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Preparation and modification of porous lightweight ceramsite and its performance investigation

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ABSTRACT

In this study, fly ash was used as the main raw material to prepare a lightweight ceramsite which has a specific density close to that of water (0.95–1.05 g/cm^3) and good wear resistance. The ceramsite was modified with positively charged iron oxide coating layer by heterogeneous coagulation and coating method. The adsorption property, iron load, bulk density, apparent porosity, compressive strength, surface morphology, surface electrical property, and phase composition of the coating layer were characterized. The optimum modification conditions determined by methylene blue adsorption experiment were: 1 mol/L $FeCl_3$ solution, calcination temperature 650°C, and calcination time 3 h. The modified ceramsite was covered with an iron oxide layer with uneven thickness. The main crystal phase of the coating layer was α-Fe_2O_3 which exhibited porous structures. The modified ceramsite has a good application prospect in water treatment and purification.

Keywords: Iron oxide; Modification; Isoelectric point; Adsorption

1. Introduction

Biofilm treatment has been proved to be a reliable approach for wastewater remediation without some of the problems encountered in activated sludge processes such as filamentous bulking, foaming, and high suspended solid content [1]. In comparison to conventional systems, the application of biofilm reactors offers many advantages including less space requirement and easy biosolid–liquid separation.

The use of moving carriers can reduce or even dispense the return sludge flow from the settler, and shows lower head loss and no clogging problems, when compared to other biofilm reactors in which biomass is attached to fixed support materials [2]. Plastic carriers (such as polyethylene and polyurethane), granular activated carbon, sand, and diatomaceous earth are commonly used as support materials for moving biofilm systems to allow growth of microorganisms [3]. In general, plastic carriers have low density and good processability and can be easily expanded as the water circulates. Nevertheless, the poor hydrophilicity and biocompatibility of plastic carriers often lead to some deficiencies in the rate and amount of biofilm culturing and the adhesion extent of biofilm [4].

Ceramics have good mechanical, chemical, and thermal resistance. Recently, a number of studies have focused on the development of ceramic carriers with light weight and high activity. Porous ceramic materials possess many pores on their surfaces and inside their structures, resulting in high porosity, excellent absorption capacity, and high specific surface area [5]. Especially, ceramic foams are regarded as a good

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candidate for simultaneously providing both aerobic and anoxic zones, due to their unique pore structure [5]. Liu et al. [6] prepared lightweight ceramsite (density 1.02–1.04 g/cm^3) with good performance from iron ore tailings.

In general, the surface of inorganic material is negatively charged in water due to the existent of many hydroxyl bonds. However, the surface of bacterial cells and organic pollutants is usually negatively charged in aqueous solution, leading to a repulsive electrostatic interaction between cells and pollutants and carrier surfaces [7]. Surface modification of inorganic materials with iron oxides has been investigated extensively and proven to be effective for the removal of heavy metals [8,9] and organic contaminants from water [10–12]. Additionally, Johnson and Logan [13] found that coating quartz with iron oxide increased bacterial retention 160% relative to uncoated quartz.

This study investigated the possibility of using fly ash as one of the starting materials to prepare porous lightweight ceramsite by a high-temperature calcination process. The ceramsite was modified with iron oxide coating layers. The properties of uncoated and coated ceramsites were investigated and compared.

2. Materials and methods

2.1. Materials

The raw materials were fly ash, feldspar, calcite, fired talc, and kaolin. All these samples were oven dried at 105℃ for 24 h, and then pulverized with a ball mill until they could pass through a 100 μm sieve.

2.2. Preparation of lightweight ceramsite

The preparation process of the lightweight ceramsite consists of slurry preparation, foaming, molding, drying, and calcination, which was performed according to Sepulveda et al. [14] with some modifications. Briefly, the sieved and dried samples of fly ash (60 g), feldspar (18 g), calcite (2 g), fired talc (5 g), and kaolin (15 g) were mixed with addition of deionized water (50 mL) and foaming agents (a mixture of equal amounts of Na_2SO_4 and $MgCO_3$, 1−4%) to produce a slurry. The mixture was then cast into molds. The sample was dried at 150℃ and then calcined in a gas furnace at 1,260℃ for 2 h with heating rate of 50℃/min. The calcined product was gradually cooled down to about 200℃ by natural ventilation, and then taken out of the furnace until cooling down to ambient temperature. The lightweight ceramsite was finally obtained.

