

Preparation and characterization of low cost porous ceramisite adsorbents based on forsterite powders and porcelain insulators wastes

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1. Introduction

Adsorption has been widely used for the treatment of industrial effluents because major advantage of that for water pollution is less investment in terms of both initial cost and land, simple design and easy operation and no effect of toxic substances compared to conventional biological treatment processes^[1]. At present, activated carbon, quartz sand, clay, as well as sewage sludge, et al. have been used as adsorbents to dispose of pollution water^[2-5]. Although activated carbon with well-developed porous structure and large active area surface is a kind of outstanding adsorbent, the high cost of it limits the development of its application. Quartz sand needs to be surface modified with inorganic acid, base, or organic matters to improve its capability of adsorption because of its drawback of small specific surface area, which will cause secondary pollution. The adsorption equipment is easy to be blocked when adopting adsorbents based on natural clay because of hard separation between solid and liquid. Therefore, developing a kind of low cost, environment friendly adsorbent will produce better economic and social benefits.

Plenty of forsterite fine sand with outstanding properties eliminated during producing, although not real wastes, needs to be used as raw materials rather than landfill disposal. The forsterite powders have been utilized as raw materials to fabricate porous materials considering making the best of the forsterite with fine granularity and its excellent properties. Nevertheless, the lack of liquid phases leads to difficulty in producing pores with small sizes that are the key factors to improve adsorption properties. Hence, introducing components into the forsterite powders which can form liquid phases is of importance to generate pores with small sizes.

SiO₂ is an important composition in the porcelain insulators wastes, which will form liquid phases during firing^[6]. Therefore, it provides authors train of thought that they can introduce the porcelain insulators wastes into the

forsterite powders to prepare porous ceramisites with small size pores.

In this pilot research, porcelain insulators wastes and forsterite powders were used as raw materials to fabricate a kind of novel low cost porous ceramisite adsorbents combining the excellent properties of forsterite with the formation of liquid phases of porcelain insulators wastes. The effects of compositions of raw materials and firing temperature on the properties of the porous ceramisite adsorbents were examined. Batches of studies of adsorption for Cu²⁺ were conducted, and the adsorption isotherms for the adsorbent to adsorbate were also investigated.

2. Materials and methods

2.1. Synthesis of porous ceramisites

The porous ceramisites were composed of porcelain insulators wastes, forsterite powders, clay, and pore-forming agent. The ratio of the raw materials was shown in Tab.1. The particle size of porcelain insulators wastes (Hefei, Anhui Ruitai New Material Technology Co. Ltd., China), forsterite powders (Henan province, China), and clay (Fujian province, China) was about 0.074 mm. The chemical compositions of the raw materials were shown in Tab. 2. Sawdust was used as pore-forming agent and the particle size (d₅₀) of it was nearly 64 μm.

The porous ceramisites were prepared as follows: first, raw materials were mixed in a polyurethane pot and transported into pelletizer; meanwhile water glass solution (27 wt.%) was injected to make powdered materials become spherical particles with a similar diameter (5-13 mm). And then the fresh pellets were dried at 110 °C for 12 h, after that fired at 1000 °C, 1050 °C, 1100 °C for 3 h, respectively. Finally, the porous ceramisites were obtained after screen separation.

Tab. 1 Batch compositions (wt.%)

Group	Porcelain insulators	Forsterite	Clay	Extra additions	
				Sawdust	Water glass solution
1 [#]	90	0	10		
2 [#]	72	18	10		
3 [#]	54	36	10		
4 [#]	36	54	10	50 wt.%	100 wt.%
5 [#]	18	72	10		
6 [#]	0	90	10		

Tab. 2 Chemical compositions of raw materials (wt.%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	IL
Porcelain insulators	71.24	21.85	2.01	0.43	0.64	2.64	0.51	0.56	0.07
Forsterite	43.25	0.36	10.09	0.42	42.09	0.02	0.02	0.01	3.92
Clay	30.99	40.58	0.82	—	—	0.71	—	0.10	19.10

2.2. Porous ceramisites as adsorbents for Cu²⁺ removal

The Cu²⁺ solution samples of various concentrations i.e. 8000, 10000, 15000, and 20000 mg/L were prepared for further studies.

10 g porous ceramisites with particle size of 5-10 mm were submerged in 100 mL prepared solution at 25 °C. The equilibrium concentration of Cu²⁺ was tested by spectrophotometer (722-2000).

2.3. Characterization

Bulk density, apparent porosity, and water adsorption ratio of porous ceramisites were analyzed according to Archimedes method with water as media. The test method for cold crushing strength was adopted according to the literature[6].

