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The diatomite purification effect on its adsorbability efficiency

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ABSTRACT

Diatomite is one of low cost, ecofriendly and abundantly available inorganic clay materials around the world. Recently, the application of inorganic clay material such as diatomite has received a great attention as the potential adsorbent for pollutants. However, various types of impurities found in diatomite, could have an effect on its adsorption properties. In this study, Raw diatomite was refined through various purification method *i.e*,: Drying at low temperature, Calcination, Hot Acid Leaching, Filter aid and Silica modified diatomite to remove the impurities. Then, the effect of diatomite treatment on its adsorbability efficiency to a kind of cationic dye rhodamine B (RB) as the adsorbate was investigated. The results suggested that, the adsorption curve of the several common modified diatomite at certain time gradient and varying with temperature showed a certain extent of difference. The analysis of SEM micrographs and adsorption kinetic revealed the factors that affected the adsorption rate and capacity of the modification procedure. Thus, the purification of diatomite showed a great potential on the improvement of its adsorption efficiency capacity.

Keywords: *Diatomite, adsorption, drying, calcination, acid leaching, Silica, Filter aid.*

1. INTRODUCTION

Environmental issue, one of the global major theme of nowadays which has been a guidance of human behavior such as daily life and manufacture, in which thousands of tons of waste materials which may include organic or inorganic contaminant and heavy metals are released every day. Typically, the removal of colored and colorless organic pollutants from industrial effluent for the environmental society is considered an important application of adsorption processes using a suitable adsorbent [1].

Traditionally, activated carbon is accepted as a good adsorbent for its good effect in adsorption. So far, with the development of the economy and industry, there is a growing attention on low cost and commercially available materials for the adsorption of pollutants. Diatomite, a siliceous sedimentary rock available in abundance around the world, has received great attention for its unique combination of physical and chemical properties (such as high permeability, high porosity, small particle size, large surface area, low thermal conductivity and chemical inertness) and low cost regarding as a prioritized material for the removal of pollutants from effluent [2]. Its feasibility makes it a good alternative to activated carbon, the charge of which involved activation and regeneration limits its widely application. Therefore, several literatures disclosed diatomite as the potential adsorbent for pollutants, especially dyes removal [3, 4]. For instance, Al-Deges in his excellent research reported that diatomite shows a significant efficiency as an adsorbent for heavy metals [5]. Furthermore, Erdem had found that the removal efficiencies of several dyes by diatomite ranged from 28.6 to 99.23% [6]. Subsequently, Khraishehand and AlGhouti used thermal treated and manganese-oxide-modified diatomite, respectively as adsorbents to methylene blue (MB) and other dyes [7-8]. Al-Qodah treated diatomite by sulfuric acid through the adsorption experiment, relatively improving the loading capacity [9]. Actually, the main component of diatomite is amorphous Silica,although it can contain several impurities such as organic matter and metallic oxides such as Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, $P_2O_5$and so on, which may drive to negative effects on its application properties.Therefore, diatomite needs to be refined to acquire the high quality and purity [12-13]. Several diatomite purification methods such as calcination, hot acid leaching, and so on were developed. Specifically, calcination can be applied to remove the organic matter in diatomite with the heighteningthe diameter of porous structure much larger.Moreover, hot acid leaching can used to treat diatomite to remove the metal oxide mineral and increase the pore size and surface area of diatomite too. In this study, the effect of diatomite treated from drying at low temperature (50°C, here in after referred to as Dried diatomite), calcination, hot acid leaching, Filter aid, and Silica on its adsorbability to rhodamine B dye removal, was monitored and compared to Raw diatomite. In this contribution, the adsorption curve and loading capacity varied with time and temperature of various modified diatomite were determined. Furthermore, the equilibrium kinetic and mechanism of those various modified diatomite adsorbent on RB were extensively discussed.

2. EXPERIMENTAL SECTION

2.1. Materials. Raw diatomite and Filter aid (90.6%) were obtained from LinjiangTianyuan catalyst Co. Ltd. Hydrochloric acid (AR), sulfuric acid (AR) were purchased from Sinopharm Chemical Regent Co. Ltd. Rhodamine (RB) (AR), sodium hydroxide (AR) were kindly supplied by Tianjin Fuchen Chemical Regent Factory.

