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Iron-glutamate-silicotungstate ternary complex as highly active heterogeneous Fenton-like catalyst for 4-chlorophenol degradation

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ABSTRACT

A novel iron-glutamate-silicotungstate ternary complex ($\text{Fe}^{\text{III}}\text{GluSiW}$) was synthesized from ferric chloride (Fe^{III}), glutamic acid (Glu), and silicotungstic acid (SiW), and used as a heterogeneous Fenton-like catalyst for 4-chlorophenol (4-CP) degradation at neutral pH value. The prepared $\text{Fe}^{\text{III}}\text{GluSiW}$ was characterized using inductively coupled plasma atomic emission spectroscopy, thermogravimetry, Fourier-transform infrared spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, X-ray diffraction, and field-emission scanning electron microscopy. The results showed that $\text{Fe}^{\text{III}}\text{GluSiW}$ has the formula $[\text{Fe}(\text{C}_5\text{H}_8\text{NO}_4)(\text{H}_2\text{O})]_2\text{SiW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$, with glutamate moiety and Keggin-structured $\text{SiW}_{12}\text{O}_{40}^{4-}$ heteropolyanion. The catalyst showed high catalytic activity in 4-CP degradation in the dark and under irradiation. Under the conditions of 4-CP 100 mg/L, $\text{Fe}^{\text{III}}\text{GluSiW}$ 1.0 g/L, H_2O_2 20 mmol/L, and pH = 6.5, 4-CP was completely decomposed in 40 min in the dark and in 15 min under irradiation. When the reaction time was prolonged to 2 h, the corresponding total organic carbon removals under dark and irradiated conditions were ca. 27% and 72%, respectively. The high catalytic activity of $\text{Fe}^{\text{III}}\text{GluSiW}$ is resulted from hydrogen bonding of H_2O_2 on the $\text{Fe}^{\text{III}}\text{GluSiW}$ surface. The enhanced degradation of 4-CP under irradiation arises from simultaneous oxidation of 4-CP through Fenton-like and photocatalytic processes respectively catalyzed by ferric iron and the $\text{SiW}_{12}\text{O}_{40}^{4-}$ heteropolyanion in $\text{Fe}^{\text{III}}\text{GluSiW}$.

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1. Introduction

The pollution of water resources has become a serious problem and is causing public concern. Chlorophenols (CPs) are one of various organic contaminants in the environment. These toxic compounds are widespread and suspected carcinogens [1]. CPs have been widely used as raw materials and synthetic intermediates in many industrial processes. Because of their broad-spectrum antimicrobial properties, CPs have also been widely used as preservatives and disinfectants. CPs are generated as side products in the disinfection of drinking water and bleaching of pulp with chlorine as well. CPs are resistant to

biodegradation; therefore, discharge of large amounts of these compounds into the environment is a threat to human health and ecosystems [2].

The Fenton process is an effective method for degrading a wide range of organic pollutants in water. The Fenton reaction is based on the catalytic decomposition of H_2O_2 by Fe^{2+} ions in aqueous solution to produce $\text{HO}^\bullet$, which can non-selectively oxidize most organic compounds. Catalysis by Fe^{2+} ions involves the $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ redox cycle shown in Eqs. (1) and (2) [3]:

However, because the reduction of Fe^{3+} to Fe^{2+} via Eq. (2) is

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much slower than the oxidation of Fe^{2+} to Fe^{3+} via Eq. (1), the traditional homogeneous Fenton process needs a high concentration of ferrous salt (50–80 mg/L). The subsequent treatment of iron-containing water and ferric hydroxide sludge therefore consumes large amounts of chemicals. Additionally, the homogeneous Fenton process typically works under acidic conditions ($\text{pH} = 2.0\text{--}3.0$), which is unfavorable in practice because of the costs of acidification during processing and neutralization after treatment [4–6]. To overcome these disadvantages of the homogeneous Fenton process, and to achieve catalyst recycling, much effort has been made to develop heterogeneous Fenton-like catalysts [7–12]. However, many of the heterogeneous Fenton-like catalysts reported in the literature still require acidic pH conditions, and some of them show significant deactivation in consecutive reaction cycles [13–17]. The development of reusable and efficient heterogeneous Fenton-like catalysts with wide working pH ranges is therefore highly desirable.

