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Preparation of ceramic-corrosion-cell fillers and application for cyclohexanone industry wastewater treatment in electrobath reactor

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ABSTRACT

As new media, ceramic-corrosion-cell fillers (Cathode Ceramic-corrosion-cell Fillers – CCF, and Anode Ceramic-corrosion-cell Fillers – ACF) employed in electrobath were investigated for cyclohexanone industry wastewater treatment. 60.0 wt% of dried sewage sludge and 40.0 wt% of clay, 40.0 wt% of scrap iron and 60.0 wt% of clay were utilized as raw materials for the preparation of raw CCF and ACF, respectively. The raw CCF and ACF were respectively sintered at 400 °C for 20 min in anoxic conditions. The physical properties (bulk density, grain density and water absorption), structural and morphological characters and toxic metal leaching contents were tested. The influences of pH, hydraulic retention time (HRT) and the media height on removal of COD_{Cr} and cyclohexanone were studied. The results showed that the bulk density and grain density of CCF and ACF were 869.0 kg m^{-3} and 936.3 kg m^{-3}, 1245.0 kg m^{-3} and 1420.0 kg m^{-3}, respectively. The contents of toxic metal (Cu, Zn, Cd, Pb, Cr, Ba, Ni and As) were all below the detection limit. When pH of 3–4, HRT of 6 h and the media height of 60 cm were applied, about 90% of COD_{cr} and cyclohexanone were removed.

1. Introduction

Sewage sludge, as a by-product of wastewater treatment, contains pollutants and unstable pathogen substance such as abundant organics, heavy metals and pathogenic bacteria [1–3], thus leading to potential hazards to human health and environment. Traditional treatments such as incineration, landfilling or composting were not economical, safe or sanitary [4,5]. The most widely used final disposal method of sludge is landfilling, with all the risk of soil contamination and degradation of the urban landscape [6,7]. Therefore, in order to prevent secondary pollution and convert sludge into useful resources, an effective and suitable method to treat large amounts of sludge should be found [8].

Scrap iron is a kind of solid waste from production process of machinery plants. The large quantity of scrap iron not only occupies a lot of land, but also causes environmental pollution. How to reduce environmental pollution induced by scrap iron and convert it into useful resources has been widely investigated [9–11].

Ceramics are widely used in construction industry, chemical industry, metallurgy, agriculture and environmental protection [12,13]. Sludge and scrap iron are utilized as additives in ceramics production, which can reduce the usage of clay. Thus wastes can be turned into valuable substances [14].

Micro-electrolysis technology was developed on the basis of electrochemistry in Europe during the 1960s [15]. It was believed to operate on the principles very similar to electrochemical methods, and the electrons were supplied from the galvanic corrosion of many micro-scale sacrificial anodes instead of external power supply. Numerous microscopic galvanic cells were formed between the particles of iron and carbon when they were in contact with wastewater (electrolyte solution). The half-cell reactions can be represented as follows [16]:

$$\text{Anode (oxidation)}: \ 2Fe \rightarrow 2Fe^{2+} + 4e^-, \quad E(Fe^{2+}/Fe) = -0.44\,V$$

$$\text{Cathode (reduction)}: \ \text{Acidic}\ 2H^+ + 2e^- \rightarrow H_2\uparrow, \quad E(H^+/H_2) = 0\,V$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O, \quad E(O_2/H_2O) = +1.23\,V$$

$$\text{Neutral to alkaline}\ O_2 + 2H_2O + 4e^- \rightarrow 4OH^-,$$

$$E(O_2/OH^-) = +0.40\,V$$

As a kind of physical–chemical methods, micro-electrolysis technology is widely used to treat refractory wastewater [17], including pesticide wastewater [18], pharmacy wastewater [19], and dye wastewater [20,21]. Micro-electrolysis technology can be used to break the construction of organic pollutants [22] and increase the ratio of BOD_5 to COD [23] which can facilitate biological treatment, remove color of wastewater, and reduce energy

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consumption and infrastructure investment. At present, the service life of the electrobath reactor of micro-electrolysis is too short and failure of the electrobath reactor is frequent. CCF and ACF have lower bulk density and grain density, which is beneficial for the backwash process. Therefore, they are suitable to be used as fillers of electrobath reactor for micro-electrolysis.

The cyclohexanone wastewater contains hazardous substance such as cyclohexanone and cyclohexane which is harmful to the blood vessel of human body and results in coagulation necrosis of viscera and brain. Therefore, it is significant to find an effective treatment method. At present, the treatment of cyclohexanone mainly includes extraction and electrochemistry. There are few studies on the application of micro-electrolysis for cyclohexanone wastewater treatment.

This research investigated the three aspects as follows:

(1) The possibility of novel media-ceramic-corrosion-cell fillers (CCF and ACF) used as fillers in electrobath of micro-electrolysis.
(2) The electrobath employed in cyclohexanone industry wastewater treatment.
(3) The optimum conditions (including pH, HRT and the height of fillers) for the wastewater treatment in terms of the removal efficiency of COD_{Cr} and cyclohexanone.

