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Preparation of magnetic steel-slag particle electrode and its performance in a novel electrochemical reactor for oilfield wastewater advanced treatment

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ABSTRACT

A novel continuous-flow electrochemical reactor was designed for oilfield wastewater advanced treatment. Magnetic steel slag particles were prepared as particle electrodes in the reactor. The best preparation condition of steel slag particle electrodes is obtained via orthogonal and single factor experiments. The resulting samples were characterized by scanning electron microscope and vibrating sample magnetometer. It was demonstrated that saturation magnetic intensity of the particle was 1.6389 emu/g. The process parameters and the total organic carbon (TOC) removal kinetics were investigated. Result showed that the reactor could remove over 85% TOC in 2 h, which was considered to be effective.

Introduction

Electrochemical oxidation, an important advanced oxidation technology (AOT), is known as “environmentally friendly” and has been used in many fields of environmental chemical engineering [1]. Conventional AOTs reactors was limited by their low mass transfer efficiency, thus many research works were conducted to ameliorate AOTs, such as preparing novel electrode materials [2–6], combine with other effective technologies [7–9] and so on. Three-dimensional electrode oxidation reactors, have developed from suchlike works, and verified to have advantages over the conventional electrochemical oxidation reactors.

The concept “using waste to treat waste” nowadays has gained much concern in the field of water treatment. Steel slag, which is a representative industrial waste, has been utilized through many approaches to treating wastewater [10–12]. The excellent adsorb and sedimentation ability of steel slag has made it useful in removing pollutants such as nitrogen, phosphorus, heavy metals and organics in water and soil environment [13,14].

However, the abundant metal resources contained in steel slag have been ignored by many present research works and consequently utilization of steel slag in the field of water treatment is limited. Previous research indicated that electro-Fenton process occurs in steel slag three-dimensional electrode system due to the existence of Fe element, which could obviously improve the degradation of organic pollutants [15–17]. Additionally, the existence of Fe element renders magnetism of the steel slag particles, which could bring a favorable recovery performance.

Oilfield wastewater, which is discharging increasingly every year with the development of petroleum industry, has a character of resisting biological treatment [18–20]. With respect to electro-catalysis technologies, three-dimensional electrode technology could remove organic pollutants from oilfield wastewater effectively by generating the nonselective oxidant hydroxyl radicals [21–23]. After conventional treatment of oilfield wastewater, some organics residual would maitain bio-toxicity [24]. And three-dimensional electrode technology could be an efficient selection for oilfield waste water advanced treatment. Furthermore, using steel slag particles as particle electrodes would improve organic pollutants degrading on account of the occurrence of electro-Fenton, and the steel slag particles would be facile to recovery owing to their magnetism.

In the present work, we demonstrate a novel continuous flow three-dimensional electrode reactor for oilfield wastewater advanced treatment, which could degrade organic pollutants effectively due to the presence of steel slag particle electrodes. The

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Table 1
Factors and levels of the orthogonal experiment.

Factors	Level 1	Level 2	Level 3
Content of steel slag (%)	40	50	60
Content of pore forming agent (%)	10	15	20
Calcination temperature (°C)	950	1000	1050
Calcination time (min)	30	45	60

steel slag particle electrodes are prepared through an optimized "four-step" strategy, and characterized by scanning electron microscope and vibrating sample magnetometer. Operation parameters of the continuous flow three-dimensional electrode reactor with steel slag particle electrode, which affect the reactor efficiency are also optimized in terms of dosage of the particles, applied voltage optimization and hydraulic retention time (HRT). The reactor is clarified to be efficiency for organic pollutants removing.

Experimental section

Preparation process optimization

In this work, steel slag, clay and pore forming agent were used as principal raw material in particle electrodes preparation. The strategy (four-step strategy) used to obtain particle electrodes was as follow: [25] washed steel slag was milled into powder by a pot mill, and then mixed with clay and pore forming agent. The mixture was then roll into particles with the diameters of 3–5 mm. The particles were then heated in a tube furnace to obtain particle electrodes.