50 g porous ceramisites were soaked in the hydrochloric acid (6 mol/L) for 30 min, during which stirring it per 10 min. Subsequently, the porous ceramisites after filtration were washed until the pH=7, and then the ceramisites were dried for 24 h at 110 °C. The solubility in hydrochloric acid was calculated according to the Eq. (1).

$$T = \frac{W_0 - W}{W_0} \times 100\% \quad \text{Eq.(1)}$$

T : solubility in hydrochloric acid (%); W_0 : weight of the adsorbents before soak (g); W : weight of the adsorbents after soak (g).

X-ray diffraction (X' Pert Pro, Philips, Netherlands) was used to analyze the phase compositions of sintered specimens. Microstructures including the pore size were examined via scanning electron microscope (SEM, JSM-6610, JEOL Company, Japan). The elemental concentration profiles of the microstructures were determined using energy dispersive spectroscopy (EDS, UANTAX200-30, Bruker, Germany).

3. Results and discussion

3.1. Physical properties

Physical properties of the specimens significantly depend on the temperature and content of forsterite powders as shown in Fig.1. Apparent porosity decreases with increasing the sintering temperature because of gradual densification (shown in Fig.1 (a)), which associates with the decrease of water adsorption ratio (shown in Fig.1 (b)). Thus, bulk density increases, which in turn improves cold crushing strength (shown in Fig.1 (c) and Fig.1 (d)). With regard to the influence of the content of forsterite powders, the growth of the content of forsterite powders will make the strength and bulk density degrade, which causes the improvement of the apparent porosity and water adsorption ratio. Closed porosity obviously increases with the temperature increasing and decreases with

the content of forsterite powders increasing (shown in Fig.1 (e)). When sintering temperature rises to 1100 °C, the mass loss of the specimens in hydrochloric acid near to 0% and changes a little with the ratio of raw materials (shown in Fig.1 (f)).

The results indicate that the liquid phases will decrease with the decrease of SiO₂ component, in other words, decreases with the reduction of the ratio of porcelain insulators wastes. Furthermore, raising temperature is conducive to the densification and formation of liquid phases. The liquid phases affect pore structures at two aspects. On one hand, the pores in specimens will be filled by liquid phases, which results in the degradation of apparent porosity and enhancing of bulk density and strength. On the other hand, the pores with small sizes will be produced due to flow of liquid phases.

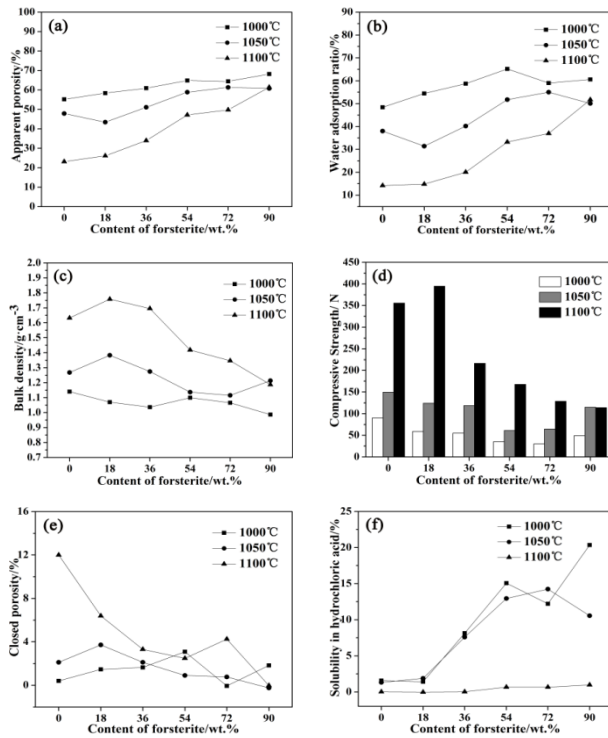


Fig.1 Physical properties of porous ceramisites((a): Apparent porosity; (b): Water adsorption ratio; (c): Bulk density; (d): Compressive strength; (e): Closed porosity; (f): Solubility in hydrochloric acid)

3.2. Phase transformation and microstructures

XRD patterns of group 3[#] specimens fired at different temperatures are shown in Fig.2. At 1000 °C, the products are mainly composed of forsterite and quartz phase. The diffraction peaks of sillimanite are observable, but their intensities are weak. When heating temperature rises to 1050 °C, sillimanite phase vanishes, and the diffraction

intensities of forsterite and quartz phase decline. Furthermore, enstatite phase is detected, but the peaks are weak. This result indicates that forsterite has reacted with quartz on some levels. Moreover, the disappearance of sillimanite illustrates that higher temperature promotes the formation of liquid phases, which is in good agreement with the results of Fig.1(a) and Fig.1(b). After sintering at 1100 °C, the diffraction peaks of forsterite and quartz phase become weaker and part of peaks of forsterite disappear, meanwhile, more diffraction peaks of enstatite are identified and the intensities increase significantly.

