



Electro-assisted heterogeneous activation of persulfate by Fe/SBA-15 for the degradation of Orange II



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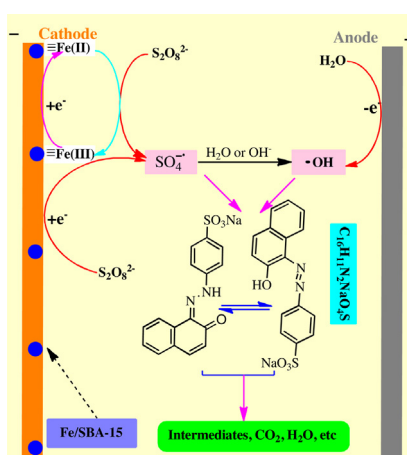
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HIGHLIGHTS

- Fe/SBA-15 was fabricated and used in an EC enhanced heterogeneous PS process.
- The effect of reaction parameters and the stability of Fe/SBA-15 were investigated.
- Primary reactive species were identified and the degradation mechanism was elucidated.
- Main intermediates were determined and a possible degradation pathway was proposed.
- The toxicity of treated solution was decreased to almost zero.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal of Orange II by activation of persulfate (S₂O₈²⁻, PS) using synthesized Fe/SBA-15 in the electrochemical (EC) enhanced process was reported in this study. The reaction rate constants, degradation mechanism, catalyst stability, and evolution of mineralization and toxicity were detailed investigated. On the basis of radical scavenger results, both the sulfate radicals (SO₄^{•-}) and hydroxyl radicals (*OH) were responsible for the degradation of Orange II. A possible pathway is suggested to describe the degradation of Orange II according to the degradation intermediates identified. The results showed that the Fe/SBA-15 catalyst maintained strong reusability and stability with a low level of iron leaching. In addition, favorable mineralization efficiency in terms of COD removal efficiency (75.4%) and TOC removal efficiency (46.3%) was obtained when the reaction time was prolonged to 24 h. The toxicity experiments implied that the toxicity of the treated solution ascended at the first 30 min but then dropped to almost zero eventually. This study provides a proof-of-concept that can be applied widely for the PS remediation of contaminated water.

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1. Introduction

Recently, synthetic dyes have been widely applied in various industries, such as printing, textile, paper, leather tanning, food

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and pharmaceutical production industries [1,2]. Among these dyes, Orange II, a kind of widely used azo dyes, covers more than 50% of the dyes employed for the textile manufacture [3,4]. Generally, the discharge of Orange II into industrial wastewater could result in serious aesthetic problem and environmental threat to the receiving water bodies [5–7]. Moreover, Orange II is chemically and photolytically stable and can remain in the ecosystem for a long time [8], and sometimes even more hazardous aromatic compounds can generate during the degradation process [9]. Therefore, it is essential to develop more effective method for the elimination of Orange II from wastewater.

Nowadays, advanced oxidation processes (AOPs) have been extensively employed for the removal of recalcitrant contaminants due to their facile operation, high efficiency, inexpensive cost, and mild condition of temperature and pressure [10]. Particularly, sulfate radical ($\text{SO}_4^{\bullet-}$) induced AOPs have been proposed as promising alternative for degrading a wide range of non-biodegradable organic compounds [11]. Compared with hydroxyl radical ($\bullet\text{OH}$) ($E^0 = 1.8 \sim 2.7$ V), $\text{SO}_4^{\bullet-}$ shows some advantages such as higher redox potential ($E^0 = 2.5 \sim 3.1$ V), longer half-life as well as stronger oxidation ability [12,13]. Usually, persulfate (PS, $\text{S}_2\text{O}_8^{2-}$) or oxone can be activated to form $\text{SO}_4^{\bullet-}$ via ultraviolet (UV) light [14], heat [15,16], transition metal [17,18], and electron transfer [19,20]. Generally, PS, a strong oxidant ($E^0 = 2.01$ V), has proved to be efficient and is commonly used since it is much cheaper than oxone and more stable than hydrogen peroxide [21,22].

In recent years, plenty of studies have reported that transitional metal in conjunction with PS are the promising methods to produce $\text{SO}_4^{\bullet-}$ for the removal of pollutants [23]. Among these transition metals (Ag^+ , Co^{2+} , Ni^{2+} , Fe^{2+} , Ru^{3+} , Mn^{2+}), iron (often as Fe^{2+}) is advantageous for activation of PS since it is relatively cost-effective, natural abundant and environmentally friendly [12,24]. However, the limitations such as the treatment of iron sludge and the reaction under acidic condition would eventually increase the overall cost [10,25]. Moreover, the rapid oxidation of Fe^{2+} to Fe^{3+} but very slow conversion from Fe^{3+} to Fe^{2+} would lead to the fast halt of the reaction and poor PS utilization [26,27]. In addition, $\text{SO}_4^{\bullet-}$ will be consumed by the excessive Fe^{2+} , leading to the decline of the oxidation efficiency [22,28]. Therefore, a novel approach named as electro/ Fe^{2+} (Fe^{3+})/PS process was successfully employed to regenerate Fe^{2+} for the degradation of contaminants [29–31]. Unfortunately, despite the activation efficiency was enhanced in this process, iron is still difficult to reuse due to the homogeneous condition [32]. The attempt of solid iron catalyst may be an alternative to overcome this drawback.

