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# Coking wastewater treatment using a magnetic porous ceramsite carrier

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A B S T R A C T

In this study, porous ceramsite was modified using a magnetic material. The modified porous ceramsite was applied to the treatment of coking wastewater in a biofilm reactor. The results showed that the COD and $NH_3$-N removal efficiencies in the modified porous ceramsite biofilm reactor were 25–30% higher than in an activated sludge reactor, and 15–20% higher than in a biofilm reactor without a magnetic carrier. Under conditions with an aeration flow of 1.5 mL/h, aeration duration of 10 h/d, and a temperature of 25–30 °C, the removal efficiencies for COD and $NH_3$-N in the porous ceramsite biofilm reactor were ~90%.

## 1. Introduction

In the process of municipal domestic sewage treatment, biofilms possess advantages for convenient operation and management, higher volume loading, good biological stability and higher microbial biomass, etc. [1,2]. However, in practical applications, the poor mass transfer of the biological filter leads to slow and limited film formation and the sloughing off of biofilm. Therefore, waste water treatment cannot achieve good results. To enhance the application of biofilms, new biomarkers must be developed [3,4]. Magnetization and magnetic biological effects have been applied to waste water treatment. After magnetization, the physical and chemical properties of water and the activities of microorganisms and enzymes can be improved [5,6].

Most magnetic field strengthening biodegradation technologies are based on laboratory studies [7,8]. This is because the addition of external magnets to practical wastewater treatment equipment is difficult due to the large volumes involved. However, modified magnetic packing in biofilm reactors is easier to implement. Similarly, the addition of nutrients and magnetic substances to polymer-based material can produce a novel magnetic biocompatible and hydrophilic packing. The magnetic and metabolism or co-metabolism effects of microorganisms can significantly improve packing surface wettability and mass transfer performance [9–11]. Therefore, the biofilm formation cycle can be reduced and wastewater treatment efficiency can be improved, especially for the treatment of organic wastewater, which is toxic and difficult to degrade.

In this study, porous ceramsite was magnetically modified using a simple method and used in biofilm reactors. The porous ceramsite biofilm reactor was used to develop a new carrier material that can enhance the treatment effect for coking wastewater. Our findings will also facilitate improvement of the $NH_3$-N and COD removal efficiencies in domestic sewage, food wastewater, pharmaceutical wastewater and chemical wastewater.

## 2. Experimental

### 2.1. Materials

The high porosity porous ceramsite was prepared in our previous researches [12]. Porous ceramic filler is prepared by using sewage sludge, quartz, coating wastewater sludge flocculation, as the main raw material, coal as the pore, and the calcination temperature of 1230–1250 °C, The porous ceramic filler performance is water absorption of 57.2%, porosity of 60.89%, bulk density of 1.065 g/m$^3$, compressive strength of 1.8 MPa, acid resistance of 97.1% and alkali resistance of 98.3%. Pure magnetite $Fe_3O_4$ was used as the magnetic seed. Porous ceramics were modified into a magnetic porous carrier. Preparation of the porous ceramsite consisted of preparation, foaming, molding, drying, and calcination. Magnetic ceramics were prepared as follows: (1) 10 g of $Fe_3O_4$ were mixed with 200 mL $Na_2SiO_3$; (2) 300 g of porous ceramic particles were added to the prepared solution and stirred for 5 min; (3) the ceramic particles were separated and dried at 100 °C in

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an oven for 6 h, followed by sintering at 500 °C in an electric furnace for 1 h; (4) after cooling to room temperature, the mass of the ceramic particles had increased by 10%. The high porous magnetic ceramic were obtained [13]. Using these methods, highly porous magnetic ceramics were obtained, and performance indicators are shown in Table 1.

Sewage was obtained from the Jingdezhen Coking Industry Group, Jiangxi, China. The properties of the sewage were as follows: $COD_{Cr}$ = 2000–3000 mg/L, concentration of $NH_3$-N = 800–1000 mg/L, BOD/COD = 0.4–0.5 and pH = 6–8. Activated sludge was obtained from a secondary sedimentation tank; it had a sludge concentration of 40–60 mg/L and an SV of 40–50%.

### 2.2. Experimental apparatus and method

Three sets of biofilm reactors were made in plexiglass, its size was the same as $\varnothing 80\ \text{mm} \times 300\ \text{mm}$ and effective volume of 1.3 L, effective volume was 1L when carrier was built-in, the carrier volume filling rate was 33.3% (v/v). The reactors were operated in batch mode with an aeration flow of 1.5 mL/h for 10 h/d. To evaluate the sewage treatment performance of the magnetic carrier, the coking wastewater was diluted 10-, 4- or 2-fold. At temperatures of 25–30 °C, activated sludge was mixed with diluted coking wastewater and transferred into three reactors to create activated sludge, non-magnetic carrier and magnetic carrier treatments, respectively. Each reactor was aerated for 10 h/d. Each day, 200 mL of supernatant were removed and another 200 mL of coking wastewater were added to the reactors to maintain the same volume of wastewater. The reaction was run for 30 consecutive days and the $COD_{Cr}$ and $NH_3$-N concentrations in the input and output water were measured daily. The schematic diagram of the experimental apparatus was shown in Fig. 1.