Polyoxometalates (POMs), which are multi-metal oxygen clusters, have been intensively studied as catalysts because of their ability to undergo multi-electron transfer reversibly. Irradiation with light of energy higher than or equal to that of the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of a POM results in charge transfer from O^{2-} to M^{6+} ($\text{M} = \text{W}, \text{Mo}$) at $\text{M}\text{--}\text{O}\text{--}\text{M}$ bonds, leading to the formation of an excited POM with strong oxidizing power [18–22]. Recently, the use of POMs in Fenton or related processes has been attracting increasing attention. Choi's group [23] reported that $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{PW}_{12}\text{O}_{40}^{3-}$ in the Fe^0/O_2 system can mediate electron transfer from Fe^0 to O_2 to produce Fe^{2+} and H_2O_2 . Sedlak's group [24] showed that addition of $\text{PW}_{12}\text{O}_{40}^{3-}$ to the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ homogeneous system extends the working pH range up to $\text{pH} = 8.5$. Taghdiri et al. [25] reported that silicotungstic acid catalyzes the oxidation of hexamethylenetetramine in the presence of H_2O_2 or $\text{H}_2\text{O}_2/\text{Fe}^{2+}$. These studies suggest potential synergies between iron and POM for catalytic oxidation of pollutants by H_2O_2 . It is therefore reasonable to infer that water-insoluble complexes containing both iron and heteropolyanions would be efficient heterogeneous Fenton-like catalysts. However, binary complexes of iron ions (Fe^{2+} or Fe^{3+}) with many heteropolyanions (e.g., $\text{SiW}_{12}\text{O}_{40}^{4-}$ and $\text{PW}_{12}\text{O}_{40}^{3-}$) are soluble in water [24].

Recently, we found that some amino acids can link Fe^{3+} ions with various heteropolyanions in aqueous solution to form water-insoluble ternary complexes; these complexes show Fenton-like catalytic activity [26,27]. Here, we report a new Fe^{III} -glutamate-silicotungstate ternary complex ($\text{Fe}^{\text{III}}\text{GluSiW}$), which acts as a highly active heterogeneous Fenton-like catalyst in the degradation of 4-chlorophenol (4-CP) at neutral pH value. The catalytic mechanism of $\text{Fe}^{\text{III}}\text{GluSiW}$ was also investigated.

2. Experimental

2.1. Reagents

Ferric chloride hexahydrate, glutamic acid, silicotungstic

acid, sodium silicate, sodium tungstate, and H_2O_2 (30%) were provided by the Sinopharm Chemical Reagent Beijing Co., Ltd. 4-CP was purchased from the Tianjin Guangfu Fine Chemical Industry Research Institute. All reagents were analytical grade and used without further purification.

2.2. Preparation and characterization of $\text{Fe}^{\text{III}}\text{GluSiW}$

$\text{Fe}^{\text{III}}\text{GluSiW}$ was synthesized by precipitation in aqueous solution at ambient temperature. Ferric chloride hexahydrate (0.27 g) and glutamic acid (0.15 g) were dissolved in water (25 mL) to form a red soluble complex of Fe^{3+} ions and glutamate. A solution of silicotungstic acid (25 mL, 0.02 mol/L) was added dropwise, precipitating $\text{Fe}^{\text{III}}\text{GluSiW}$. The precipitate was aged for 24 h at room temperature, and red-brown $\text{Fe}^{\text{III}}\text{GluSiW}$ powder was obtained by washing the precipitate with water and drying at 50 °C under vacuum.

The prepared $\text{Fe}^{\text{III}}\text{GluSiW}$ was characterized using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Shimadzu ICPS-7510), thermogravimetry (TG; Seiko TG/DTA6300), Fourier-transform infrared (FT-IR) spectroscopy (Shimadzu IRAffinity-1), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS; Shimadzu UV2550), X-ray diffraction (XRD; XD-2, $\text{Cu K}\alpha$ radiation), and field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800).

2.3. 4-CP degradation

Degradation of 4-CP was performed at 25 ± 2 °C in an $\text{Fe}^{\text{III}}\text{GluSiW}/\text{H}_2\text{O}_2$ system under both dark and irradiated conditions. All experiments were performed in a cylindrical quartz tube under magnetic stirring. A 400 W high-pressure mercury lamp was used as the irradiation source; it was surrounded by a quartz jacket to enable water cooling. A cutoff filter was placed around the lamp to remove radiation below 350 nm. In a typical procedure, $\text{Fe}^{\text{III}}\text{GluSiW}$ powder was added to 4-CP solution (100 mg/L) with stirring to maintain a uniform suspension. The suspension pH was adjusted using dilute H_2SO_4 or NaOH solution, and then H_2O_2 was added. No pH control was applied during the process. In the photo-assisted Fenton-like process, H_2O_2 addition and irradiation of the reaction system were performed simultaneously. Specimens were withdrawn at regular time intervals and analyzed immediately after filtration through a 0.22 μm filter to remove the $\text{Fe}^{\text{III}}\text{GluSiW}$ powder. Experiments were performed in triplicate, and all the results were expressed as mean values.

