Experimental Study on Purification of Low Grade Diatomite

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Abstract. This paper presented an innovation for purification of low grade diatomite (DE) by grinding, ultrasonic pretreatment, acid leaching of closed stirring and calcination. The optimum process parameters of DE purification were obtained, the characterizations of original and purified DE were determined by SEM and BET. The results showed that the specific surface area of DE increased from 12.65 m\textsuperscript{2}/g to 23.23 m\textsuperscript{2}/g, which increased by 45.54%. SEM analysis revealed that the pore structure of purified DE was dredged highly.

1. Introduction

DE is a non-metallic mineral composed of the deposition of unicellular algae, the surface was composed of a large number of regular and orderly micropores, thus DE had a large surface area, strong adsorption properties and high chemical stability, light weight, low density, acid-proof, alkali resistance, high temperature resistant, sound insulation and heat insulation\textsuperscript{[1-2]}. It was widely used in environmental protection, coatings, building materials, functional fillers, filter aid, catalyst carrier, sustained-release agent and other fields\textsuperscript{[3-4]}. DE deposits in China were mostly secondary, tertiary or even lower grade, and the distribution of high grade DE ores was rare\textsuperscript{[5]}. So the DE purification is the key to improving the utilization of DE.

2. Experimental process

Purification process was as followed: the original DE→ grinded→ ultrasonic pretreated→ acid leached→ washed→ filtered→ dried→ calcination→ cooled→ pure DE. According to the ratio of liquid to solid of 2.5:1, DE and H\textsubscript{2}SO\textsubscript{4} of different mass fraction were taken. A certain amount of distilled water was placed in a conical flask and sealed according to the ratio of liquid to solid of 16:1. After sealing, it was placed in a magnetic stirrer at 60°C for a period of time, the mixture was washed into neutral PH =7, filtered, dried, calcination in a muffle furnace for a certain time, then mixture was cooled to room temperature, so purified DE was obtained.

3. Experimental results and analysis

3.1. Grind Time

Fig.5 showed the specific surface area of diatom soil at the same rotation 300 rpm and different grind time, Fig.1-4 was the scanning electron microscope micrograph of DE at the different grind time.

It can be seen from Fig.5, the specific surface area of original DE was 12.65 m\textsuperscript{2}/g, and the specific surface area of DE kept increasing with the increase of grind time, it increased by 3.7\%, 6.0\% and 7.1\% respectively after grinding for 0~1 min, 1~3 min and 3~5 min; The Fig.1-4 SEM has been observed: the total number of diatoms decreased and debris increased when grind time was 0~5 min. In
order to keep the original porous morphology of diatom, grind time should not be too long, so 1 min was the optimum grind time.

Fig 1. SEM of raw soil  Fig 2. SEM of 1 min grind  Fig 3. SEM of 3 min grind  Fig 4. SEM of 5 min grind

3.2. Ultrasonic Pretreatment Time

Figure 6 showed the specific surface area of the diatom soil that grinded for 1 min after ultrasonic pretreatment for different time; Fig. 8-11 were SEM at different ultrasonic pretreatment time.

As shown in Figure 6, the specific surface area of DE became larger with the increase of ultrasonic time, specific surface area increased by 17.0%, 17.9%, 18.7% respectively when ultrasonic time was 0~5 min, 5~10 min, 10~15 min; The diatom shells exposed to porous structure when ultrasonic for 5~10 minutes and the number of diatom shells had almost no change. When the ultrasonic time was 15 min, diatom shells were crushed, its integrity was undermined. So the optimal time of ultrasonic pretreatment was 5~10 min. From the point of view of energy conservation, ultrasonic pretreatment time was 5 min in this experiment.

Fig 5. Effect of different grind on specific surface area of DE  Fig 6. Effect of ultrasonic time on specific surface area of DE  Fig 7. Effect of mass fraction of time H2SO4 on specific surface area of DE

3.3. H2SO4 mass fraction

After grinding for 1 min and ultrasonic for 5 min, the DE was immersed in H2SO4 for 1h, the temperature of water bath was 60℃, the specific surface area of obtained DE was shown in Fig. 7.

From Fig.7, the specific surface area of DE after acid leaching had been improved significantly, which mainly due to H2SO4 reacted with impurities (Fe2O3, Al2O3, MgO, etc.) of DE, generating soluble salts, but the main component of DE (SiO2) did not react with sulfuric acid, and the surface of diatom exposed some new micropores. From the above analysis: 50% sulfuric acid leaching made the specific surface area of DE increase from 14.80 m2/g to 18.96 m2/g.
3.4. H$_2$SO$_4$ Acid Leaching Time
After grinding for 1 min and 5 min of ultrasonic, the DE was immersed in 50% H$_2$SO$_4$ for different time by closed magnetic stirring, the temperature of water bath was 60°C, and the specific surface area of DE was shown in Fig.22. And it can be seen from Fig.22, the specific surface area of DE reached to 18.96 m$^2$/g after acid leaching for 1h.

3.5. Calcination Temperature
Fig.23 was the specific surface area of DE after grinding for 1min, ultrasonic for 5min, 50% H$_2$SO$_4$ acid leaching for 1h, calcination for 2h at different temperatures. Table 1 was the PH value of calcination of DE at different temperatures.

As can be seen from Fig.23, the specific surface area increased to 21.23 m$^2$/g when the calcination temperature was from 25°C to 600°C, then it decreased with increasing temperature. Therefore, 600°C was the best calcination temperature.

It can be seen from Table 1, from 25°C to 600°C, the surface area of DE increased, the number of inner superficial hydroxyl of hole per square meter increased, the more H$^+$ were ionized, acidity was enhanced, PH value became smaller; When the temperature was risen, the specific surface area decreased, the number of the inner superficial hydroxyl of hole per square meter was lower, the less H$^+$ were ionized, PH value became larger.

| Calcination temperature (°C) | 25 | 400 | 600 | 800 |
|-----------------------------|----|-----|-----|-----|
| PH value                    | 6  | 5   | 5   | 7   |

3.6. Calcination Time
Fig. 2.4 was the specific surface area of DE after grinding for 1min, ultrasonic pre-treatment for 5min, with 50% concentrated sulfuric acid leaching for 1h, 600°C calcination at different time. It can be seen from Fig. 2.4, the specific surface area increased to 23.23m$^2$/g when the calcination time was 4h, so the optimum calcination time was 4h.

According to the pore size distribution of BJH before and after the purification of DE, the DE had a pore size distribution of 2~3nm, and the peak value of pore size distribution of 100~110nm increased. It indicated that the pore structure of purified DE was dredged, the specific surface area and pore volume were increased and the number of small pores and large pores were increased.

4. Conclusions

In this experiment, the structure of diatom shell was influenced by acid concentration, acid leaching time, calcination temperature and time, the specific surface area of purified DE increased from 12.65m$^2$/g to 23.23m$^2$/g, which increased by 45.54%, the internal pore structure was dredged highly.

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