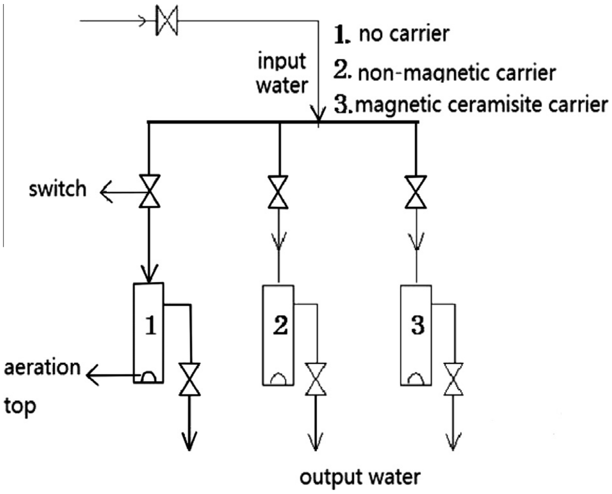

**Fig. 1.** Schematic of the experimental apparatus.

### 2.3. Analysis

Chemical composition of the sludge was analyzed by Dutch PAN alytical Axios X-ray fluorescence spectrometer, ceramsite phase composition was determined by the Germany Bruker 8D-advance production-type X-ray instrument, cross-section morphology of the sample was observed by JSM-6700F scanning electron microscope (scanning electron microscope, SEM), the sample water absorption Wa, porosity Pa and the volume density D were determined with hydrostatic weighing method, compressive strength was expressed with Ningxia machinery research Institute TZS-4000 flexural strength test, acid and alkali resistance were determined as a percentage of the weight and the original to after weight ratio, the determination of acid and alkaline soak for 24 h immersion, in 98% sulfuric acid solution and 20% sodium hydroxide solution respectively. Magnetic field strength was measured by Gauss Meter TES-1390 production with TES Electronic Industrial Co., Ltd., water treatment installations was made in Shanghai Tongguang Education Equipment Co., Ltd. production of industrial sewage biodegradability testing device TG-249. Carrier biofilm formation observation and analysis were used DA1-180M digital biological microscope (Ningbo Ouyi microscope Co., Ltd.), MLSS, Determination of biofilm volume and SV were used gravimetric method. According to Chinese EPA standard methods [14], potassium dichromate method was used for chemical oxygen demand (COD) analysis, Nessler reagent colorimetric method was used for $NH_3$-N analysis.

## 3. Results and discussion

### 3.1. Porous ceramsite characterizations

The XRD of the test samples are shown in Fig. 2. The analysis results shows that the main crystalline phase of sintering samples is calcium melilite $Ca_2Al_2SiO_7$. Ingredients containing $SiO_2$, $Al_2O_3$, formed in the firing process of the silicate in the crystal structure having the silicon–oxygen tetrahedral. Si–O total key force is a strong covalent bond, and therefore its structure is stable, with good resistance to credibility.

The scanning electron microscope (SEM) image are shown in Fig. 3. It can be seen that the internal ceramsite has a lot of ravines and pore channels crossing uneven size, the pore size is about 0.5–1 mm, this create the conditions for magnetic modified and microorganisms sticking. The kind photos of the porous ceramsite magnetic modified are shown in Fig. 4(a) before and (b) after, respectively. The porous ceramsite (Fig. 4(a)) is surface rough, porous, low smoothness, the larger surface area. It has high water absorption and apparent porosity, its bulk density is slightly larger than the water, the compressive strength is greater, not be broken, acid and alkali resistance are large. The magnetic ceramsite (Fig. 4(b)), its surface become black, the strength increase, that is the result of adhesion of the magnetic $Fe_3O_4$ on the ceramsite surface and internal.

### 3.2. Performance of different reactors

The input water had COD and $NH_3$-N concentrations of 1346.5–1371.2 mg/L and 474.1–493.8 mg/L, respectively. Biochemical

**Table 1**
Physical and chemical nature of porous ceramsite and magnetic carrier.

| Ceramics particles | Particle size (mm) | Filler density ($g\ cm^{-3}$) | Bulk density ($g\ cm^{-3}$) | Porosity (%) | Compressive strength (MPa) | Breakage rat (%) | Acid and alkali resistance (%) | Magnetic field intensity/mGs |
|---|---|---|---|---|---|---|---|---|
| Porous ceramics | 8–15 | 0.8–1.2 | 1.13–1.15 | 50–60 | 6–6.5 | ⩽1.2 | >98 | – |
| Magnetic carrier | 8–15 | 1.2–1.3 | 1.18–1.24 | 45–50 | 7–7.5 | ⩽1.4 | >96 | 80–100 |