2.3. Modification of ceramsite

The iron oxide modified ceramsite used in this study was prepared by mixing 20 g of ceramsite (geometric mean size = 1.1 cm) in 50 mL of $FeCl_3$ solution (0.25–2.0 mol/L, adjusted to pH 5 with hydrochloric acid) for 1 h. The ceramsite was dried at 110℃ for 4 h and then calcined in a gas furnace (200–800℃) for a time period of 1–5 h. The calcined ceramsite was gradually cooled down and the iron oxide modified ceramsite was finally obtained. To obtain the optimum modification conditions, the concentration of $FeCl_3$ solution, calcination temperature, and calcination time were varied.

2.4. Static adsorption test

To evaluate the effects of modification conditions on the property of modified ceramsite, the adsorption experiments were carried out by adding a fixed amount of modified ceramsite (20 g) to a series of 250 mL conical flasks filled with 100 mL methylene blue solutions (1 mg/L). After a desired time, the supernatant was analyzed for methylene blue using a 722 UV–Vis spectrophotometer operated at 668 nm. The data obtained from the adsorption experiments were then used to calculate the decolorization efficiency of methylene blue by Eq. (1):

$$E_{\text{decoloration}} = \frac{(C_0 - C_t)}{C_0} \times 100\% \tag{1}$$

where C_0 and C_t are the concentrations of methylene blue in solution at time $t = 0$ and $t = t$, respectively.

All decolorization experiments were performed in triplicates to get reliable data, and the results represented the average of three parallel experiments.

2.5. Characterization

The apparent porosity was measured by the water immersion method. Isoelectric point of metal oxide was determined by measurement of contact angles at the hexadecane/aqueous solution interface as a function of pH of the aqueous phase [15]. Compressive strength was determined using the loop test [16]. Mineralogy was characterized by an X-ray diffraction (XRD) meter (Bruker, Germany). Crystal size and morphology were investigated using scanning electron microscopy (SEM) on a JEOL JSM-6380 field emission SEM (Japan).

3. Results and discussion

3.1. Effect of foaming agent dosage

In this study, porous lightweight ceramsite was prepared by using a chemical foaming method. This incorporates some carbonates, sulfates, and/or sulfides in the ceramic slurry as foaming agents. The foaming agents may be treated so as to evolve gas which creates bubbles in the mixture during high-temperature calcination. Both open cell and closed cell foams can be made by this process.

The dosage of foaming agents is a major factor affecting the synthesis of lightweight ceramsite. The temperature range of gas evolution is 1,200−1,350℃ and 600−650℃ for Na_2SO_4 and $MgCO_3$, respectively. Considering the calcination temperature of the ceramsite and the price factor, the mixture of equal amounts of Na_2SO_4 and $MgCO_3$ was used as foaming agents in the present study. Fig. 1 illustrates the effect of foaming agent dosage on the bulk density and compressive strength of lightweight ceramsite. As shown, when the foaming agent dosage was 2 wt%, the prepared ceramsite has a bulk density of 0.98 g/cm^3 and compressive strength of 2.8 MPa on average. This bulk density is slightly less than that of water. The bulk density of the ceramsite would be close to that of water after biofilm growth, therefore only gentle agitation or aeration was needed to produce good carrier expansion.

In this study, the bulk density and compressive strength of the lightweight ceramsite decreased with increasing the dosage of foaming agents (Fig. 1). The bulk density of the prepared lightweight ceramsite should be controlled around 1.0 g/cm^3, thus 2 wt% of foaming agents was used in the following experiments. The excess of foaming agents would produce large amounts of gas, and large gas pressure could break glass phase surface tension, thus many large bubble and connected bubble were formed, leading to a significant decrease in the bulk density and compressive strength of the ceramsite. Contrastly, too small dosage of foaming agents would result in difficult foaming, excessive density, and small pore size of ceramsite.