The 4-CP concentration was determined using a high-performance liquid chromatography (HPLC) system (Shimadzu LC-20AD) equipped with C18 reverse-phase column and UV detector. The mobile phase was a mixture of methanol (65%) and 1% acetic acid aqueous solution (35%) at a flow rate of 0.5 mL/min. The total organic carbon (TOC) content was determined using a TOC analyzer (Shimadzu TOC-V CPH).

3. Results and discussion

3.1. $\text{Fe}^{\text{III}}\text{GluSiW}$ characterization

Fig. 1. TG and DTG curves of Fe^{III}GluSiW.

The ICP-AES, TG, and FT-IR results show that the chemical formula of Fe^{III}GluSiW is [Fe(C₅H₈NO₄)(H₂O)]₂SiW₁₂O₄₀·13H₂O. The ICP-AES data for the Fe, Si, and W contents in Fe^{III}GluSiW are close to the values calculated based on the suggested chemical formula. Calcd for Fe^{III}GluSiW (%): Fe 3.15, Si 0.79, W 62.2; found (%): Fe 3.62, Si 0.75, W 61.1.

The TG curve of Fe^{III}GluSiW in Fig. 1 shows a multi-step mass loss in the range 30–425 °C. The 6.4% mass loss in the first step, from 30 to 174 °C, arises from loss of the 13 crystallization water molecules (anal., calcd: 6.6%). The 9.5% mass loss in the subsequent steps, from 174 to 425 °C, is caused by loss of the coordinated water molecule and stepwise destruction of the glutamate moiety (anal., calcd: 9.3%). The TG data are in agreement with the proposed chemical formula.

The FT-IR spectrum of a POM reflects the structure of the heteropolyanion, i.e., the primary structure. The FT-IR spectrum of Fe^{III}GluSiW is shown in Fig. 2(1) and the assignments of the main absorption peaks, based on literature values [28,29], are listed in Table 1. The FT-IR spectrum of Fe^{III}GluSiW has the characteristic peaks of Keggin-structured SiW₁₂O₄₀⁴⁻ at 986, 920, 881, and 793 cm⁻¹; these are respectively attributed to the stretching vibrations of terminal W=O bonds, tetrahedral Si–O bonds, and two types of bridging W–O–W bonds in SiW₁₂O₄₀⁴⁻.

Fig. 2. FT-IR spectra of (1) Fe^{III}GluSiW, (2) Fe^{III}GluSiW used under irradiation, and (3) Fe^{III}GluSiW used in the dark.

Table 1

Main relevant FT-IR data (in cm⁻¹) of Fe^{III}GluSiW and their assignments.

Fe ^{III} GluSiW	Fe ^{III} GluSiW used in the dark	Fe ^{III} GluSiW used under irradiation	Assignment
793	795	797	$\nu_s(\text{W-O-W})$
881	883	883	$\nu_s(\text{W-O-W})$
920	918	920	$\nu_s(\text{Si-O})$
986	986	986	$\nu_s(\text{W=O})$
1349 (m)	1349 (m)	1349 (m)	$\delta(\text{CH})$
1437 (w)	1438 (w)	1437 (w)	$\delta(\text{CH}_2)$
1459 (w)	1459 (w)	1459 (w)	$\delta(\text{CH}_2)$
1507 (w)	1507 (w)	1507 (w)	$\delta(\text{NH}_3^+)$
1617 (sh)	1617 (sh)	1617 (sh)	$\nu_s(\text{CO}_2^-)$
1630 (vs)	1630 (vs)	1630 (vs)	$\nu_s(\text{CO}_2^-)$

m: medium, w: weak, sh: shoulder, vs: very strong.

Structural information on the glutamate moiety can also be obtained from the FT-IR spectrum. The peaks at 1630 and 1617 cm⁻¹ correspond to the asymmetric vibrations of two COO⁻ groups of glutamate. The absorption at 1507 cm⁻¹ is assigned to the bending vibration of NH₃⁺. The CH₂ and CH bending modes are observed at 1459, 1437, and 1349 cm⁻¹. The FT-IR data verify the presence of Keggin-structured SiW₁₂O₄₀⁴⁻ and glutamate moiety in Fe^{III}GluSiW.

The UV-Vis DR spectra of silicotungstic acid and Fe^{III}GluSiW are shown in Fig. 3. The spectrum of silicotungstic acid has a wide absorption band in the region 200–450 nm, with peaks at 210 and 265 nm; these are attributed to charge transfer from O²⁻ to W⁶⁺ in the Keggin unit for W=O and W–O–W bonds, respectively [30]. It is worth noting that the spectrum of Fe^{III}GluSiW shows a clear red shift of the absorption onset compared with that of silicotungstic acid. This may be favorable for photocatalysis because of the relatively narrow HOMO–LOMO gap of Fe^{III}GluSiW.

