent will be oxidized to generate Fe^{2+} by O₂ (Eq. (6)) [28]. Meanwhile, the generation of superoxide radical (Eq. (7)) will have a positive effect for the degradation of pollutants. When the pH of wastewater was reduced to a certain extent, it provides the conditions for the Fenton reaction between BL-nZVI and hydrogen peroxide (H₂O₂). On the side of cathode, O₂ will be reduced by H⁺ and generate a certain amount of H₂O₂ according to Eq. (8). Therefore, a large

amount of \cdot OH with strong oxidizing capacity are generated due to the Fenton reaction between Fe²⁺ and H₂O₂ according to Eq. (9) [29]. Meanwhile, although Fe³⁺ may be generated but instantly being reduced to be Fe²⁺ (Fig. 8) thus forming a cycle. Transformation in the form of the iron ions can keep the Fenton reaction running constantly. Therefore, such a cycle can not only reduce the consumption of nZVI but also oxidize organic substances efficiently.

$$2Fe^{0} + O_{2} + 2H_{2}O \rightarrow Fe^{2+} + 4OH^{-}$$
 (6)

$$O_2 + 2e^- \to O_2 \cdot^- \tag{7}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{8}$$

$$Fe^{2+} + H_2O_2 \rightarrow OH + OH^- + Fe^{3+}$$

4. Conclusions

In this work, organosolv lignin was used as an effective stabilizer and applied to the synthesis of Bentonite-Lignin nano zero-valent iron (BL-nZVI). Various of characterization methods demonstrated that organosolv lignin can prevent the oxidation and aggregation of nano zero-valent iron particles. Subsequently, BL-nZVI was used as particle electrodes added into 2D system to form 3D system for the tertiary treatment of pulp and paper wastewater. Results proved the 3D system with BL-nZVI electrode particles possessed excellent performance in COD degradation and decolorization. The COD of the wastewater decreased from 256 mg/L to 32 mg/L and the decolorization rate reached 93.1% when current density was 40 mA/cm², electrolysis time was 50 min, distance of electrode plates was 4 cm, pH value was 4.0 and dosage of BL-nZVI was 2.0 g/L. Furthermore, the results of GC-MS detection indicated the 3D system with BL-nZVI particle electrodes was efficient to remove the organic pollutants in pulp and paper wastewater. The indicators (COD and color) of the target water can reach the national discharge standard (GB3544-2008). BL-nZVI supported 3D electrode system may become a prospect technology in treating the secondary wastewater of pulp and paper industries in the future.

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Highlights

- Organosolv lignin was used as stabilizer to synthesis BL-nZVI.
- Organosolv lignin can prevent the aggregation of nZVI particles effectively.
- BL-nZVI was acted as electrode particles and exhibited excellent performance.
- Degradation mechanism of pollutants was proposed.

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