Efficient Desilication by Adsorption with Aluminum Salt-modified Bentonite from Green Liquor

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The objective of this work was to investigate the possibility of using Na-bentonite as a raw material to produce aluminum salt-modified bentonite (AlMB) for desilication of green liquor. Batch experiments were carried out by varying the experimental parameters to find the optimum conditions. The optimum adsorbent dose was 20 g/L. The maximum adsorptions of 96.37% and 87.22% took place at pH 7.4 when the initial concentrations of silicate in green liquor were 4 and 6 g/L, respectively. The kinetic models showed that the process included physical adsorption and chemical adsorption. Finally, this study showed that the extent of desorption was 56.78% for silicate after desorption of AlMB in 2 M NaOH solution. The AlMB is an efficient and novel adsorbent for desilicating that can provide a good reference for the “silicon influence” in a papermaking mill.

Keywords: Bentonite; Modification; Aluminum salts; Adsorption; Desilication; Green liquor

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INTRODUCTION

Owing to the shortage of wood resources, non-wood materials are being used for papermaking in Europe and Asia. However, non-wood materials generally have a higher ash content than wood materials. For instance, the wheat straw ash content is 3 to 5%; straw contains up to 15%, and bamboo contains 1 to 3% (Zhong 2002). During the kraft digesting process, the silicon in the raw material reacts with sodium hydroxide to form sodium silicate. The silicate enters the black liquor and then gets into the green liquor, which causes a series of problems in the alkali recovery system that are known as “silicon influence” (Isono and Ono 1967; Rao *et al.* 1988; Taylor and McGuffie 2007; Tutus and Eroglu 2003). The primary issue is that sodium silicate in green liquor forms calcium silicate after recausticizing, and the product is so fine that it is difficult to precipitate and filter. The presence of calcium silicate leads to serious consequences for white mud.

The black liquor after cooking is extracted, evaporated, and concentrated. Then black liquor is burned in the furnace and formed into solid melt. When the solid is dissolved in water, the resulting liquid is called “green liquor”. The main component of green liquor is sodium carbonate. Lastly, quick lime is added in the green liquor. Sodium carbonate reacts with calcium oxide to generate sodium hydroxide (white liquid). Meanwhile, calcium carbonate as the main composition of white mud is also obtained (Wang 2013). The white mud is difficult to wash since it contains a high content of residual alkalis; the silicate causes high energy consumption during lime calcination, especially while recycling of white mud, since it exacerbates the silicon influence. The alkali recovery system could ultimately collapse. To avoid this silicon influence or silicon effect, some pulping mills choose to landfill or stack the white mud, which is not only a waste of resources but also results in environmental pollution. Alleviating or eliminating non-wood pulp's silicon effects has already become a key issue that has affected the development of non-wood resources and biomass resources recycling (Tutus and Eroglu 2004).

Bamboo is a kind of non-wood raw material that grows quickly. It has been used in the production of ordinary paper, dissolving pulp, fluff pulp, microcrystalline cellulose, and other products (Tsuji and Ono 1966). Therefore, there is huge potential for the development and use of bamboo. In this work, green liquor from kraft bamboo pulping was chosen as the research subject.

Silicon in green liquor comes from three main sources (Pada 1963): conjugated raw materials, which are in plants due to a physiological need to absorb silicon; sediment contained in raw materials, which is unconjugated silicon and is easy to remove in material preparation; and silicon accumulated in the black liquor. Moreover, in the alkali recovery system, 90% of the silicon comes from raw materials, while 10% comes from caustic lime. Accordingly, silicon removal in green liquor consists of adding a certain amount of chemicals to the green liquor so that the silicon deposits in the form of a precipitate.

One of the main methods for removing silicon is the combustion method. Vehmaan-Kreula (2000) proposed adding magnesium or aluminum salt to black liquor. Such treatment leads to formation of an insoluble silicate compound that can then be filtered from the green liquor. This is a novel method, which means that there is little literature on the subject. It was the first report of adding a metal salt into the black liquor, and the silicon removal rate reached 90%. Additionally, magnesium or aluminum salts are prone to deposition of scale onto the equipment during the black liquor combustion process and can be adjusted according to equipment load.