The XRD patterns of H₄SiW₁₂O₄₀·xH₂O and Fe^{III}GluSiW are shown in Fig. 4. The XRD pattern of a POM reflects its secondary structure, i.e., the three-dimensional arrangements of the heteropolyanions, cations, and other components. Usually, the primary structure of POM is stable (Fig. 2); however, the secondary structure is variable. As shown in Fig. 4, H₄SiW₁₂O₄₀·xH₂O is highly crystalline, whereas Fe^{III}GluSiW is less crystalline and possibly contains an amorphous phase.

Fig. 3. UV-Vis DRS spectra of (1) silicotungstic acid and (2) Fe^{III}GluSiW.

Fig. 4. XRD patterns of (1) silicotungstic acid and (2) $\text{Fe}^{\text{III}}\text{GluSiW}$.

The SEM image of $\text{Fe}^{\text{III}}\text{GluSiW}$ in Fig. 5 shows irregular particles of size 100–200 nm.

3.2. Catalytic performance of $\text{Fe}^{\text{III}}\text{GluSiW}$

Zero-valent iron (ZVI) has been used as a heterogeneous Fenton-like catalyst for the degradation of 4-CP at ambient temperature [13]. For comparison, the catalytic activity of $\text{Fe}^{\text{III}}\text{GluSiW}$ was evaluated under similar conditions: 4-CP 100 mg/L, H_2O_2 20 mmol/L, $\text{Fe}^{\text{III}}\text{GluSiW}$ 1.0 g/L, and temperature $25 \pm 2^\circ\text{C}$. The natural starting pH was 6.5, and no pH control was applied throughout the process. All experiments were

Fig. 5. SEM image of $\text{Fe}^{\text{III}}\text{GluSiW}$.

conducted under dark and irradiated conditions separately.

Control experiments indicated that no significant 4-CP degradation occurred in 40 min when $\text{Fe}^{\text{III}}\text{GluSiW}$ or H_2O_2 was used alone. However, as shown in Fig. 6, rapid degradation was observed when both $\text{Fe}^{\text{III}}\text{GluSiW}$ and H_2O_2 were present, and the reaction was significantly accelerated by irradiation. The time required to degrade 4-CP completely was ca. 40 min in the dark and ca. 15 min under irradiation. Similar to most heterogeneous Fenton-like systems, the reaction rate is also influenced by experimental parameters such as catalyst dosage, H_2O_2 concentration, and initial pH value; these issues will be discussed in Section 3.4.

The catalytic performance of $\text{Fe}^{\text{III}}\text{GluSiW}$ at initial pH = 6.5 was also evaluated based on TOC removal. The results (Fig. 7)

Fig. 6. 4-CP removal in the $\text{Fe}^{\text{III}}\text{GluSiW}/\text{H}_2\text{O}_2$ system. Except for the investigated parameter, others fixed on $\text{Fe}^{\text{III}}\text{GluSiW}$ 1.0 g/L, H_2O_2 20 mmol/L, and pH = 6.5.

Fig. 7. TOC removal from 4-CP solution in $\text{Fe}^{\text{III}}\text{GluSiW}/\text{H}_2\text{O}_2$ system. Reaction conditions: $\text{Fe}^{\text{III}}\text{GluSiW}$ 1.0 g/L, H_2O_2 20 mmol/L, pH = 6.5.

show that TOC removal after 2 h was 27% in the dark and 72% under irradiation. The $\text{Fe}^{\text{III}}\text{GluSiW}$ ternary complex therefore showed high Fenton-like catalytic activity in the degradation of 4-CP, without any pH adjustment (at natural pH = 6.5), and the reaction rate clearly increased under irradiation. In contrast, it has been reported that ZVI has no catalytic activity in 4-CP degradation at pH > 4.0 [13].