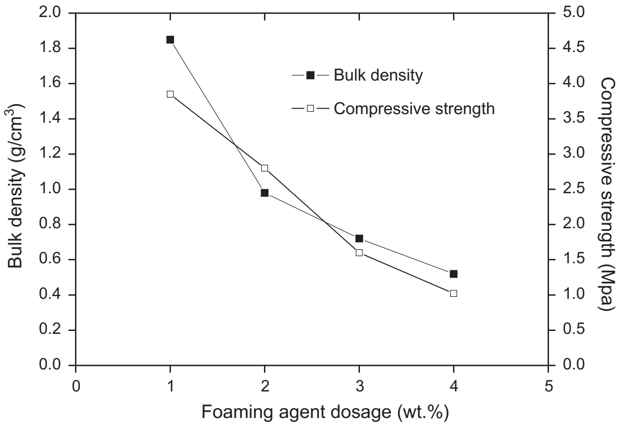

Fig. 1. Effect of foaming agent dosage on the bulk density and compressive strength of lightweight ceramsite.

3.2. Optimization of ceramsite modification

In the present study, results demonstrated that the absorption equilibrium was achieved after 20 min of reaction for all the experimental sets (data not shown). For simplicity, thus, the data after 20 min of reaction are presented.

3.2.1. Effect of $FeCl_3$ concentration

Twenty grams of ceramsite were soaked in 50 mL of $FeCl_3$ solution (0.25, 0.5, 1.0, or 2.0 mol/L, pH 5) for 1 h. The ceramsite was dried at 110℃ for 4 h and then calcined at 650℃ for 3 h. The calcined ceramsite was used in the static adsorption test.

As shown in Fig. 2, a remarkable increase in decolorization efficiency was observed for the modified ceramsite. The decolorization efficiency was found to be 28.0, 65.4, 74.6, 86.3, and 81.7% for the ceramsite modified with 0 (unmodified), 0.25, 0.5, 1.0, and 2.0 mol/L $FeCl_3$ solution, respectively. The low decolorization efficiency occurring in the case of 0.25 and

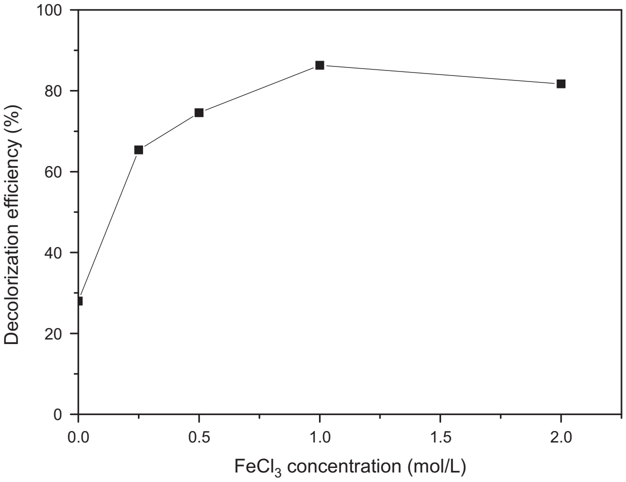

Fig. 2. Effect of $FeCl_3$ concentration on methylene blue decolorization by modified ceramsite. The experimental conditions were: room temperature (25℃); initial dye concentration 1 mg/L; solution volume 100 mL; and static adsorption.

0.5 mol/L $FeCl_3$ indicated that the coated amount of iron oxide was not enough. The highest decolorization efficiency was obtained in the case of 1.0 mol/L $FeCl_3$, suggesting that there was enough absorbing sites on the surface of modified ceramsite. When the $FeCl_3$ concentration was increased from 1.0 to 2.0 mol/L, however, decolorization efficiency decreased. This could be attributed to hole plugging on the surface of modified ceramsite caused by the excessive accumulation of iron oxide coating, leading to a decrease in the amount of absorbing sites and, thus, the declining decolorization efficiency. Thus, in all subsequent experiments, 1.0 mol/L $FeCl_3$ solution was used to modify the ceramsite.

