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Application for oxytetracycline wastewater pretreatment by Fe-C-Ni catalytic cathodic-anodic-electrolysis granular fillers from rare-earth tailings

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ABSTRACT

Fe-C-Ni catalytic cathodic-anodic-electrolysis granular fillers (REGF) coupled with a reactor was studied for oxytetracycline (OTC) wastewater pretreatment. In this study, the REGF were manufactured from the rare-earth tailing (RET), powdered activated carbon (PAC), scrap iron and nickel by balling and calcining. The REGF was characterized by X-Ray Diffraction and Scanning Electron Microscope analysis. The influences of pH value (2−7), OTC concentrations, hydraulic retention time and aeration on the removal efficiency of OTC and total organic carbon (TOC) were studied. This system had good removal efficiency of TOC of 80.0% and OTC of 98.2% under the optimal conditions, which were influent pH of 3, aeration rate of 0 mg L^{-1}, and HRT of 3 h. After running for 50 d, the REGF did not become hardened and the ability of reaction was more lasting. The system was back-washed by acid solution (pH = 1) in the 25th day. The removal mechanisms were electrophoresis, redox and flocculation. The nickel, which was as the catalyst, was added into REGF to enhance the reduction of pollution with the absorbed atomic hydrogen. This paper provides a way for the recycle of the rare earth tailings and an effective application for wastewater.

1. Introduction

Rare earth tailings is one of the products of the sorting operation in rare earth separation, which contains the useful target components. The useful mineral grade of accumulation was very high. A large amount of tailings not only caused great waste of resources, but also damaged the ecological environment (Gupta et al., 2011; Khani et al., 2010; Yang et al., 2017b). The composition of tailings contains a lot of oxides with different valence states. According to the previous introductions, the rare earth reserves of bayan obo were 43.5 million tons (Dong et al., 2017). Since 1958, the resource has been mined 12.5 million tons, and about 2 million tons had been lost in the process of selecting, smelting, and storage. Thus, the actual use of rare earth resources is only about 1.2 million tons, and more than 9 million tons of rare earth resources has been discharged into the tailings dam (Gupta et al., 2015; Saleh and Gupta, 2012a; Wang et al., 2016; Yang et al., 2017b). Therefore, it is necessary to recycle the rare earth tailings.

In modern society, due to its unique physical and chemical properties, the rare-earth minerals have a wide range of applications in the development of economy (Gupta et al., 2013; Ramasamy et al., 2017; Sadri et al., 2017; Saleh and Gupta, 2014). Over the past 25 years, scientists had launched many sided researches about the application of rare-earth minerals (Saravanan et al., 2016; Zhuang et al., 2017). The application scope of the rare earth minerals have been expanded to various fields of modern science and technology (Ramasamy et al., 2017). The rare earth mineral will play a more and more important role in the development of the society (Devaraj et al., 2016; Huang et al., 2017; Peng et al., 2017; Yi et al., 2017). In 2007, the production of rare earth was about 12.08 t in China, which accounted for 97% of the world's rare earth minerals output (Dong et al., 2017; Gupta et al., 2014a). The technological process of rare earth ore mining are dressing, comprehensive mining and smelting, resulting the resources utilization rate is low. Therefore, the manufacture process will bring a lot of rare earth tailings (Hu and Sun, 2016; Karthikeyan et al., 2012; Mohammadi et al., 2011). The disposal methods of rare earth tailings were mainly displayed as follows: (1) the physical methods for

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Nomenclature

OTC	oxytetracycline
TOC	total organic carbon ($mg\,L^{-1}$)
RET	rare-earth tailing
PAC	powdered activated carbon
HRT	hydraulic retention time (h)
FFRT	The filler was separately granulated by the rare earth tailings
SFRT	The filler was made by FFRT, powder and carbon
REGF	Fe-C-Ni catalytic cathodic-anodic-electrolysis granular fillers
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction

recycling useful minerals from the tailings were flotation, magnetic separation, etc; (2) the chemical methods were leaching, roasting, etc; (3) the directly way for the recycle of tailings were backfilling mined-out area or made as a building material (Editorial Board/Publication Information (2015)).

Oxytetracycline (OTC) is a broad spectrum antibiotic, which has been extensively used for the treatment of illness of animals and humans (Hu et al., 2016; Liu et al., 2016; Saravanan et al., 2013c). OTC is extensively used all over the world. Some papers stated that the human organism function could be disturbed if the OTC was abused. Additionally, the bioactivity of majority microorganisms would be affected by the OTC in the environment (Boonsaner and Hawker, 2015; Ghodsi et al., 2016; Robati et al., 2016; Saravanan et al., 2015). Therefore, OTC has received a wide range of attention around the world, and the treatment methods of OTC wastewater with low-cost and high efficiency became a research focus.