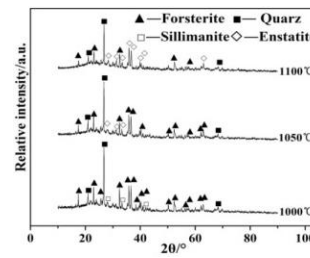


Fig.2 XRD patterns of specimens firing at different temperatures

Fig.3 shows the SEM and EDS photographs of the group 3[#] samples sintering at 1050 °C. A lot of pores are found with irregular morphologies in the specimens. The pores consist of two kinds of groups, one group includes the bigger pores formed by ignition loss of sawdust about 130 μm, and another group contains the pores with smaller size about 5 μm attributing to flow of liquid phases. Elements distributions are shown in Fig.3 B, the result shows dense Mg-Si-rich particles and loosened Al-Si-rich particles exist in the specimens. It can be inferred that the dense particles are forsterite or enstatite and the loosened particles mainly compose of quartz and liquid phase according to the results of XRD analysis. These results obviously bear out that introducing porcelain insulators wastes into forsterite powders should be in favor of the generation of small size pores owing to the liquid phases.

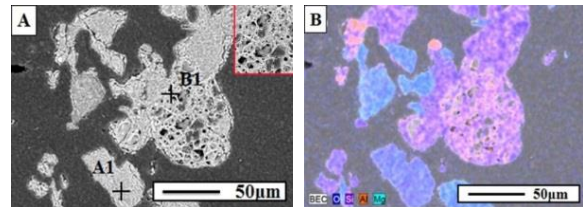


Fig.3 SEM and EDS photographs of samples 3[#] firing at 1050 °C(A: SEM; B: EDS)

3.3. Adsorption for Cu²⁺

The CuSO₄ • 5H₂O solution with different Cu²⁺ initial concentrations was fed to 10g porous ceramisites with particle

size of 5-10 mm. The percentage removal of Cu^{2+} and amount adsorbed were calculated according to paper [7].

It is found that adsorption efficiency of Cu^{2+} decreases as we increase the initial concentration of Cu^{2+} , which is owing to increase in adsorbate to adsorbent ratio for the same amount of porous ceramisites. Adsorption capacity of Cu^{2+} which defines as the gross of Cu^{2+} ions adsorbed on per g porous ceramisites trends to increase with initial Cu^{2+} ions concentration increasing. The phenomenon can be explained by the fact that more adsorption sites will be occupied by the Cu^{2+} . The results are depicted in Fig.4.

The Langmuir and Freundlich models of linear forms are employed to describe the adsorption behavior of Cu^{2+} uptake by varying the initial Cu^{2+} concentration, and the equations can be described by referencing to literature [7].

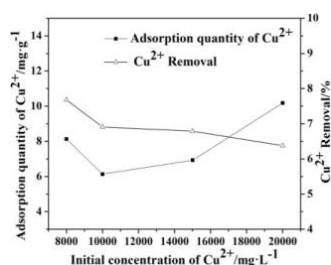


Fig.4 Adsorption quantity and removal of Cu^{2+} varies with different initial concentration

The correlation coefficient (R^2) is found to be 0.752 for Langmuir model while 0.988 for Freundlich model, demonstrating a good fitness with Freundlich model for the adsorption process which takes place at specific inhomogeneous reactive sites on the rough surface of these samples and is probably multilayer incorporation.

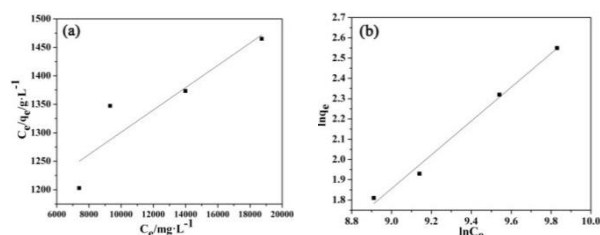


Fig.5 The fitted curves of adsorption isothermal adsorption equations for Cu^{2+} ((a): Langmuir isothermal adsorption equation; (b): Freundlich isothermal adsorption equation)

4. Conclusions

Low cost and easy separation for solid-liquid porous ceramisite adsorbents were successfully fabricated with high strength and porosity using porcelain insulators wastes and

forsterite powders.

When the firing temperature is 1050 °C, the ratio of forsterite powders to porcelain wastes is 36:54, samples show better complex properties with strength of 119 N, apparent porosity of 51%, closed porosity of 2.12%, bulk density of 1.27 g cm^{-3} , water adsorption ratio of 40.17%, solubility in hydrochloric acid of 7.59%.

The porous ceramisite adsorbents are capable of removing the Cu^{2+} in the pollution water ascribing to its high apparent porosity and existence of pores with small sizes. The adsorption process is well fitted with Freundlich isotherm, which demonstrating that the adsorption takes place at the heterogeneous surface.

References

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