Metallic oxides/hydroxides are good sorbents of organic compounds, heavy metals, and bacteria. This has led to the development of iron oxide-coated sand and ceramic membrane as a filtration/adsorption medium in water and wastewater treatment. Iron oxide-coated sand and ceramic membrane was shown to be highly efficient in removing different organics, heavy metals, micro-organisms, and turbidity [17,18]. Additionally, Zhao et al. [19] investigated the performance of iron oxide-coated zeolite in the removal of methylene blue and methyl orange from aqueous solution in single-dye system.

3.2.2. Effect of calcination temperature

Twenty grams of ceramsite were soaked in 50 mL of 1 mol/L $FeCl_3$ solution (pH 5) for 1 h. The ceramsite was dried at 110℃ for 4 h, and then calcined at 200, 350, 500, 650, or 800℃ for 3 h. The calcined ceramsite was used in the static adsorption test.

As shown in Fig. 3, the modified ceramsite calcined at 200 and 650℃ exhibited the lowest and highest decolorization efficiencies, respectively. This is because at low calcination temperatures, the strength of coating layers was not enough, the channel feature was not prominent, and the surface crystal may be amorphous, leading to declining adsorption sites. When calcination temperature was too high, however, the ceramsite lost hydroxyl water, the collapse of micro-fibrous structure of ceramsite occurred, micropores were destroyed [20], and the amount of surface adsorption sites decreased, thereby reducing the decolorization efficiency of the dye. Thus, the ceramsite calcined at 650℃ was used in all subsequent experiments.

3.2.3. Effect of calcination time

Calcination time determines the stability of iron oxide coating, thus determining the property of modified ceramsite. Twenty grams of ceramsite were soaked in 50 mL of 1 mol/L $FeCl_3$ solution (pH 5) for 1 h. The ceramsite was dried at 110℃ for 4 h and then calcined at 650℃ for 1, 2, 3, 4, or 5 h. The calcined ceramsite was used in the static adsorption test.

As shown in Fig. 4, the modified ceramsite calcined for 1 h demonstrated the lowest decolorization efficiency. With prolonging calcination time, the decolorization efficiency increased and reached the maximum for 3 h of calcination, and then dropped. The

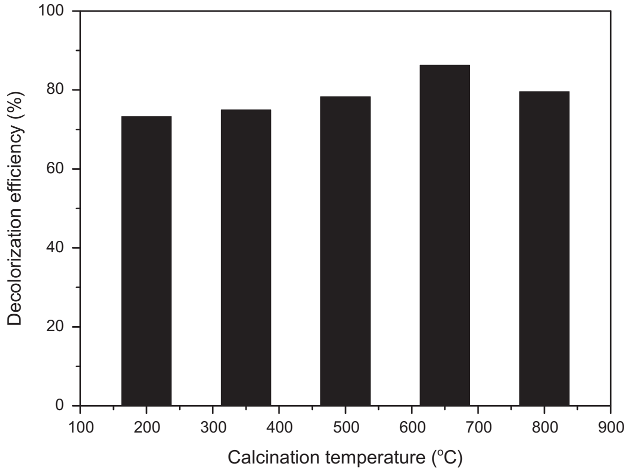

Fig. 3. Effect of calcination temperature on methylene blue decolorization by modified ceramsite. The experimental conditions were: room temperature (25℃); initial dye concentration 1 mg/L; solution volume 100 mL; and static adsorption.

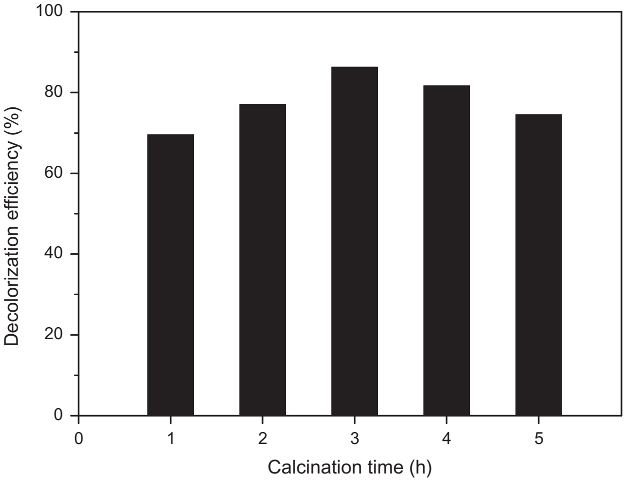

Fig. 4. Effect of calcination time on methylene blue decolorization by modified ceramsite. The experimental conditions were: room temperature (25℃); initial dye concentration 1 mg/L; solution volume 100 mL; and static adsorption.