2.2. Adsorbent preparation.

2.2.1. Drying diatomite at low temperature.

51.25g Raw diatomite was put in oven for 24 hours under 50°C. Thereafter, theDried diatomite was weighed and found to be 48.70g. Consequently, the rate of the water lost was 4.98%.

2.2.2. Calcination of diatomite.

A weighed amount of Raw diatomite was put in Muffle furnace (GWL-80) to calcine for 2 hours under high temperature controlled at 500°C, and then followed by cooling naturally at room temperature to get the Calcined diatomite.

2.2.3. Hot Acid Leaching of diatomite.

60g of Calcined diatomite was dispersed in 500ml beaker filled with 240mLof 10% hydrochloric acid prepared obviously under mechanical agitation. Then, the beaker was heated under oil bath at 100 °C for 1 hour. Thereafter, the beakerwas taken out followed by cooling naturally. And then, the mixture was filtrated and the solid was washed by diluted hydrochloric acid(concentrated hydrochloric acid: water =1: 4) for four times. Finally, the purified solid was put in Muffle furnace (GWL-80) and calcined at 500 °C for 2 hours to obtain the dried Acid leached diatomite.

2.2.4. Silicapreparation.

100g Calcined diatomite, 300ml water and 60g sodium hydroxide were added to 1 L beaker and boiled under mechanical stirring for 5 min. The mixture was cooled and adds400ml water to the beaker followed by filtration. Then, the water was continuously added up to 800ml. Thereafter, the mixture was boiled again and simultaneously adds40mL concentrated sulfuric acid until there would be a lot of precipitate occurring,followed by filtration. Finally, the Silica can be obtained by drying and milling the purified solid at 80°C for 12 hours.

2.3. Adsorbate preparation.

The aqueous solution of 100mg/L rhodanmine B was prepared by dissolvingrhodanmin B solid intodeionizedto get theadsorbate.

2.4. Adsorption isotherms determination.

Adsorption isotherm experiments were conducted by immersing1.5g adsorbent (Raw diatomite ,Dried diatomite, Calcined diatomite, Acid leached diatomite, Filter aid, Silica) to 150mL of 100g/L rhodanmine B solution in conical flask deposited on a thermostatic oscillator(rotation rate :180rpm/min), respectively. The rate of adsorption was measured at the time gradient (1,2,4,6,8,10,15,20,30,40,60,90, and 120min). At the corresponding time gradient, 10mL adsorption solution was taken out followed by centrifugation (3000rpm/min, 5min), and the filtrate was analyzed by spectrophotometer(scanning speed:600nm/min; scanning range:450nm-650nm; scanning spacing:2nm; the wavelength of maximum absorbance: 554nm). The temperature of the adsorption process was set at 20,30,40,50 °C, respectively.

The amount of the adsorption was calculated by the following formula:

$$Q=\frac{(C_0 - C_t)\times V}{m}$$

Where C_0 is the initial concentration of the rhodanmine B solution; C_t is the concentration of the adsorbate when adsorption took place at t min; V is the volume of the solution; m is the mass of the adsorbent; Q is the amount of the adsorption.

3. RESULTS SECTION

3.1. Effect of adsorption time on the adsorption of modified diatomite.

The adsorption of rhodanmine B(100mg/L) onto Raw diatomite, Dried diatomite, Calcined diatomite, Acid leached diatomite, Silica and Filter aidat various times was studied at 20°C and depicted in Fig.1.

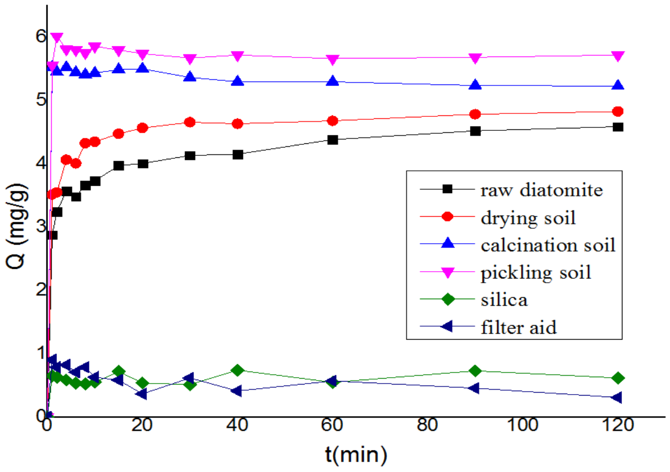

Figure 1. Adsorption of RB onto different modified diatomit.

