



Full Length Article

Design of a novel immobilized solid acid coating and its application in Fenton-like oxidation of phenol



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ABSTRACT

A novel immobilized solid acid coating on Q235 carbon steel was successfully prepared via plasma electrolytic oxidation. Sulfate functionalized $\text{Fe}_3\text{O}_4/\text{FeAl}_2\text{O}_4$ was confirmed by XRD, TEM and XPS analysis and surface acidic property was verified by NH_3 -TPD measurement. Fenton-like degradation performance was evaluated by employing phenol as target pollutant. Fast phenol degradation under the wide range of pH (pH 6–9) was accomplished within only 11 min. Without sulfate functionalization, phenol could hardly be degraded by Fenton-like oxidation which meant that after sulfate functionalization the existence of acidic microenvironment on the catalyst surface not only provided an optimal circumstance for enhanced Fenton-like reaction, but also avoided adjusting pH of the treated wastewater. A reasonable Fenton-like degradation mechanism was proposed. This paper offered a novel design thought for synthesizing excellent Fenton-like coating catalyst under circumneutral pH.

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1. Introduction

In recent years, Fenton reaction as one of the advanced oxidation processes (AOPs), which is based on the Fe^{2+} and H_2O_2 , has been widely researched for the removal of the organic pollutant, especially the recalcitrant contamination in the wastewater [1–10]. However, the drawbacks of narrow pH (pH 2–4), sludge production during operation, pH adjustment before treatment and neutralization of the treated wastewater before discharge and sludge recyclability constrain its commercial application [3]. Although Fenton-like catalysts, which mainly utilize iron based materials in the form of powder, such as Fe_2O_3 [11], Fe_3O_4 [5], iron oxyhydroxide [12], zeolite supported iron oxide [13] et al., have been developed on the basis of Fenton catalyst, the poorer catalytic activity under near-neutral condition and centrifugation or filtration for reuse still hindered their industrial process [5,14]. Therefore, the development of high efficient under near-neutral pH environment and easier recyclable Fenton-like catalyst is still a great challenge.

Intriguingly, solid acid as Fenton-like catalyst which has acidic microenvironment on the solid surface and then enhances catalytic activity without adjusting pH of wastewater, was proposed. Indeed, solid acid catalysts replacing of traditional inorganic acids in the liquid phase such as HF, HCl, H_2SO_4 et al., have been widely utilized

in the acid-catalyzed organic reactions, like esterification, isomerization, acylation, etc [15–17] which are in favor of solving the separation, corrosion and environmental issues caused by conventional catalysts. However, although some literature on solid acid Fenton-like catalysts have been published in recent years [18,19], these catalysts in the form of powder have the disadvantages of separation difficulty, catalyst loss during recycling and complex synthesis method. In brief, facile preparation of immobilized solid acid coating catalyst was never reported.

In view of the superior catalytic activity of Fenton-like catalyst and strong oxidant capacity of hydroxyl radicals under acidic environment (pH 2–4) [4,5,20,21], in this paper, a novel immobilized solid acid coating catalyst on Q235 carbon steel was prepared in situ via plasma electrolytic oxidation technique which was environmental benign. This solid acid coating as Fenton-like catalyst was employed to degrade phenol pollutant in the wastewater. The results signified that phenol could be degraded rapidly in the wide range of pH. In the end, the reasonable degradation mechanism was proposed.

2. Experimental section

2.1. Chemicals and materials

Phenol and NaAlO_2 were obtained from Sinoharm Chemical Reagent Co. Ltd., China. Hydrogen peroxide (analytical grade, 30%, w/w) was purchased from Xilong Chemical Co., Ltd in

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China. $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ were derived from Tianjin Zhiyuan Chemical Reagent Co. Ltd., China. All solutions used were prepared with deionized water.

2.2. Preparation of immobilized solid acid coating catalyst

The immobilized solid acid coating on Q235 carbon steel was successfully prepared by PEO technique. The detailed procedure is as follows: the rectangular Q235 carbon steel with a dimension of 20 mm \times 20 mm \times 0.5 mm, the composition of which is C 0.14–0.22%, Mn 0.30–0.65%, Si \leq 0.30%, P \leq 0.045%, S \leq 0.05%, the rest Fe, wt.%, was as anode. Before the PEO process, the Q235 carbon steel was polished with 500, 1000, 1500, 2000, 2500 mesh abrasive paper in sequence and then washed with deionized water, ethanol and finally thoroughly dried with a drier. A home-made unipolar pulsed DC power source with pulse peak current waveform was utilized for PEO process. The PEO process was operated in a water-cooled electrolyser which is made of stainless steel as cathode and can maintain the electrolyte temperature 25 °C. The electrolytic solution was composed of 10 g/L NaAlO_2 , 1.5 g/L $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and 1.0–4.0 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The peak current was 150 A and the pulse frequency was 2000 Hz. The reaction time was 10 min. After PEO process, the coated specimen was taken out and rinsed with deionized water and then dried naturally.