3.3. Stability and reusability of $\text{Fe}^{\text{III}}\text{GluSiW}$

The stability of a solid heterogeneous catalyst during reactions is crucial to its reusability. In solution, $\text{SiW}_{12}\text{O}_{40}^{4-}$ can be hydrolyzed to SiO_3^{2-} and WO_4^{2-} at neutral or alkaline pH values [18]. In reaction systems of initial pH = 6.5, $\text{Fe}^{\text{III}}\text{GluSiW}$ is therefore expected to be unstable and prone to decomposition through hydrolysis of $\text{SiW}_{12}\text{O}_{40}^{4-}$ in $\text{Fe}^{\text{III}}\text{GluSiW}$. Furthermore, the glutamate moiety in $\text{Fe}^{\text{III}}\text{GluSiW}$ is possibly oxidized during this procedure, which also results in the decomposition of $\text{Fe}^{\text{III}}\text{GluSiW}$. If $\text{Fe}^{\text{III}}\text{GluSiW}$ decomposes during 4-CP degradation, Fe, Si, and W at appropriate concentrations should be detected in the bulk solution by ICP-AES. The stability of $\text{Fe}^{\text{III}}\text{GluSiW}$ during 4-CP degradation at pH = 6.5 was investigated by separating the $\text{Fe}^{\text{III}}\text{GluSiW}$ powder from the solution after the reaction (recovery yield ca. 80%–90%). The concentrations of Fe, Si, and W in the solution were ca. 0.018, 0.0086, and 0.096 mmol/L, respectively, for the dark system, and ca. 0.030, 0.012, and 0.14 mmol/L, respectively, for the irradiated system. This shows that in addition to the unavoidable loss of catalyst during separation, ca. 5% of $\text{Fe}^{\text{III}}\text{GluSiW}$ decomposed during the reaction. The separated $\text{Fe}^{\text{III}}\text{GluSiW}$ was characterized using FT-IR; the results are shown in Fig. 2 and Table 1. There are no obvious differences between the FT-IR spectra of the freshly prepared $\text{Fe}^{\text{III}}\text{GluSiW}$ and used $\text{Fe}^{\text{III}}\text{GluSiW}$ samples. Experiments confirmed that there were no significant differences in the $\text{Fe}^{\text{III}}\text{GluSiW}$ activity after three cycles for both the dark and irradiated systems. The $\text{Fe}^{\text{III}}\text{GluSiW}$ catalyst is therefore stable during 4-CP degradation.

$\text{SiW}_{12}\text{O}_{40}^{4-}$ immobilized in water-insoluble $\text{Fe}^{\text{III}}\text{GluSiW}$ is more resistant to hydrolysis than $\text{SiW}_{12}\text{O}_{40}^{4-}$ dissolved in water. This is similar to the reported observation that $\text{PW}_{12}\text{O}_{40}^{3-}$

immobilized in a SiO_2 matrix is stable in a neutral pH medium [31]. Also, in contrast to the fast oxidation of 4-CP, oxidation of the glutamate moiety in the $\text{Fe}^{\text{III}}\text{GluSiW}$ catalyst is retarded. The exact reasons for the stabilities of the $\text{SiW}_{12}\text{O}_{40}^{4-}$ and glutamate moiety in $\text{Fe}^{\text{III}}\text{GluSiW}$ remain unknown, and further investigation is needed.

3.4. Possible catalytic mechanism of $\text{Fe}^{\text{III}}\text{GluSiW}$

The widely accepted catalytic mechanism in heterogeneous Fenton-like systems using iron-based solid catalysts is similar to that in homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ systems; these involve a redox cycle between Fe^{3+} and Fe^{2+} ions on the catalyst surface and production of $\text{HO}^\bullet$ from H_2O_2 decomposition. However, previous studies have indicated the formation of ferryl (Fe^{IV}) species under some conditions; this is a weaker oxidant than $\text{HO}^\bullet$ and cannot oxidize aromatic compounds [32]. It has been suggested that in POM photocatalysis, $\text{HO}^\bullet$ can be formed through H_2O activation by an excited POM [33].

The oxidative intermediate species formed in the $\text{Fe}^{\text{III}}\text{GluSiW}/\text{H}_2\text{O}_2$ system were detected by performing control experiments involving addition of 0.3 mol/L *n*-butanol (an $\text{HO}^\bullet$ scavenger) to the reaction system at pH = 6.5. The results show that 4-CP degradation was significantly retarded in both the dark and irradiated systems, indicating that $\text{HO}^\bullet$ is the dominant oxidative intermediate species in the $\text{Fe}^{\text{III}}\text{GluSiW}/\text{H}_2\text{O}_2$ system.

Control experiments were performed in two homogeneous mixed solutions, each containing 100 mg/L of 4-CP, to investigate possible degradation of 4-CP in the bulk solution. One solution contained 0.028 mmol/L Fe^{3+} (ferric chloride), 0.014 mmol/L SiO_3^{2-} (sodium silicate), and 0.168 mmol/L WO_4^{2-} (sodium tungstate), and the other contained 0.028 mmol/L Fe^{3+} and 0.014 mmol/L $\text{SiW}_{12}\text{O}_{40}^{4-}$ (silicotungstic acid). The two aqueous solutions are equivalent to the bulk solution phase of the $\text{Fe}^{\text{III}}\text{GluSiW}/\text{H}_2\text{O}_2$ system, on the basis that 5% of the catalyst decomposes during the reaction, as mentioned in Section 3.3. The former solution corresponds to the case in which $\text{Fe}^{\text{III}}\text{GluSiW}$ decomposes through hydrolysis of $\text{SiW}_{12}\text{O}_{40}^{4-}$, and the latter represents decomposition of $\text{Fe}^{\text{III}}\text{GluSiW}$ through oxidation of glutamate. Both solutions were adjusted to pH = 6.5, followed by addition of H_2O_2 to a final concentration of 20 mmol/L. The changes in 4-CP concentration were monitored. The results show that 4-CP degradation was negligible under both dark and irradiated conditions. The formation of $\text{HO}^\bullet$ and degradation of 4-CP in the heterogeneous $\text{Fe}^{\text{III}}\text{GluSiW}/\text{H}_2\text{O}_2$ system therefore probably occur on or near the $\text{Fe}^{\text{III}}\text{GluSiW}$ surface.