Carbon dioxide or flue gas can also be used to remove silicon using the seeding method. The decrease in pH due to the introduction of CO_2 leads to the formation of silicic acid colloid (Xia *et al.* 2013; Yu *et al.* 2008). The method is simple, easy, and low-cost. The India Amerit Paper Company (Idrees and Veeramani 1977) found that when the pH reached 9.5 and the temperature was 60 to 80 °C, the desilication rate was as high as 85%. However, considerable dust and powder residue of impurities are present in the flue gas. Such impurities would mix in the white mud. The lime resulting from calcination of white mud was not reusable because of its low quality. The pH value of green liquor decreased and required the addition of NaOH to return to the original pH.

The addition of calcium oxide (CaO) or alternatively, pre-causticizing silicon removal, is a third method for silicon removal. The CaO can slow the decrease of pH in wastewater, which is better than the method utilizing CO_2 or flue gas. The rate of desilication can reach 80 to 90% through a multi-stage method (Barnes *et al.* 1999). This high desilication rate can only be obtained in the lab and is reduced to 40% in practical production due to the high content of impurities in industrial quicklime (Bohmer 1984). After desilication, the $CaCO_3 \cdot SiO_2$ does not easily decompose into CaO and thus is difficult to recycle, which increases costs.

Magnesium ions, aluminum salts, and iron ions are popular desilicating agents (Akgül and Karabakan 2011; Jolsterå *et al.* 2010) and can be used to precipitate the silicate. Although the rate of desilication is high, the introduction of metal ions affects the quality of the green liquor, which can aggravate the scaling problem in the alkali recovery processes. Additionally, the products aluminosilicate and magnesium silicate are difficult to filter because of their fine particles.

Sodium bentonite has received much attention for water and wastewater treatment due to its low cost, easy modification, powerful adaptability, abundance, and high adsorption efficiency (Zamparas *et al.* 2012; Gibbs and Özkundakci 2011; Lin *et al.* 2014). However, there has been a considerable amount of work on adsorption of metal ions (Yapar *et al.* 2005), dye (Ma *et al.* 2011), organics (Ma *et al.* 2007), and gas (Wang *et al.* 2013). Silicate ions are anions, and since the surface of bentonite has a negative charge, the bentonite does not readily adsorb the anions. However, Ma *et al.* (2007; 2012) found that when bentonite is modified with acid and quicklime (*i.e.*, CaO), it will produce the novel adsorbent hydroxyl calcium bentonite (HO-CaBen) and increase the adsorption capacity for anionic pollutants such as fluoride, phosphate, acid dyes, and anionic surfactants. It was concluded that the modified bentonite adsorbs not only cations, but anions as well.

The purpose of this research is to find a simple, efficient, inexpensive, and recyclable adsorbent using aluminum salt-modified bentonite. Manohar *et al.* (2005) used polyaluminium chloride to change the spacing of bentonite and absorb metal ions, while Bosetto *et al.* (1993) used aluminum salts to modify bentonite and to absorb organic compounds by hydrogen bonds. Pusino *et al.* (1995) used the same method with bentonite to adsorb metal compounds by means of precipitation adsorption. Therefore, different mechanisms can be adapted for the adsorption of different particles on aluminum-modified bentonite.

In this work, Na-bentonite was modified with aluminum salt to produce a high efficiency adsorbent, which can increase the absorption capacity of silicate. The effects of adsorbent dose, pH, contact time, and ionic strength on desilication and the adsorption capacity for silicate ions were studied in batch systems. Finally, the kinetic process was analyzed using kinetic data and the desorbed rate was measured.

EXPERIMENTAL

Materials

All chemical reagents used in the experiments were of analytical grade from the Chemical Corporation of Tianjin. The water used in all experimental work was double distilled unless stated otherwise. The green liquor was provided by Guizhou Chitianhua Paper Industry Co. Ltd. Its composition was as follows: total alkali 137.21 g/L, active alkali 39.88 g/L, Na_2CO_3 97.27 g/L, Na_2S 31.94 g/L, and SiO_2 4.36 g/L. For adsorption experiments, silicate with 2000 to 8000 mg/L of green liquor was prepared, which was achieved by both diluting and concentrating the green liquor with 4000 mg/L silicate. The raw material used for this work was Na-bentonite, which was obtained from AMCOL International Corporation.