The results for this experiment showed that the tendency of Raw diatomite and Dried diatomite on adsorption varying with time was almost similar. Theinclination of calcined and Acid leached diatomite on adsorption varying with time was found to be the same; and the tendency of Silica was equal to Filter aid.

When referring to Raw diatomite and dried soil, the adsorption rate is quite fast at the beginning of the adsorption. With the extent of adsorption time, the amount of adsorbate onto adsorbent (Q) was increasing, while the adsorption rate was dropping down. When the time was long enough, the adsorption tended to equilibrium. Sustaining 90 minutes approximately, the adsorption equilibrium of RB could be attained. The ultimate value of equilibrium adsorption indicated that the loading capacity of dried was enhanced compared to Raw diatomite, though the enhancement was not enough. This demonstrated that the diatomite lost water partially and increased its surface area at a certain extent when drying, though it was not so evident,but it provided a good direction.

When referring to Calcined diatomite and Acid leached diatomite, the adsorption rate is much faster. The adsorption process can be finished within 1min and attained the loading capacity. At 40 min approximately, the adsorption equilibrium can be achieved. Compared to Raw diatomite and Dried diatomite, the equilibrated loading capacity of Calcined diatomite and Acid leached diatomite was also enhanced and the adsorption curve showed an obvious change. Furthermore, the tendency is far from Raw diatomite and Dried diatomite, and the adsorption rate also increased considerably.

As mentioned above, seeing from the whole procedure and the effect of the modification on the adsorption, we could conclude that the calcination step played a considerable role. Specifically, compared to Raw diatomite, drying step just increased a little for the adsorption of RB onto diatomite and the adsorption law seeing from the adsorption curve didn't change a lot. However, after calcination step, the Acid leached diatomite had a great improvement on RB adsorption rate and equilibrated loading capacity. Moreover, the adsorption law seeing from the adsorption curve also changed a lot.

When come to Silica and Filter aid, we could see that they seldom have adsorptivity compared to Raw diatomite, Dried diatomite, Calcined diatomite and Acid leached diatomite. It is already known that Silica and Filter aid had already crystallized inner and the surface area was much smaller compared to the porous structure of diatomite. The above results suggest that the adsorption of RB onto diatomite was mainly determined by its inner porous structure. In addition, the adsorption capacity and rate was also positively influenced by the inner diameter of pores and surface area, which can be confirmed by the SEM micrographs as Fig.2.

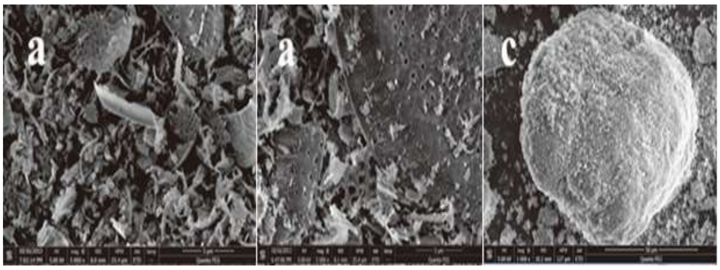

Figure 2. SEM micrographs of (a) Raw diatomite at 5,000X, (b) Acid leached diatomite at 5,000X, and (c) Silica at 1,000X.

3.2. The Q_e of different modified diatomite.

All the modified steps above would have an impact on the diameter and size of the pores, which made the diatomite porous structure a good attribute for adsorptivity. Consequently, the maximum equilibrium adsorption capacity (Q_e)of RB adsorbed on the modified diatomite would surely be affected by the modified procedure. The data of the $Q_e$that was tested at different temperature of different adsorbent are showed in Table1.

To make the tendency and difference of the $Q_e$more clear and easy to distinguish, the Table 1 can be convertedinto column diagram, Figure 3.

It is clear from Table 1 and Figure 3 that the Q_e of diatomite on RB was increasingly improving as follow "Raw diatomite →drying (low temperature)→cooling→ calcination (high temperature) → cooling→ acid leaching →filtration→ washing→ calcination→ modified diatomite" going on at low temperature (20°C and 30°C) relatively. While at high temperature (40°C and 50°C) relatively, the Q_e of calcined and Acid leached diatomite were higher than raw and Dried diatomite instead. But, throughout, the Q_e of the Dried diatomite was always higher than Raw diatomite. According to the result, the Q_e of diatomite adsorbent (raw, dried, calcined, Acid leached diatomite) were considerably higher than Silica and Filter aid whatever the temperature was.