For a heterogeneous Fenton-like process, the adsorption of H_2O_2 on the catalyst surface is crucial to the formation of $\text{HO}^\bullet$. Tang's group [34] reported that ethylenediaminetetraacetic acid (EDTA) can significantly enhance the catalytic activity of nano- BiFeO_3 for oxidative degradation of bisphenol A. The carboxyl and amino groups in EDTA can concentrate H_2O_2 within local areas on the catalyst surface by hydrogen bonding with H_2O_2 ; this facilitates $\text{HO}^\bullet$ formation. In the case of $\text{Fe}^{\text{III}}\text{GluSiW}$, because of the presence of glutamate moieties and

SiW₁₂O₄₀⁴⁻ heteropolyanions on the catalyst surface, H₂O₂ is also prone to adsorption on the surface via hydrogen bonding. This may be an important reason for the high catalytic activity of Fe^{III}GluSiW.

We propose a possible mechanism for Fe^{III}GluSiW catalysis, based on our experimental results and those reported in the literature. When the reaction is performed in the dark, the catalytic mechanism for Fe^{III}GluSiW is similar to those for iron-based materials, in which H₂O₂ reacts with iron ions on the catalyst surface (denoted by ≡Fe^{III} and ≡Fe^{II}), resulting in the formation of HO• and oxidation of 4-CP (Eqs. (3)–(5)) [13–17]:

The hydrogen-bonded H₂O₂ on the Fe^{III}GluSiW surface is highly reactive with Fe^{III} and Fe^{II}, resulting in fast production of HO•, and therefore rapid degradation of 4-CP.

When the reaction is conducted under irradiation, the reduction of ≡Fe^{III} to ≡Fe^{II} via Eq. (3) is accelerated, resulting in enhanced production of HO• via Eq. (4) [35]. More importantly, 4-CP is also oxidized through a photocatalytic route mediated by SiW₁₂O₄₀⁴⁻ in Fe^{III}GluSiW. For POM photocatalysis, the oxidation of organic compounds is suggested to occur via two parallel reaction routes, i.e., oxidation by an excited POM (POM*) and by HO• produced via activation of H₂O by an excited POM [33]. The reduced POM (POM⁻) is oxidized by O₂ to close the catalytic cycle. Photocatalysis by Fe^{III}GluSiW of the degradation of 4-CP is expressed by Eqs. (6)–(8):

We noted that the Fe^{III}GluSiW powder changed to dark brown from red-brown during the irradiated reaction. This confirms reduction of SiW₁₂O₄₀⁴⁻ during the reaction. It is worth noting that most POMs by themselves are not good photocatalysts because of slow oxidation of POM⁻ by O₂ (Eq. (9)) [18]. This may be why 4-CP degradation under irradiation is slow when Fe^{III}GluSiW is used alone without addition of H₂O₂. However, in the presence of both Fe^{III}GluSiW and H₂O₂, H₂O₂ can oxidize SiW₁₂O₄₀⁵⁻ to SiW₁₂O₄₀⁴⁻, producing additional HO• species (Eq. (10)) [25]. This proposal is supported by the fact that the redox potential of H₂O₂ to HO• and H₂O (+0.71 V versus the normal hydrogen electrode [36]) is more positive than that of SiW₁₂O₄₀⁴⁻ to SiW₁₂O₄₀⁵⁻ (+0.057 V versus the normal hydrogen electrode [37]). Additionally, the hydrogen bonding of H₂O₂ on the Fe^{III}GluSiW surface may promote oxidation of SiW₁₂O₄₀⁵⁻ by H₂O₂. The photocatalytic activity of Fe^{III}GluSiW is therefore enhanced by the presence of H₂O₂. In summary, the increased rate of 4-CP degradation under irradiation is ascribed to simultaneous oxidations of 4-CP through Fenton-like and photocatalytic routes mediated by ferric iron and SiW₁₂O₄₀⁴⁻ heteropolyanions, respectively, in Fe^{III}GluSiW.