Methods

Preparation of aluminum salt-modified bentonite (AlMB)

Aluminum salt-modified bentonite (AlMB) was prepared as follows. First, 15 g of Na-bentonite was dispersed in 1 L of double-distilled water, and the suspension was named bentonite suspension. Second, 72 g of aluminum salt ($Al_2(SO_4)_3$) was added to the solution. After stirring for 2 h at 1000 rpm, the suspensions were allowed to age for 10 h. The supernatant was decanted, and the residue was placed in an oven at 105 °C for 24 h. Finally, the dried residue was ground, filtered through a 200-mesh screen, and stored in an airtight bag.

Adsorption experiments

The adsorption experiments were carried out in a series of 100-mL beakers. The adsorbent dose (4 to 50 g/L), pH of solution (1 to 14), and contact time (0 to 30 min) were tested. Green liquor in factories generally has a high temperature, so the experiment was carried out at 90 °C. After sedimentation, silicate concentrations in the aqueous phase were determined by measuring the absorbance at 680 nm using a 722N spectrophotometer (Jingke Company; Shanghai, China) (Shi *et al.* 2004). All experiments were carried out in duplicate.

The efficiency of adsorption with different adsorbent doses was studied at 90 °C with a 4 g/L silicate solution, contact time of 10 min, and equilibrium time of 24 h. The final pH of different doses was also studied. The effect of pH on adsorption was investigated in the pH range from 1 to 14 at 90 °C with 4 g/L and 6 g/L silicate solutions, contact time of 10 min, and equilibrium time of 24 h. The effect of contact time on adsorption was studied in the range from 0 to 30 min at 90 °C with 2 g/L, 4 g/L, 6 g/L, and 8 g/L silicate solutions. The equilibrium time was also 24 h.

Adsorption performance

The silicon molybdenum blue method (Shi *et al.* 2004) was used to measure the concentration of silicate by colorimetric analysis. Sodium silicate was converted into silicic acid under slight acid environment, and the molybdate formed a silicon-molybdenum blue complex

The adsorption capacity of silicate by the adsorbent was calculated by the difference in concentrations using the following equation,

$$\eta\ (\%) = \frac{C_0 - C}{C_0} \times 100\% \tag{1}$$

$$\mathrm{q_t}\ (\mathrm{mg/g}) = \frac{C_0 - C_t}{m} \times V \tag{2}$$

where η is the adsorption rate of silicate, q_t is the adsorption capacity of silicate on the adsorbent at time t, c_0 is the initial silicate concentration (g/L), c_t is the equilibrium concentration of silicate in solution at time t (g/L), V is the volume of the working solution (mL), and W is the weight of the adsorbent used (g).

Ions introduce detection by EDX analysis

Prior to analysis, 32 g of AlMB were added to 1 L of green liquor containing 4.36 g silicate and stirred for 10 min at 90 °C. After standing for 24 h, the mixture was filtered. The filter mud and the filtrate were dried at 105 °C. The filter mud was the AlMB that adsorbed the silicate in the green liquor (called spent AlMB), and the filtrate was the green liquor after treatment of AlMB. After drying, the green liquor after treatment by AlMB and the spent AlMB were analyzed by energy dispersive x-ray fluorescence spectroscopy (EDX) (EDAX GENESIS XM, USA) on a Hitachi S4800 scanning electron microscope (SEM; Japan) to detect the ions introduced to the green liquor.

Desorption of AlMB

Four grams of AlMB were added to 100 mL of green liquor with 4 g/L silicate, stirred for 10 min at 90 °C and filtered. The filter mud, which was the spent AlMB, was dried. In the desorption tests, 4 g of spent AlMB was added to 100 mL of either 2 M NaOH or 2 M HCl. The mixtures were shaken at room temperature on a rotary shaker at 500 rpm for 12 h. The suspension was filtered, and the filtrate absorbance at 680 nm analyzed to determine how much silicate leached from AlMB.