It is reported that the introduction of appropriate support can bring outstanding catalyst performance and practicability [13,33]. Mesoporous silica SBA-15, a kind of ordered mesoporous molecular sieve, has attracted more and more attention as a promising support owing to its high stability, large pore size and high surface area [34,35]. Furthermore, some studies have proved that the SBA-15 supported metal catalysts were of high stability, and the leaching of metal species could be effectively inhibited [33].

SBA-15 supported iron (Fe/SBA-15) particles have been fabricated and accepted as excellent catalyst in Fenton process for wastewater treatment in our previous studies [36,37]. Additionally, the active species of low-valent metal could be continuously obtained at the cathode during the electro-assisted process. Despite of that, to the best of our knowledge, there is no report on the combination of electrochemical (EC) method with Fe/SBA-15 activated PS process. Hence, Fe/SBA-15 catalyst was synthesized for the activation of PS to remove Orange II in an electrolytic cell in this study. Detailed work was investigated on the removal of Orange II under EC/Fe/SBA-15/PS system. The influence of the principal reaction parameters like current density, initial pH (pH_0), PS concentration, and catalyst addition were studied. The probable mechanism for

Orange II degradation under this process was clarified. Moreover, the intermediates were identified by GC–MS technique and a possible degradation pathway was elucidated. Finally, the changes of mineralization and toxicity during the process were determined as well under this process.

2. Materials and methods

2.1. Preparation and characterization of Fe/SBA-15

The support SBA-15 was synthesized based on previously published reports [37,38] (Supplementary data). Fe/SBA-15 particles were prepared via an in situ auto-combustion method [13,38] (Supplementary data). X-ray diffraction (XRD) of the SBA-15 and Fe/SBA-15 catalysts was scanned by a PANalytical X'Pert Pro XRD system. The morphology of the Fe/SBA-15 catalyst was detected at 120 kV using a Philips CM120 transmission electron microscope (TEM) equipped with the EDX analyzer to detect the iron spot.

2.2. Experimental setup

Batch electrolyses were conducted in a 250 mL glass beaker with 150 mL Orange II solution ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaO}_4\text{S}$). A plate anode (Ti/RuO₂-IrO₂, 5.0 cm × 11.9 cm) and a stainless steel plate (cathode) with same dimensions were placed in parallel. A water bath was used to immerse the reactor for keeping the temperature at 20 ± 2 °C. Sodium sulfate (Na_2SO_4) was kept at 50 mM as electrolyte. A direct current (DC) power supply was utilized to obtain constant current. The solution was mixed at a constant rapid (500 rpm). Prior to each test, the fresh Orange II (0.3 mM) was prepared using deionized water. The initial pH (pH_0) of Orange II was adjusted with 0.1 M sulfuric acid or with 0.1 M sodium hydroxide and measured via a Mettler-Toledo FE20 pH-meter. PS and the catalyst were added into the electrolytic cell simultaneously as the DC power supply started. At each selected time interval, aliquots were taken from the reactor, filtered through 0.22 μm membranes (Millipore Co.), and immediately mixed with the same volume of methanol prior to analysis.

2.3. Analytical methods

The concentrations of Orange II samples were determined at $\lambda_{\text{max}} = 485$ nm by the Rayleigh UV-9100 spectrophotometer (Rayleigh Co., China), and the color removal efficiency was obtained based on Eq. (1), where C_0 was the initial concentration of Orange II and C was the concentration at time t .

$$\text{Decoloration efficiency}(\%) = (C_0 - C) / C_0 \times 100 \quad (1)$$

Residual concentration of PS was detected using an iodometric titration method [39]. Iron leaching concentration was determined via an atomic adsorption spectrophotometer (AAS, Perkin Elmer Analyst). The intermediates during the process were identified by gas chromatography-mass spectrometry (GC–MS, VARIAN 450-GC/320-MS) (Supplementary Data). TOC data was collected from a Jena multi N/C 3100 analyzer and the value of COD was determined using the closed reflux spectrophotometric method (Supplementary Data). The toxicity experiments with activate sludge were conducted similar to the previous work by Arslan-Alaton and co-authors, and the conditions were adjusted for proper oxygen uptake rates (OUR, in mg/(L h)) [40,41] (Supplementary Data). The percentage inhibitory on oxygen uptake rates (I_{OUR} , in%) for each tested sample was calculated according to Eq. (2), where OUR_S is the OUR for the samples reacted and OUR_B is the OUR for the sample blank.

$$I_{\text{OUR}}(\%) = [(\text{OUR}_B - \text{OUR}_S) \times 100] / \text{OUR}_B \quad (2)$$

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