Three critical factors were considered in particle electrodes preparation: ratio of raw materials, calcination temperature and calcination time. Therefore, an L9 3^4 Orthogonal test was applied to analyze the influence of the three factors on performance of the particle electrodes. In this orthogonal test, ratio of raw materials were split into two factors: proportion of steel slag and proportion of pore forming agent. RhB degradation rate was regarded as evaluation criteria. Table 1 shows the factors and levels of the orthogonal test. Results of the orthogonal test were displayed in Table 2, K an R values were calculated and listed too.

Since we can not select the best condition of particle electrodes preparation based on the results showed in Table 2, we just chose the better condition that listed in Table 2: content of steel slag 50%, content of pore-forming agent 10%, calcination temperature 1000 °C and calcination time 60 min. Furthermore, it can be observed in Table 2 that influence on performance of steel slag particle electrodes in 3-D oxidation system decrease in the order: calcination temperature > proportion of steel slag > proportion of pore forming agent > calcination time. In consideration of results that mentioned above, we could running single influnce factor experiments in the order: ratio of raw materials, calcination temperature, and then calcination time.

The strategy of single influence factor experiment is as follow: (1) Ratio of materials: steel slag powder, clay and pore forming agent were mixed by the mass ratio of 4.5:4.5:1, 5:4:1 and 5.5:3.5:1, respectively. Calcinate the particles at 1000 °C for 30 min. The particles were then utilized in a three dimensional electrode system for RhB degradation under a 6 V voltage and 0.1 mol/L electrolyte concentration, measure the absorbance of the RhB solution intervals of 10 min, calculate the degradation ratios. (2) Calcination temperature: steel slag powder, clay and pore forming agent were mixed by the optimized mass ratio. Calcinate the particles at 950 °C, 1000 °C and 1050 °C for 30 min, respectively. The particles were then utilized in a three dimensional electrode system for RhB degradation under a 6 V voltage and 0.1 mol/L electrolyte concentration, measure the absorbance of the RhB solution intervals of 10 min, calculate the degradation ratios. (3) Calcination time: steel slag powder, clay and pore forming agent were mixed by the optimized mass ratio. Calcinate the particles at the optimized temperature for 30 min, 60 min and 90 min, respectively. The particles were then utilized in a three dimensional electrode system for RhB degradation under a 6 V voltage and 0.1 mol/L electrolyte concentration, measure the absorbance of the RhB solution intervals of 10 min, calculate the degradation ratios.

Characterization

In order to investigate the morphology and elementary composition of steel slag particle electrodes, particles that prepared with the optimized conditions were characterized by a Quanta 200F field emission scanning electron microscope (SEM) and the Energy Dispersive Spectroscopy (EDS). Vibrating sample magnetometer (lake shore 7040, VSM) was employed to investigate the magnetic characteristic of the particle electrodes. RhB decoloration ratio was analyzed at 554 nm on a UV–vis spectrometer (UV2550). TOC values were measured by a Multi N/C 3100 total organic carbon analyzer.

Description of the continuous flow reactor

The continuous flow reactor can be deemed as a dynamic three dimensional electrode unit for waste water treatment. Schematic of the dynamic reactor is as shown in Fig. 1. The whole reactor is divided into a three-chambers electrochemical system by two interlayer. The inside volumes of the three chambers were

Table 2
Analysis of the L9(3^4) test results.

No.	Content of steel slag (%)	Content of pore forming agent (%)	Calcination temperature (°C)	Calcination time (min)	RhB degradation ratio(%)
1	40	10	950	30	46.2
2	40	15	1000	45	51.5
3	40	20	1050	60	50.4
4	50	10	1000	60	71.9
5	50	15	1050	30	55.2
6	50	20	950	45	49.8
7	60	10	1050	45	54.8
8	60	15	950	60	49.3
9	60	20	1000	30	50.9
K1	49.367	57.633	48.433	50.767	
K2	58.967	52	58.1	52.033	
K3	51.667	50.367	53.467	53.2	
R	9.6	7.266	9.667	6.433	