reason for this phenomenon is similar with the effect of calcination temperature. A prolonged calcination time could enhance the strength of coating layers. Nevertheless, too long calcination time may result in the loss of hydroxyl water and the distortion of ceramsite crystal configuration, thus reducing the decolorization efficiency of the dye.

According to the results obtained from the above experiments, the optimum modification conditions were: 1 mol/L of $FeCl_3$, calcination temperature of 650℃, and calcination time of 3 h. The modified ceramsite was colored as dark red.

3.3. Characterization of ceramsite

3.3.1. Coating amount, bulk density, apparent porosity, and compressive strength

Twenty grams of unmodified ceramsite weighed an average of 23.31 and 22.98 g after modification and water rinsing, respectively. The unmodified ceramsite has an average bulk density of 0.98 g/cm^3 (0.95–1.05 g/cm^3) and an average compressive strength of 2.8 MPa (2.5–3.0 MPa). The load rate and failure rate of the coating layers were 14.9 and 1.65%, respectively. The bulk density, apparent porosity, and compressive strength of the modified ceramsite were 0.97–1.06 g/cm^3, $\geq$50%, and 2.5–3.0 MPa, respectively, which were nearly the same as those of unmodified ones. These results indicated that the mechanical property of ceramsite was not significantly altered by modification.

3.3.2. Acid and alkali resistance

The modified ceramsite was soaked in 3 mol/L HCl and 3 mol/L NaOH for 24 h, respectively. After drying, the surface of ceramsite porous coatings hardly changed and no coatings flaked away from the substrates. This indicated that the modified ceramsite was resistant to acid and alkali. This property of the modified ceramsite is of significance for its actual application.

3.3.3. Surface isoelectric point

It is known that the outermost surface of an oxide or an oxide film is covered with a layer of hydroxyl groups [15]. In aqueous solutions, these hydroxyl groups may remain undissociated, in which case the pH of the aqueous solution is the same as the isoelectric point of the oxide. If the pH is less than the isoelectric point, the surface of the oxide will acquire a positive charge [15]:

$$-\mathrm{MOH_{surface}} + \mathrm{H^+} \leftrightarrow -\mathrm{MOH^+_{2surface}} \quad (2)$$

If the pH is greater than the isoelectric point, the surface of the oxide will acquire a negative charge:

$$\begin{aligned} &-\mathrm{MOH_{surface}} + \mathrm{OH^-} \leftrightarrow -\mathrm{MO^-_{surface}} + \mathrm{H_2O} \\ &\text{or} \quad -\mathrm{MOH_{surface}} \leftrightarrow -\mathrm{MO^-_{surface}} + \mathrm{H^+} \end{aligned} \quad (3)$$

The nature of the surface charge on an oxide film is of importance with regard to a number of applications involving metals such as adhesion, corrosion, and catalysis [15]. Table 1 lists the surface isoelectric point of unmodified and modified ceramsite as well as soild-phase α-Fe_2O_3. The XRD pattern of modified ceramsite is shown in Fig. 5. As shown, the main crystal phase in the coating layers was α-Fe_2O_3, which was in accordance with the result of surface isoelectric point. Thus, the introduction of iron oxide coating altered the surface charge state of ceramsite, which was determined by the α-Fe_2O_3. In such cases, the surface isoelectric point of modified ceramsite increased to around 8.3 compared to the unmodified ones, thereby the surface of modified ceramsite was positively charged. Thus, wastewater treatment efficiency could be enhanced by using this modified ceramsite, because the adsorption ability of modified ceramsite to organic pollutants and micro-organisms increased due to that the surface of organic compounds and microbial cells are usually negatively charged [11,17].

