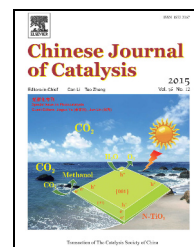


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Iron-glutamate-silicotungstate ternary complex as highly active heterogeneous Fenton-like catalyst for 4-chlorophenol degradation



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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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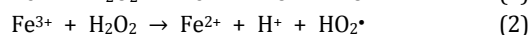
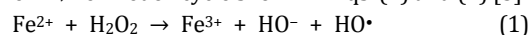
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1. Introduction

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 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 (pH = 2.0–3.0), 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 $\text{M}-\text{O}-\text{M}$ 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 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

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