Study on Purification Diatomite with nitric acid by Thermal Closed System

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Abstract. In this research, a purification approach using nitric acid leaching at thermal closed system was developed to improve the porous structure of raw diatomite by removal of impurities from its surface and clogged pores. The feasibility and efficiency of this approach were determined by XRF for chemical constitution of diatomite, SEM for morphology and BET for specific surface area of purified diatomite. The investigations indicated that the content of SiO_2 was in order of 85.14% for raw diatomite and 98% for purified diatomite, the content of Fe_2O_3 decreases after purified; the integrity of the porous structure was confirmed by SEM, and increase in specific surface area from $18m^2 \cdot g^{-1}$ to $36m^2 \cdot g^{-1}$.

Keyword: thermal closed system; diatomite; low temperature; purification

1 Introduction

Diatomite, is a sort of biologic sedimentary rock which composed of fossilized skeletons of diatoms with porous structure, it consists of amorphous silica (SiO_2) was derived from skeletons of diatoms, the remainder being Al_2O_3, Fe_2O_3, CaO, MgO, K_2O and Na_2O were adopted from clays and other minerals [1]. Due to well-developed porous structure with large specific surface area, diatomite possesses lots of excellent physical and chemical characteristics, such as low bulk density, chemical stability, high mechanical strength, and relatively low price owing to its abundance, etc. As a result of these features, it has been widely employed in variety of other applications: filter aid [2], adsorbents [3], and as support for catalysts [4].

China has massive diatomite resources, but the vast majority of which are of low or moderate quality, and raw diatomite commonly contain several types of impurities, which block the porous and limit the performance. Therefore, it is purification of diatomite that will improve the property before its industrial and commercial utilization. It can be purified

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by physical and chemical methods; these technologies have been basically mature that large grain minerals and clay minerals were removed by physical methods: scrubbing method, high-speed shear and ultrasonication. But these oxides where adhered at surface was removed by chemical methods: alkali leaching [5], acid leaching [6], and acid leaching-calcinations [7]. With these methods, nevertheless, have some drawbacks: destruction of the porous structure (alkali leaching); inefficiency, high operational cost, the pollution caused by sour vapors pours into air in open system (acid leaching and acid leaching-calcinations) could compromise the results.

Furthermore, the purification process can be accelerated if acid leaching temperatures were raised. For this reason, our idea was the raw materials (diatomite and nitric acid) were mixed in hydrothermal synthesis reactor (the model number is KH-500), heated. More specifically, the objective of our work was using acid leaching at thermal closed system and developed to improve the porous structure of raw diatomite by removal of impurities from its surface and clogged pores, loss of ignition (LOI) were removed by calcination at 450°C.

2 Experimental Part

2.1 Materials

Nature diatomite from region of Jilin province in China was used in this investigation, after mining, primary crushing, blending and classifying of the raw diatomite, the natural powder was ready for use (with particle size distribution of d_{50}=20μm, S_{BET}=18$m^2 \cdot g^{-1}$). The chemical composition of which is shown in Table 1. HNO_3 (A.R 65%, by mass).

TABLE 1 CHEMICAL CONSTITUTION OF DIATOMITE (MASS FRACTION/%)

SiO_2	Al_2O_3	Fe_2O_3	K_2O+Na_2O	CaO+MgO	MnO_2+TiO_2	LOI
85.14	4.31	1.98	1.52	1.15	0.62	5.3

2.2 Purification of Diatomite

The purified diatomite was prepared by mixing raw diatomite with HNO_3 equilibrated for various contact time 4-14h. In this experiment, 80g of diatomite, 150ml of HNO_3 (in order to obtain complete reacted product, $HNO_3$was exceed the need) were mixed in hydrothermal synthesis reactor, sealed, and keep these samples at a constant temperature of 120°C. The residual solid was separated from the mixture by washed several times with distilled water in centrifuge until Fe^{3+} can not be detected. The obtained samples were then dried in an oven at 70°C, reground, and then samples were calcined at 450°C, the purified diatomite were stored in tightly closed plastic bottles.

2.3 Evaluation and Characterization

For characterization of purified diatomite, several methods were used. The study of the samples included: (i) elemental analysis of the samples was carried out measurement X-ray fluorescence (S4 Pioneer), (ii) microstructural analysis using SEM (S-3400), and (iii) determination of specific surface areas by BET (BELSORP-mini Ⅱ).

3 Results and Discussion

3.1 Results of Purification

Acid leaching process was solid-liquid multiphase reaction; this reaction can be described as:

$$\sum\left(T_x^n O_y^m + (x \cdot n)\mathrm{HCl} \rightarrow xT(\mathrm{Cl})_n + yH_2O\right) \quad (1)$$

Where $T^n{}_xO^m{}_y$ are K_2O, Na_2O, CaO, MgO, Al_2O_3 and Fe_2O_3; based on the motion of above oxides, $T^n{}_xO^m{}_y$ in proper order with HNO_3 start reaction. These results can be described as Table 2; it was found that the amount of SiO_2 was in order of 85.14% for raw diatomite and 98% for purified diatomite, the content of Fe_2O_3 decreases after purified. $T^n{}_xO^m{}_y$ and partial organics were removed by acid leaching, then samples were washed, desiccations, calcined at 450°C, adsorbed water and other organics were removed. As shown as in Table 2, acid leaching time was 8h, the reaction was basically over. From this knowable, the optimal conditions of acid leaching at 120°C for 8h and calcination at 450°C for 2h.