2.3. Catalysts characterization

X-ray diffraction (XRD) measurement of the samples was performed by a Rigaku D/max- γ B diffractometer with Cu K α ($\lambda = 0.15406$ nm) radiation. The morphology of the coatings was characterized with field-emission scanning electron microscope (NanoLab 600i scanning electron microscope). Transmission electron microscopy (TEM) characterization with energy dispersive X-ray detector (EDX) was performed by using FEI Tecnai G2 F30, America. The TEM specimen preparation was as follows: the ceramic coating was scraped off from the surface and grinded into powder; the powder was suspended into the ethanol under ultrasonic dispersion and then several microliters sample was added onto carbon coated copper grid for subsequent TEM analysis. Surface composition of the sample was analyzed by X-ray photo-

electron spectroscopy (XPS) equipped with PHI 5400 ESCA System with Al K α radiation at 1486.6 eV. NH_3 -TPD was performed to evaluate surface acidic property of catalyst on a Finetec FINESORB-3010 instrument. The sample used in NH_3 -TPD measurement existed in the form of powder which originated from ceramic coating. The test procedure was carried out according to the reported literature [22] and the detailed experimental process was as follows: firstly, the sample was pretreated for 60 min at 450 °C under argon atmosphere (20 mL/min) and cooled to 30 °C, and then treated with NH_3 for 60 min; Ar gas was allowed to flow the whole sample under 120 °C in order to eliminate physisorbed ammonia; finally, after a stable baseline was achieved the NH_3 -TPD was run between 34 °C and 765 °C at 20 °C/min.

2.4. Phenol degradation experiment

The catalytic activity of the as-prepared solid acid coating was evaluated by degradation phenol through Fenton-like reaction. In a typical batch experiment, 6 cm² coating catalyst was immersed into 50 mL 35 ppm phenol solution with the original pH (pH 6.0) without the adjustment by H_2SO_4 or NaOH in a 100 mL beaker. Phenol solution was placed into water bath to keep the temperature 303 K with constant stirring speed. The phenol degradation was initiated once a given amount of H_2O_2 (0.034 mL 30%) was added. During degradation, a desired amount of sample was withdrawn with a pipette at a given interval time for phenol concentration measurement.

2.5. Sample analysis

Phenol concentration was determined by 4-aminoantipyrine spectrophotometric method at 510 nm on a UV/Vis spectrophotometer (Lambda XLS, PerkinElmer) [23,24]. 1, 10-phenanthroline method was adopted to measure the concentration of the ferrous ion and total iron leaching from the catalysts [24,25].

3. Results and discussion

3.1. Characterization of catalysts

The surface morphology of the as-prepared PEO coatings under different sulfur source content in the aluminate electrolyte system was shown in Fig. S1. All of the PEO coatings had the porous structure which was the residual discharge channels and just like volcanic crater. Abundant bulges were distributed randomly to the coating surface, which were sintered substances and formed by quenching effect of electrolyte during the discharge reaction process. With the increase of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ content, amount of the discharge sparks was increased, but the intensity and size became small which led to the results that less molten substances were ejected through the breakdown-channels and much smaller pores were kept on the coating surface. In addition, more and more micro/nano sized particles were gathered on the bulges. The pore size of the PEO coatings was presented in Fig. S2. The average pore size decreased with the sulfur source increases from 0.0 g to 3.0 g, and then changed little. It is well acknowledged that the more pores and the smaller pore size could lead to the larger specific area, so PEO coating with 3.0 g sulfur source might have the largest specific area. In a word, the PEO coatings with different pore and bulges size were successfully prepared in the aluminate electrolyte containing different content of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

The elemental composition of the coatings was investigated by EDS analysis. As shown in Table S1 which was achieved from SEM-EDS, the coatings were mainly comprised of Fe, Al, O, P and Na, among which Fe was from the substrate and other elements were derived from the electrolyte. Moreover, after addition of

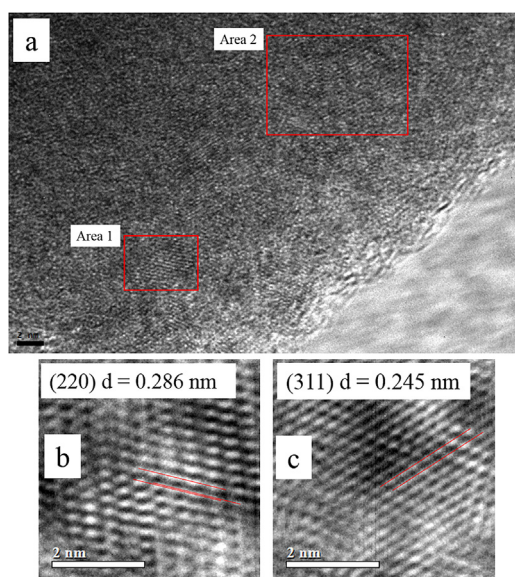


Fig. 1. TEM images of S modified $\text{Fe}_2\text{O}_4/\text{FeAl}_2\text{O}_4$ composite coating prepared with 3 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (a); (b and c) are obtained by fast Fourier transform (FFT) on area 1 and 2 of (a) respectively, and smoothing edge by mask then inverse FFT.

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