Table 1. Equilibrium absorption capacity of different adsorbent

Adsorbent	Q_e(mg/g)			
	20°C	30°C	40°C	50°C
Raw diatomite	4.411 ± 0.1912	4.839 ± 0.1434	5.1500 ± 0.1292	5.5807 ± 0.2083
Dried diatomite	4.730 ± 0.0896	5.215 ± 0.1007	5.2641 ± 0.1868	5.6549 ± 0.2200
Calcined diatomite	5.264 ± 0.0365	5.110 ± 0.0830	5.2156 ± 0.0893	5.0587 ± 0.0269
Acid leached diatomite	5.694 ± 0.0279	5.309 ± 0.0143	5.0074 ± 0.0647	4.8790 ± 0.0479
Silica	0.660 ± 0.0933	0.423 ± 0.1314	0.1780 ± 0.1104	0.3377 ± 0.2761
Filter aid	0.437 ± 0.1087	0.714 ± 0.2619	0.3234 ± 0.1573	0.4889 ± 0.5304

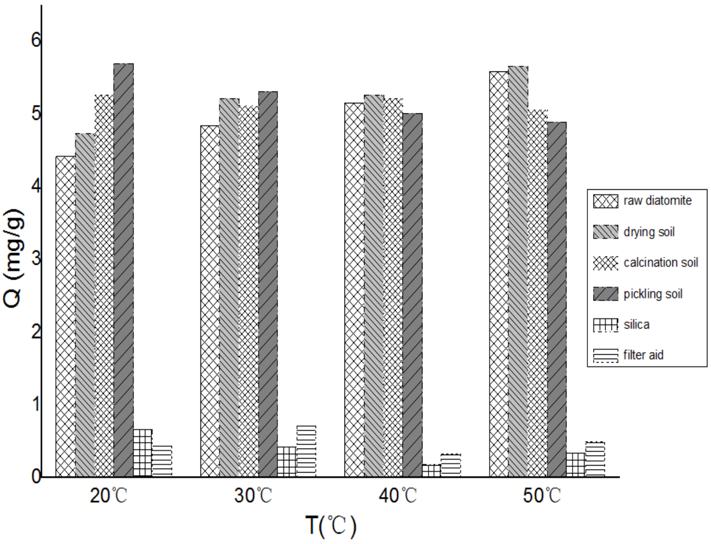

Figure 3. The maximum equilibrium absorption capacity of different adsorbent at different temperature.

Judging from the SEM micrographs, we could discuss the adsorption mechanism. When the diatomite was shaped in the amorphous structure, the inner porous surface made it present a good adsorptivity. However, when the diatomite was exposed to ultra-high temperature and the inner structure crystallized the adsorptivity would decrease evidently just like the Filter aid. In addition, the adsorptivity of diatomite was also closely related to surface area, while the surface area was simultaneously affected by crystal form. Therefore, crystal form was the major factor that determined the adsorptivity.

3.3. The Q_e of different adsorbent at various temperatures.

Figure 4. demonstrate the curves of the $Q_e$of four different modified diatomite adsorbent(Raw diatomite, Dried diatomite, Calcined diatomite, acid leached) on RB absorptionat various

temperatures.

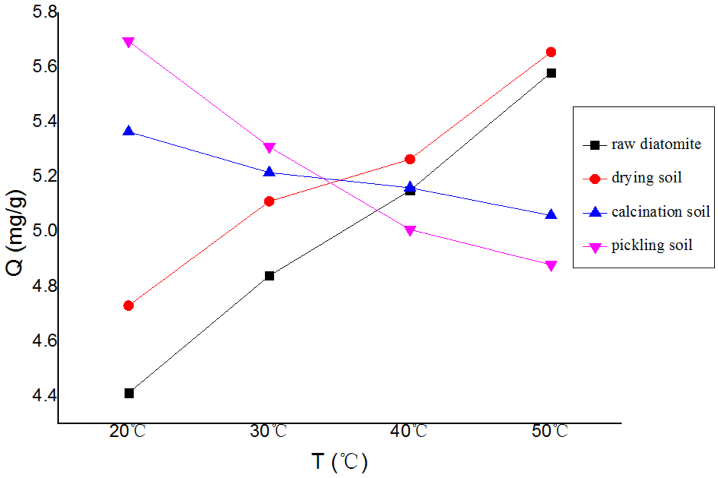

Figure 4. Equilibrium absorption capacity of adsorbent at different temperature.