Micro-electrolysis technology is a kind of electrochemical method with the iron and carbon used as the anodic and cathodic respectively, which can form the electrolyte battery in the system (Chen et al., 2012; Huang et al., 2014; Saravanan et al., 2013b, 2013d, 2013e; Xu et al., 2016). The mechanism of micro-electrolysis pretreatment in wastewater can be concluded as the oxidation reduction, coagulation, deposition, electrophoresis effect, physical adsorption (Gupta and Saleh, 2013; Rajendran et al., 2016; Saleh and Gupta, 2011, 2012b; Saravanan et al., 2013a, 2013d; Zhang et al., 2017). Compared with other wastewater pretreatment technologies, the micro-electrolysis has longer service life, lower operation cost and universal applicability (Ghaedi et al., 2015; Gupta et al., 2014b; Huang et al., 2014). The objective of this study was to explore the availability of the Fe-C-Ni catalytic cathodic-anodic-electrolysis granular fillers for the pretreatment of oxytetracycline wastewater.

2. Materials and methods

2.1. Materials

The REGF was made by powdered activated carbon, scrap iron, rare earth tailing and nickel sulfate solution. PAC was bought from Kermel Company in Tianjin. Scrap ion was purchased from Jinan Machinery Plant in Shandong. In addition, nickel sulfate ($NiSO_4{\cdot}6H_2O$), gathered from Henan shunbo chemical products co. LTD, was used to prepare the concentration of Ni^{2+} ($1.0\,g\,L^{-1}$). The rare earth tailing was gathered from Inner Mongolia baotou bayan obo tailings. The compositions of RET are demonstrated in Table 2. The rare-earth tailing, PAC and scrap iron were dried for 2–4 h at 105 °C, which were grinded and passed through a 154 µm sieve (NO. 100) 200 mesh griddle.

The purity for the used OTC, HCL and NaOH were all analytical pure. The oxytetracycline (> 95%, purity) sample was bought from Hubei Xing Galactic Chemical Company (China). The molecular weight was 460.58, whose molecular formula of OTC was $C_{22}H_{24}N_2O_9$. Sodium hydroxide (0.5 M) was bought from Guang Cheng Chemical Reagent Company (Tianjin, China) and Hydrochloric acid (0.5 M) was bought from Kant Chemical Company (Shandong, China). The composition of OTC simulation wastewater is shown in Table SM-1.

2.2. REGF synthesis and characterization

Firstly, the RTE, PAC and scrap iron dry powders were poured into a container and stirred for 10–15 min. Then, the mixed materials were added into Pelletizer (QJ300, China). The rotate speed of apparatus was about 700–800 rpm, and a predetermined amount of nickel sulfate solution (10.0 wt%) was added to produce raw pellets. Then, the raw pellets with diameter of 5.0–6.0 mm were sieved and were air-dried at room temperature for later experiments. The dried pellets were moved into muffle furnace (SX2–4–13, made in China) for sintering, and the temperature was gradually increased from room temperature to the calcined temperature (800–850 °C). The temperature of furnace was kept at 800–850 °C in nitrogen atmosphere for 30–40 min. Finally, the sintered pellets were cooled to room temperature in anaerobic conditions.

The characters of REGF was determined in terms of the previous study (Zhang et al., 2017). The grain density ($1998.8\,kg\,m^{-3}$), bulk density ($998.8\,kg\,m^{-3}$) and water absorption (14.3%) of the sintered pellets were measured by the national standard (GB/T 17431.2e2010).

2.3. Equipment and operational procedures

Schematic diagram of the continuous system for OTC simulate wastewater pretreatment is shown in Fig. 1. The cylindrical reactor (150 mm of inner diameter, 1100 mm in height) was made of polypropylene. A percolated plate was located 150 mm from the bottom of column, leaving a bottom space for air and water distribution zone. In the process of backwashing, a headspace of 200 mm in the reactor was need to retain fillers. The wastewater and air were provided into the column through a pump.

The potential adsorption effect by the REGF was avoided by immersing the fillers in the wastewater for a period of time before the formal experiment. The single factor influence of the system had been explored, including: hydraulic retention time, pH value, OTC concentrations and aeration. The hardened performance of the REGF also be verified by the long running in the system. The system was carried out in the laboratory of Shan Dong University. The temperature was 25 °C, the humidity was 54%, the climate was the continental monsoon

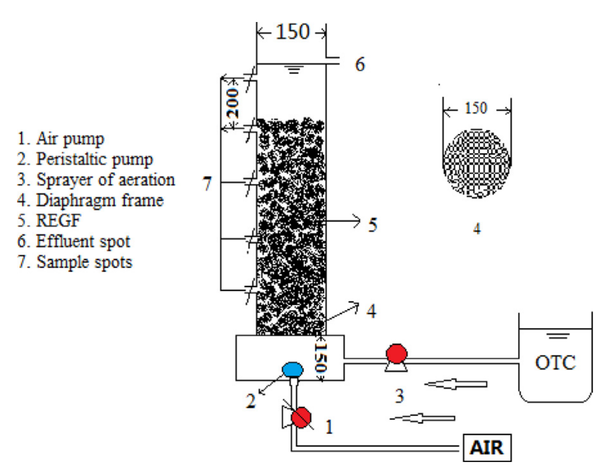

Fig. 1. Schematic diagram of the reactor.