The proposed catalytic mechanism explains the effects of catalyst dosage, H₂O₂ concentration, and initial pH value. As shown in Fig. 6(a) and (d), 4-CP degradation was hindered by

decreasing the catalyst dosage from 1.0 to 0.2 g/L, and did not change significantly with increasing dosage from 1.0 to 2.0 g/L. The formation of HO• and oxidation of 4-CP mainly occur on the catalyst surface. A lower catalyst dosage (e.g., 0.2 g/L) provides fewer active sites; therefore, smaller amounts of H₂O₂ and 4-CP are attached to the catalyst surface, resulting in a lower reaction rate. However, addition of an excess of catalyst to the reaction system (e.g., 2.0 g/L) leads to considerable agglomeration of catalyst powder, reducing the increase in the number of active sites caused by increasing the catalyst dosage. When the reaction is carried out under irradiation, the presence of excess catalyst reduces light penetration through water, and this retards the photocatalytic degradation of 4-CP.

Fig. 6(b) and (e) shows that decreasing the H₂O₂ concentration from 20 to 10 mmol/L inhibited the reaction. A lower H₂O₂ concentration results in decreased adsorption of H₂O₂ on the catalyst surface, leading to reduced production of HO• via Eqs. (3) and (4), and slower oxidation of SiW₁₂O₄₀⁵⁻ by H₂O₂ via Eq. (10). The oxidation of 4-CP through both the Fenton-like and photocatalytic routes is therefore hindered. However, the reaction rate did not increase correspondingly when the concentration of H₂O₂ was increased from 20 to 30 mmol/L because of scavenging of HO• by excess H₂O₂ [7,13]. Furthermore, coverage of too many active sites on the catalyst by H₂O₂ molecules, i.e., a too high H₂O₂ concentration, restrains the adsorption of 4-CP, which is unfavorable for 4-CP oxidation.

The degradation of 4-CP was enhanced by lowering the initial pH from 6.5 to 3.0, and was significantly retarded by increasing the initial pH to 8.0 (Fig. 6(c) and (f)). This is because of the higher redox potential of HO• and less decomposition of H₂O₂ to O₂ and H₂O at lower pH [14,38,39]. Although a low pH (e.g., 3.0) favors 4-CP degradation in the Fe^{III}GluSiW/H₂O₂ system, the reaction rate at an initial pH = 6.5, with no pH adjustment, is still considerable. Fe^{III}GluSiW is therefore a promising heterogeneous Fenton-like catalyst for the treatment of CPs.

4. Conclusions

An iron-glutamate-silicotungstate ternary complex, Fe^{III}GluSiW, was synthesized from ferric chloride, glutamic acid, and silicotungstic acid. The chemical formula of Fe^{III}GluSiW is [Fe(C₅H₈NO₄)(H₂O)]₂SiW₁₂O₄₀·13H₂O, with glutamate moiety and Keggin-structured SiW₁₂O₄₀⁴⁻ heteropolyanion. The prepared Fe^{III}GluSiW showed high catalytic activity in 4-CP oxidation by H₂O₂ at neutral pH under both dark and irradiated conditions. The high catalytic activity of Fe^{III}GluSiW is related to the formation of hydrogen-bonded H₂O₂ on the catalyst surface. The enhanced degradation of 4-CP under irradiation is ascribed to the synergetic effect of Fenton-like and photocatalytic oxidations catalyzed by ferric iron and SiW₁₂O₄₀⁴⁻ heteropolyanions, respectively, in Fe^{III}GluSiW.

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Graphical Abstract

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Iron-glutamate-silicotungstate ternary complex as highly active heterogeneous Fenton-like catalyst for 4-chlorophenol degradation

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The high catalytic activity of the catalyst is due to the hydrogen bonding of H_2O_2 on the surface. The enhanced degradation of 4-chlorophenol (4-CP) under irradiation is due to simultaneous oxidation of 4-CP through Fenton-like and photocatalytic processes.

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铁-谷氨酸-硅钨酸三元配合物作为高活性非均相类Fenton催化剂降解4-氯酚

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摘要: Fenton氧化法通过 Fe^{2+} 离子催化分解 H_2O_2 产生羟基自由基, 能够氧化降解绝大多数有机污染物. 但是传统的均相Fenton氧化法使用高浓度二价铁盐作为催化剂, 催化剂不便于回收利用, 而且还会引发新的环境问题. 另外, 均相Fenton氧化法通常需要在pH约为3的酸性条件下进行, 在较高pH条件下, 有机物氧化降解速率降低, 同时铁盐水解产生铁泥. 文献报道了一些含铁固体材料作为非均相类Fenton催化剂, 能够解决催化剂回收和重复利用问题, 但是许多固体催化剂仍然只在酸性条件下表现出较高催化活性. 多金属氧簇是除过渡金属氧化物之外的一类光催化剂. 近年来, 多金属氧簇在Fenton氧化过程中的应用开始受到关注. 可以预计, 含铁的多金属氧簇固体化合物有可能同时具有类Fenton催化活性和光催化活性.