It is evident from Figure 4 that raising adsorption temperature could increase the Q_e at a certain extent for Raw diatomite and Dried diatomite.In other words, raising temperature could enhance the adsorption though the degree was not so the same. Briefly speaking, the $Q_e$of Raw diatomite on RB at 50°C increased by 25% approximately than it was at 20°C, while the $Q_e$of Dried diatomite on RB at 50°C increased only by 20% . Contrary to Raw diatomite and Dried diatomite, the Q_e of Calcined diatomite and Acid leached diatomite on RB were not favored by the raising of adsorption temperature at a certain extent. Specifically, the Q_e of Calcined diatomite on RB at 50°C decreased by 4% approximately than it was at 20°C, while the $Q_e$of Acid leached diatomite on RB at 50°C decreased by 18% compared to 20°C.

3.4. The adsorption curve of different adsorbent varying with temperature.

To understand the adsorption of RB onto the four modified diatomite more deeply, and know about its mechanism, the adsorption curves of them under the certain time gradient varying with temperature were depicted in Figures 5-8, respectively.

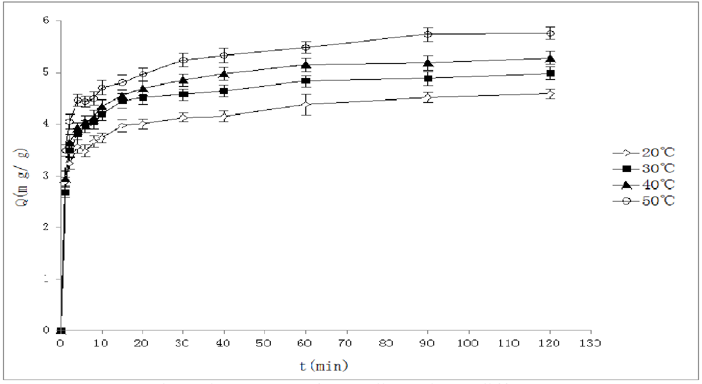

Figure 5. Adsorption curves of Raw diatomite at different temperature

Figures 5 and 6 showed that the adsorption of RB onto Raw diatomite and Dried diatomite last for nearly 90 minutes before reaching the equilibrium. The tendency showed almost no difference as the temperature risen from 20°C to 50°C, though the loading capacities have increased, i.e.: 25% for Raw diatomite and 20% for Dried diatomite. Figures 7 and 8 showed that the adsorption of RB onto Calcined diatomite and Acid leached diatomite could be finished instantly and reach the maximum within one minute. Then, with some fluctuation of data, the equilibrium still could be reached in 40 minutes. The adsorption tendency remained unchanged as the temperature risen from 20°C to 50°C. As the temperature rose for 20°C to 50°C, the loading capacities showed a decreasing trend, specifically, 4% and 18% for calcined and Acid leached diatomite, respectively.