RESULTS AND DISCUSSION

Silicate Adsorption Studies

Effect of adsorbent dose

Figure 1a displays the effect of adsorbent dose on the adsorption of silicate by Na-bentonite and AlMB. It is clear that the percent adsorption increased with an increasing adsorbent dose, since for a fixed initial silicate concentration, increasing the adsorbent dose provided a greater surface area for adsorption sites.

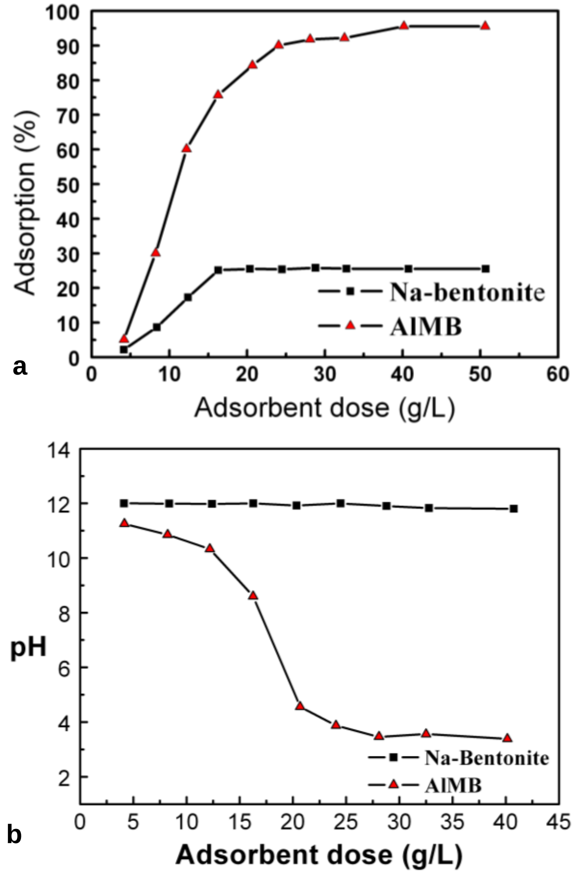

Fig. 1. Effect of adsorbent dose on the (a) adsorption and (b) final pH on Na-bentonite and AlMB. Initial concentration, 4.17 g/L; temperature, 90 °C; equilibrium time, 24 h; contact time, 10 min; and initial pH, 12.01

The results showed that for the complete desilication from an initial concentration of 4 g/L, the maximum adsorbent dosage for AlMB was 40 g/L. No matter how much Na-bentonite was used, the maximum desilication was only 25%. Na-bentonite has so little Al atom on its surface that it is unable to adsorb the Si-OH groups in green liquor by chemical adsorption. So the adsorption of 25% mainly can be attributed to physical adsorption at gaps on the surface of Na-bentonite, and small parts of silicate can come into the gaps during stirring in the green liquor. This indicated that AlMB is more effective than Na-bentonite for the adsorption of silicate. However, Fig. 1b shows the effect of adsorbent dose on final pH by Na-bentonite and AlMB, which can explain why AlMB had a higher efficiency than Na-bentonite. The final pH of AlMB decreased with increasing adsorbent doses, and pH equilibrium was reached at 3.00. However, the adsorbent dose of Na-bentonite had few effects on the final pH. After displacing Na^+ with Al^{3+}, one end of aluminum atoms linked to OH and formed Al-OH (Reaction 1). The other bond linked to bentonite. When AlMB was added to the silicate solution, the bond of Al-OH reacted with Si-OH of the silicate solution to form Al-O-Si (Reaction 2) (Doula *et al.* 2002; Xu and Smith 2012). Because of the increasing hydrogen ionic content, which is shown in Reaction 2, the solution was acidic. This process was chemical adsorption. The adsorption of Na-bentonite was probably caused by the increase of interlayer pacing, which was stretched by van der Waals forces. This process was physical adsorption. There was only a small amount of silicate that was adsorbed in Na-bentonite. Therefore, subsequent adsorption experiments with silicate were performed only on AlMB.