本文以三价铁盐(Fe^{III})、谷氨酸(Glu)和硅钨酸(SiW)为原料在水溶液中合成了一种不溶性的三元固体配合物 $\text{Fe}^{\text{III}}\text{GluSiW}$, 并用电感耦合等离子体原子发射光谱(ICP-AES)、热重分析(TG)、傅里叶变换红外光谱(FT-IR)、紫外-可见漫反射光谱(UV-vis DRS)、

X射线衍射(XRD)和场发射扫描电镜(FE-SEM)对 $\text{Fe}^{\text{III}}\text{GluSiW}$ 进行了表征. 根据ICP-AES, TG和FT-IR结果推断, $\text{Fe}^{\text{III}}\text{GluSiW}$ 可能的化学组成为 $[\text{Fe}(\text{C}_5\text{H}_8\text{NO}_4)(\text{H}_2\text{O})]_2\text{SiW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$, 其中含有铁、谷氨酸根单元和Keggin结构的 $\text{SiW}_{12}\text{O}_{40}^{4-}$ 阴离子. FE-SEM和XRD测试结果表明, $\text{Fe}^{\text{III}}\text{GluSiW}$ 是由结晶度较低、尺寸为100–200 nm的无规则颗粒组成, 并含有无定形相.

通过考察在自然初始pH 6.5条件下100 mg/L 4-氯酚(4-CP)在 $\text{Fe}^{\text{III}}\text{GluSiW}$ (1.0 g/L)/ H_2O_2 (20 mmol/L)体系中的氧化降解反应, 我们发现在暗态和光照条件下, 4-CP完全降解所需时间分别为40和15 min, 延长反应时间至2 h, 总有机碳(TOC)去除率分别达到27%和72%. 结果表明, $\text{Fe}^{\text{III}}\text{GluSiW}$ 具有很高的催化活性, 而且在光照条件下活性更高. 进一步研究发现, $\text{Fe}^{\text{III}}\text{GluSiW}$ 在pH 3–6.5范围内均表现出高的催化活性, 而且在酸性条件下活性更高. 用ICP-AES测定Fe元素在溶液中的析出量, 证实4-CP氧化降解主要发生在固体催化剂表面. 在反应体系中加入正丁醇能显著抑制4-CP降解, 说明4-CP降解反应涉及羟基自由基的氧化作用. 在光照反应条件下, 催化剂颜色明显变深, 表明光照条件下的反应机理涉及催化剂中 $\text{SiW}_{12}\text{O}_{40}^{4-}$ 阴离子的还原. 考虑到催化剂中含有谷氨酸根和 $\text{SiW}_{12}\text{O}_{40}^{4-}$ 杂多阴离子, 推测 H_2O_2 有可能通过氢键吸附于催化剂表面, 这可能是 $\text{Fe}^{\text{III}}\text{GluSiW}$ 表现出高催化活性的重要原因.

结合文献报道的含铁固体材料类Fenton催化机理和多金属氧簇光催化机理, 可以很好地解释4-CP降解反应实验结果. 在暗态条件下, $\text{Fe}^{\text{III}}\text{GluSiW}$ 的催化机理归因于催化剂表面 Fe^{III} 的氧化还原循环 $\text{Fe}^{\text{III}} \rightleftharpoons \text{Fe}^{\text{II}}$, 即 H_2O_2 分子在催化剂表面分解产生羟基自由基, 从而导致4-CP氧化; 而在光照条件下, 除了催化剂中 Fe^{III} 的类Fenton催化作用之外, 催化剂中 $\text{SiW}_{12}\text{O}_{40}^{4-}$ 杂多阴离子的光催化作用同时发生, 导致4-CP降解速率加快. 在光催化过程中, 4-CP可以被激发态 $\text{SiW}_{12}\text{O}_{40}^{4-}$ 直接氧化, 也可以被激发态 $\text{SiW}_{12}\text{O}_{40}^{4-}$ 与 H_2O 相互作用产生的羟基自由基氧化. 被还原的杂多阴离子可以被 O_2 氧化, 也可以被 H_2O_2 氧化, 因而 H_2O_2 的存在也促进了 $\text{Fe}^{\text{III}}\text{GluSiW}$ 的光催化作用.

关键词: 多金属氧簇; 硅钨酸; 非均相催化; Fenton氧化; 4-氯酚降解

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