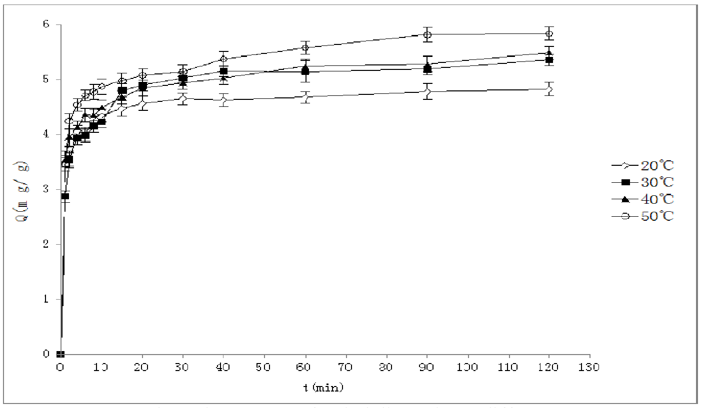

Figure 6. Adsorption curves of Dried diatomite at different temperature

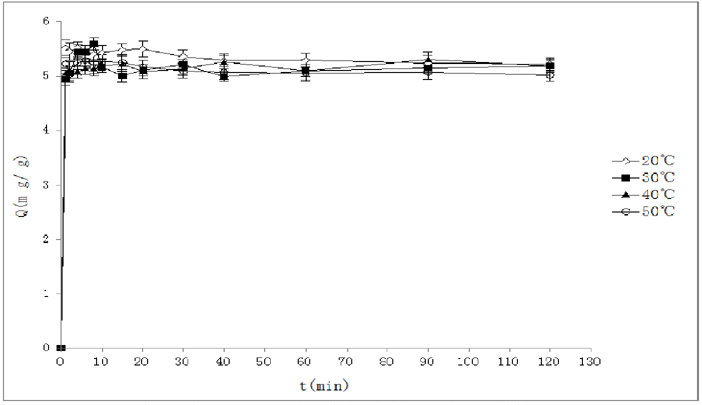

Figure 7. Adsorption curves of Calcined diatomite at different temperature

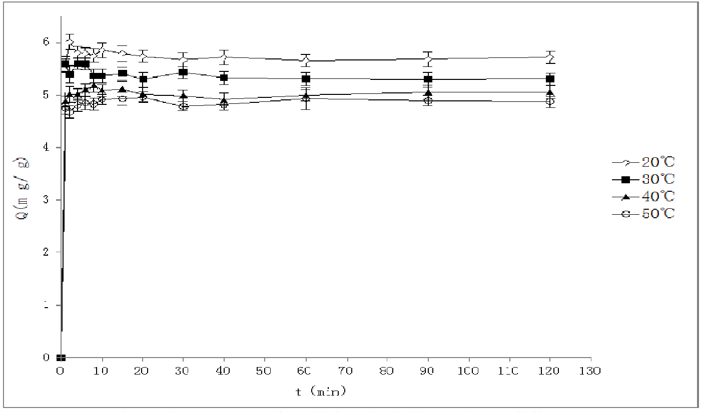

Figure 8. Adsorption curves of Acid leached diatomite at different temperature.

It is evident from Figures 5 and 6 that the adsorptivity of Raw diatomite and Dried diatomite would be enhanced with the rise of temperature at a certain extent, which indicted the adsorption was endothermic reaction. Table 2 suggests that the adsorption of Raw diatomite and Dried diatomite is a chemical adsorption controlled. Its adsorption rate could be explained by chemical kinetic law. As for Calcined diatomite and Acid leached diatomite, the rise of temperature didn't favor the adsorption, instead, it would weaken the adsorption at a certain extent, which suggested the adsorption was a exothermic reaction. The adsorption mechanism of them fits the process that physical adsorption is controlled well judging from the Table 2.

Table 2. Comparison of chemical and physical absorption

	Physical adsorption	Chemical adsorption
Adsorption force	Van der Waals force	Chemical bond
Selectivity or not	Not	Yes
Adsorption rate	Much faster	Much slower
Adsorption heat and energy	Low,close to condensing heat, just several kJ/mol	high, close to chemical reaction heat, near several hundred kJ•mol^{-1}
Temperature affect	Not so obvious	Raising temperature favor adsorption

4. CONCLUSIONS

It was shown in the present investigation that the treatment of diatomite went through the procedure “Raw diatomite →drying(low temperature)→ cooling→ calcination (high temperature)→ cooling→ pickling→ filtration→ washing→ calcination→ modified diatomite” could not only refine the Raw diatomite to obtain high-quality and purified diatomite, but also enhance the adsorption capacity and increase the adsorption rate. Just like the four different modified diatomite as adsorbents, the adsorption curve gave us the most visualized reflection. The consequence of modified steps that could increase the $Q_e$was able to be explained by SEM micrographs. Compared with Silica and Filter aid, the Q_e of the modified diatomite was considerably increased.Therefore, the modified diatomite could be a more effective and novel Filter aid. In addition, the tendency of the adsorption varying with temperature suggested that the adsorption processes of raw and Dried diatomite were endothermic reaction, while the adsorption of calcinedand Acid leached diatomite were exothermic reaction. The former was predominated by chemical adsorption, and its adsorption rate fitted with chemical kinetic law. The latter was predominated by physical adsorption, and its adsorption rate was pretty fast at the beginning and soon reached the adsorption equilibrium.

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6. ACKNOWLEDGEMENTS

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