$$\mathrm{Al^{3+} + Na\text{-}bentonite \rightarrow OH\text{-}Al\text{-}Bentonite + Na^{+} + H^{+}} \qquad \text{(Reaction 1)}$$

$$\mathrm{Si\text{-}OH + OH\text{-}Al\text{-}bentonite \rightarrow Si\text{-}O\text{-}Al\text{-}bentonite{+}H_2O} \qquad \text{(Reaction 2)}$$

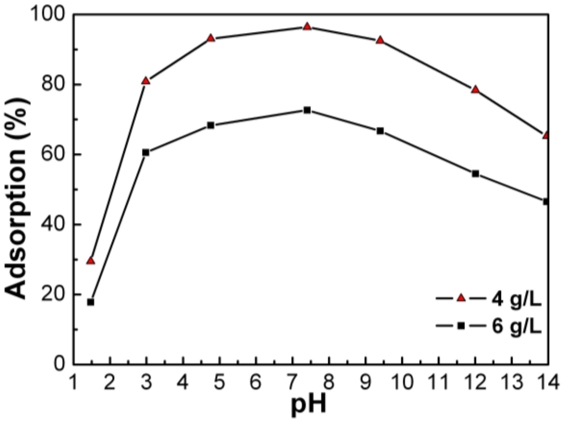

Fig. 2. Effect of pH on the adsorption of silicate onto AlMB. Temperature, 90 °C; contact time, 10 min; adsorbent dose, 16 g/L; and equilibrium time, 24 h

Effect of pH on the adsorption of silicate onto AlMB

The influence of pH on the adsorption of silicate was examined over the pH range 1.00 to 14.00. As shown in Fig. 2, the adsorption increased with increasing pH, flattened from pH 4 to 9, and then decreased with an increase in pH over 10.00. The plat values at an initial concentration of 4 g/L and 6 g/L were found to be 96.36% and 87.23%, respectively. However, green liquor is also strongly alkaline; the pH change in the acid condition is more obvious than in the alkaline condition. The silicate is capable of forming different hydrolyzed species in aqueous solution. According to the literature (Crawlord and Alderfer 1990), SiO_3^{2-} predominates in solutions above pH 13.5, while between pH 10.9 and 13.5, $Si_2O_5^{2-}$ exists in the solution. The two ion forms SiO_3^{2-} and $Si_2O_5^{2-}$ were hydrolyzed to form Si-OH, which react with Al-OH in the AlMB from pH 4 to pH 9; the increase of OH^- ions competed with Si-OH in a strong alkaline (Zamparas *et al*. 2012); thus the rate of desilication decreased. At a highly acidic pH from 1.00 to 3.00, silicic acid polymerized into poly-silicate, which has little Si-OH, and the rate decreased. Consequently, the optimum pH ranged from 3.0 to 10.9. In reality, to save resources, adjusting the pH is unnecessary in green liquor.

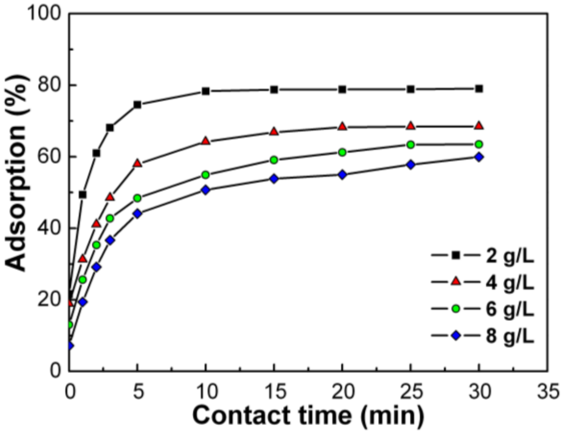

Fig. 3. Effect of contact time and initial concentration on the adsorption of silicate onto AlMB. Initial pH, 12.01; adsorbent dose, 16 g/L; and temperature, 90 °C

Effect of contact time and initial concentration on the adsorption

The rate of silicate adsorption increased with time up to 30 min (Fig. 3). It is evident that most of the adsorption occurred within the first 10 min, beyond which the change of adsorption was very small. Hence, an adsorption time around 10 min for AlMB is sufficient to reach the equilibrium concentration. At a fixed adsorbent dose of 16 g/L, the total available sites on AlMB were limited, resulting in the phenomenon that the lower the initial concentration, the earlier equilibrium was reached. Therefore, this method is more suitable for the desilication of relatively low concentrations of silicate in wastewater from a papermaking mill.