2. Materials and methods

2.1. Raw materials

Clay and dried sewage sludge (DSS) were utilized as raw materials to prepare CCF, and clay and scrap iron were used as raw materials for ACF production. Clay was obtained from a brickfield (in Zibo, Shandong Province), and dried sewage sludge and scrap iron were obtained from Jinan Wastewater Treatment Plant and Jinan Machinery Plant. Clay, DSS and scrap iron were dried at 105 °C for 4 h, crushed to pass sieve No. 100 (the diameter of mesh was 0.154 mm), and stored until being used in polyethylene vessels to avoid humidification.

2.2. Preparation of CCF and ACF

The raw pellets were thermally treated according to the following three steps as shown in Fig. 1:

Step 1: Dosage, mixing and drying. Raw pellets were prepared with clay and DSS or clay and scrap iron, which were completely mixed, respectively. Then, the mixture was poured into a pelletizer (DZ-20 equipment) to produce pellets (about 7.00 wt% of water was added). Two sieves (the diameters of meshes were 5.00 mm and 6.00 mm, respectively) were used to sift the pellets, which were selected for the following treatment. Before thermal treatment, raw pellets were stored in draught cupboard at room temperature (22 °C) for 24 h.
Step 2: Sintering treatment. The dried raw pellets were transferred into electric tube furnace (KSY-4D-16, made in China) and sintered at 400 °C for 20 min in anoxic conditions. The pellets were placed in the center of the heated zone.
Step 3: Cooling treatment. After the sintering process, the pellets were kept in draught cupboard until they cooled down to room temperature (22 °C).

2.3. Characterization of CCF and ACF

Water absorption and bulk density were determined according to GB/T 17431.2-1998 [24]. Before the tests, sintered pellets were kept in an exsiccator (105 °C) for 4 h. Then 100 g of dried pellets were put in a measuring cylinder (500 mL) and leveled completely. The bulk volume of dried pellets was determined. 200 mL of water was added into the measuring cylinder to cover the pellets completely. A dry towel was used to dry the surface of the wet pellets after 1 h, and 1 h saturated wet pellets were weighed. Water absorption and bulk density were calculated by Eqs. (1) and (2), respectively:

$$\text{Water absorption} = \frac{\text{mass of 1 h saturated wet pellets} - \text{mass of dry pellets}}{\text{mass of dry pellets}} \times 100\% \tag{1}$$

$$\text{Bulk density}\,(\text{kg m}^{-3}) = \frac{\text{mass of dry pellets}}{\text{bulk volume of dry pellets}} \tag{2}$$

Grain density was determined by the dry mass (M_{dry}) and the volume of the sintered pellets (V_{grain}). Individual grain density was calculated according to the Archimedes' principle [25].

Structural and morphological analysis was conducted by scanning electron microscopy (Hitachi S-520) both in the surface and in the cross-section (Au coated).

1000.00 g of CCF (or ACF) was soaked into 1.00 L of hydrochloric acid (0.20 mol L^{-1}; HCl: $\rho = 1.19\,\text{g mL}^{-1}$ Guaranteed Reagent (GR)) for 24 h. 1.00 mL of leach solution obtained from the supernatant was collected for leaching test of the toxic metal elements. Toxic metal concentrations (Cu, Zn, Pb, Cr, Cd, Hg, Ba, Ni, and As) of 1000.00 g of CCF (or ACF) were determined by ICP-AES (IRIS Intrepid II XSP equipment) and were compared with GB 5085.3-2007 [26].

2.4. Electrobath reactor

An electrobath reactor was set up as shown in Fig. 2. The cylindrical reactor made from polymethyl methacrylate had a diameter of 200 mm and an effective volume of 12.5 L with a height of 1.15 m.

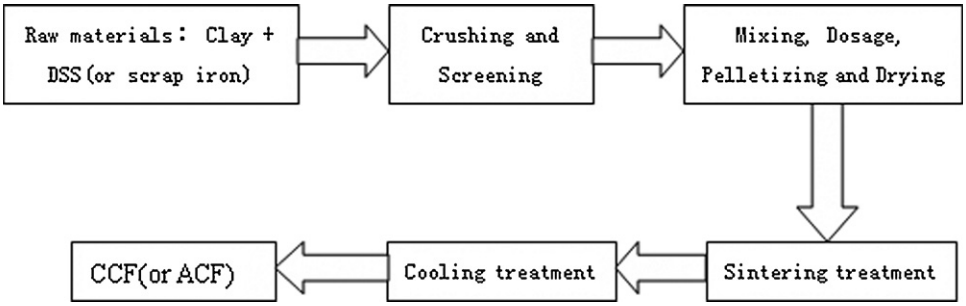

Fig. 1. Flow chart for preparation of CCF and ACF.