TABLE 2 CHEMICAL CONSTITUTION OF DIATOMITE BEFORE AND AFTER PURIFICATION (MASS FRACTION/%)

Samples	SiO_2	Al_2O_3	Fe_2O_3	K_2O+Na_2O	CaO+MgO	MnO_2+TiO_2	LOI
Raw diatomite	85.14	4.31	1.98	1.52	1.15	0.62	5.3
4h	94.02	3.03	1.44	0.74	0.54	0.23	-
6h	97.88	1.01	0.36	0.48	0.13	0.13	-
8h	98.09	0.82	0.32	0.52	0.12	0.13	-
10h	98.16	0.78	0.33	0.44	0.14	0.15	-
12h	98.39	0.70	0.24	0.48	0.10	0.12	-
14h	98.51	0.64	0.30	0.29	0.10	0.16	-

Note: Purified diatomite was treated using nitric acid concentration of 65% for 4h to 14h and calcined at 450°C for 2h.

3.2 SEM of Diatomite

The fresh sample was characterized by SEM, and selection of images of purified diatomite is presented in Fig. 1. The micrograph of 30μm diameter particles covered with diatoms and the shapes of diatom have disc and cylinder is shown in image (a); the porous structure of purified diatomite was well-developed and some holes could be seen in the surface more clearly, which suggests a porous and hollow structure as described previously is shown in image (b); in light of the above findings, microstructural analysis was done to verify the success of this approach in producing high purity diatomite and in maintaining

the integrity of the porous structure of diatomite after purification is shown in (c) and (d). These results were in accordance with those of the preceding chemical analysis.

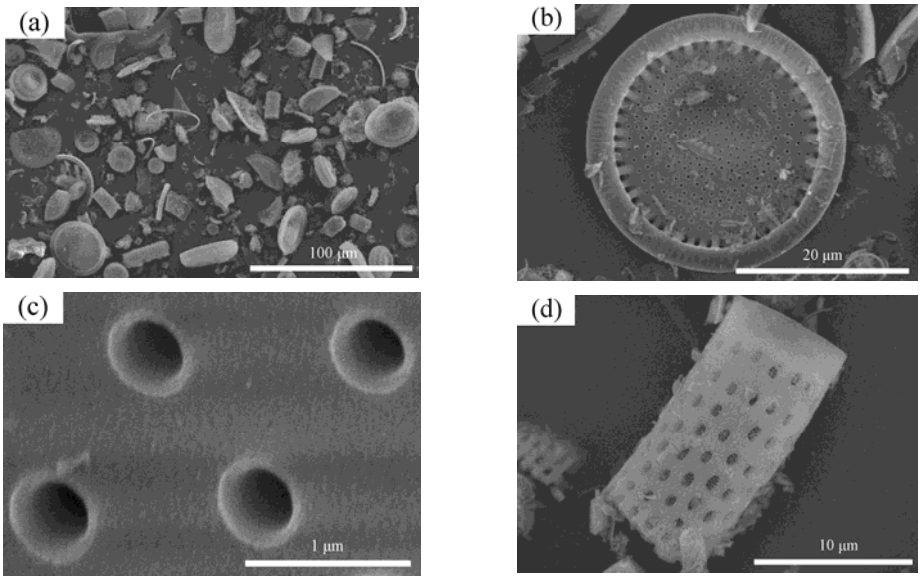

Fig. 1 Scanning electron microscope (SEM) photographs of purified diatomite

3.3 BET Analysis

Fig. 2 displays the nitrogen adsorption/deadsorption isotherms measured at 77k and pore size distributions was investigated using BJH method applied to purified diatomite. As shown as in Fig.2, the nitrogen adsorption isotherms for purified diatomite was classified as type II and pore size were 2.33nm, 4.50nm, 7nm, 25.72nm and 40nm, this means diatomite was mesoporous material according to International Union of Pure and Applied Chemistry (IUPAC).

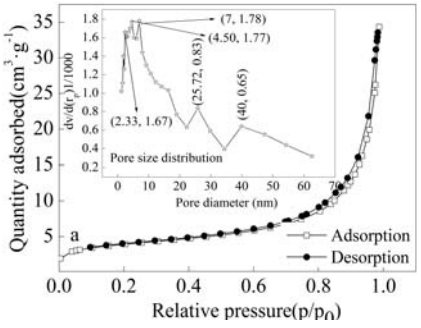

Fig.2 Isotherm for adsorption of N_2 and pore size distribution on purified diatomite

Table 3 reveals the variation law of specific surface area, as shown as in it, increase in specific surface area from $18m^2 \cdot g^{-1}$ to $36m^2 \cdot g^{-1}$.

TABLE 3 VARIATION LAW OF SPECIFIC SURFACE AREA OF PURIFIED DIATOMITE

Times (h)	0	4	6	8	10	14
Specific surface area ($m^2 \cdot g^{-1}$)	18	27.31	35.76	36.96	35.19	34.79

4 Conclusions

It was shown in the present work that the treatment of diatomite with HNO_3 in thermal closed system improved its purity. The amount of SiO_2 was in order of 85.14% for raw diatomite and 98% for purified diatomite, the content of Fe_2O_3 decreases after purified. The well-develop porous structure was confirmed by SEM, and increase in specific surface area from $18m^2 \cdot g^{-1}$ to $36m^2 \cdot g^{-1}$.

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