Table 1
Surface isoelectric point of different materials

Item	Unmodified ceramsite	Modified ceramsite	Soild-phase α-Fe_2O_3
Isoelectric point	2.2	8.3	8.5

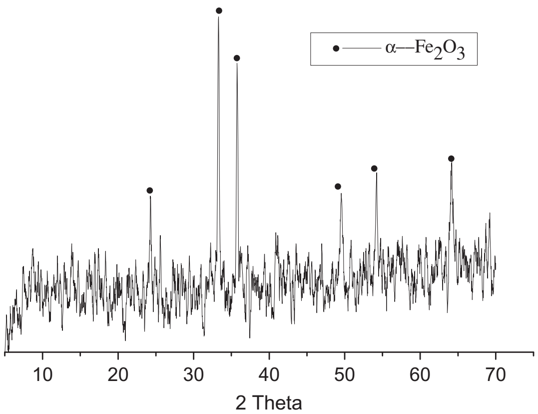

Fig. 5. XRD pattern of modified ceramsite.

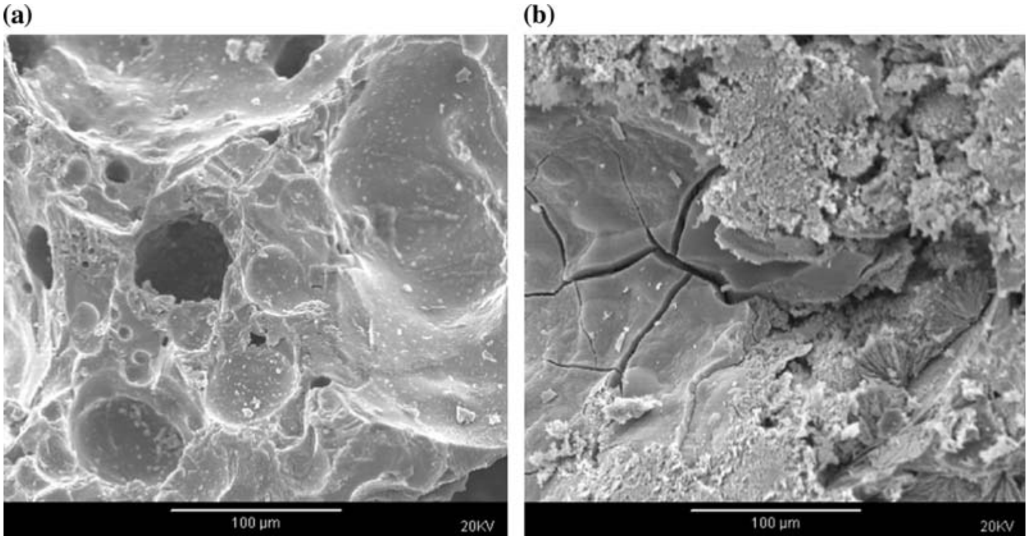

Fig. 6. SEM images of ceramsite. (a) Before modification and (b) after modification.

3.3.4. Scanning electron microscopy

The SEM photographs of the ceramsite samples before and after modification are shown in Fig. 6(a) and (b), respectively. As shown in Fig. 6(a), before modification, the surface crystal of ceramsite was mainly characterized by glass phase, the distribution of surface pore was uneven and the pore diameter was in the range of 60–70 μm, presenting the combination of open holes and closed hole. Thus, it can be found that the porous lightweight ceramsite is a good biocarrier, and the inner surface of the ceramsite is suitable for the coating adhesion.

As shown in Fig. 6(b), after modification, an iron oxide coating layer with uneven thickness was formed on the ceramsite surface. The iron oxide coating layer was characterized by multilayer accumulation, uneven thickness, and rough surface. Thus, the specific surface area of ceramsite was significantly increased after modification, leading to an enhanced adsorption ability of modified ceramsite to organic pollutants.

4. Conclusions

In this study, lightweight ceramsite was produced of the five compositions (fly ash, feldspar, calcite, fired talc, and kaolin) by using the equal amounts of Na_2SO_4 and $MgCO_3$ as the foaming agent. The prepared ceramsite has high strength, density close to that of water, and high porosity. The ceramsite modified with iron oxide coating has strong adsorption ability to methylene blue. The modified ceramsite has a good application prospect in water treatment and purification.

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