Ions introduced

Aluminum and silicon were not detected in the green liquor treated with AlMB (Table 1). However, 13.17% aluminum and 19.88% silicon were detected in the AlMB (Table 2), verifying that the AlMB adsorbed silicate from the green liquor. Likewise, it demonstrated that aluminum bound tightly on the bentonite and was not free during the desilication process. Excessive aluminum ions were introduced in the alkali recovery system and added to the cooking system. The raw materials containing silicate reacted with the aluminum ions to form aluminosilicate precipitate, which bound to the cooking equipment (Ulmgren 1987).

Table 1. Concentration of Green Liquor after the Treatment of AlMB as determined by EDX

Element	C	O	Na	Cl	S	K
Wt%	6.40	28.8	23.61	2.77	17.75	20.67

Table 2. Concentration of the Spent AlMB in Green Liquor as determined by EDX

Element	C	O	Na	Cl	S	K	Al	Si
Wt%	3.63	17.67	24.53	6.67	5.46	8.99	13.17	19.88

Kinetics of Adsorption Reaction

Figure 4 shows that the adsorption capacities of AlMB increased with an increase in adsorption time. The adsorption process included two stages. The rate of silicate adsorption onto the surface of AlMB was fast in the initial stage, but it slowed down to reach equilibrium. In the second stage, the silicate bound on the AlMB surface must be rearranged so that more chemical binding sites are available. The remaining silicate can be then be continually adsorbed, which is the reason the second stage was too slow. This will be analyzed by kinetic models.

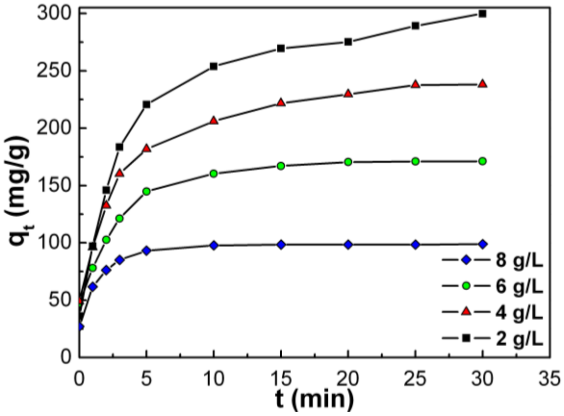

Fig. 4. Adsorbent kinetics of different initial concentrations of silicate on AlMB

The kinetic model

Adsorption kinetic data linearly fit the models of the pseudo-first-order kinetic equation, the pseudo-second-order kinetic equation, and intra-particle diffusion equation (von Oepen *et al.* 1991).

The pseudo-second order kinetic model is based on the assumption that the adsorption follows second-order chemisorption. It is used to describe the adsorption process, and is shown below (Ho 2006):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

In this equation, k_1 (g/(min mg)) is the rate constant of the pseudo-second order model. Also, q_t and q_e are the amount of silicate adsorbed onto the AIMB surface at time t and at equilibrium, respectively. At initial condition of the adsorption, q_t, is equal to zero. Therefore, the two equations can be integrated to yield:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

Rate parameters, k_2 and q_e, can be directly obtained from the intercept and slope of the plot of (t/q_t) against t. The equilibrium concentration can be further calculated as the value of q_e as obtained from the fitting of Eq. (4),

$$q_t = k_p t^{1/2} + b \tag{5}$$

where q_t is the adsorption capacity (mg/g) at time t (min), k_p is the rate constant of intra-particle diffusion model, and b is a constant related to the interfacial layer, which represents the layer of AlMB adsorbing the silicate.

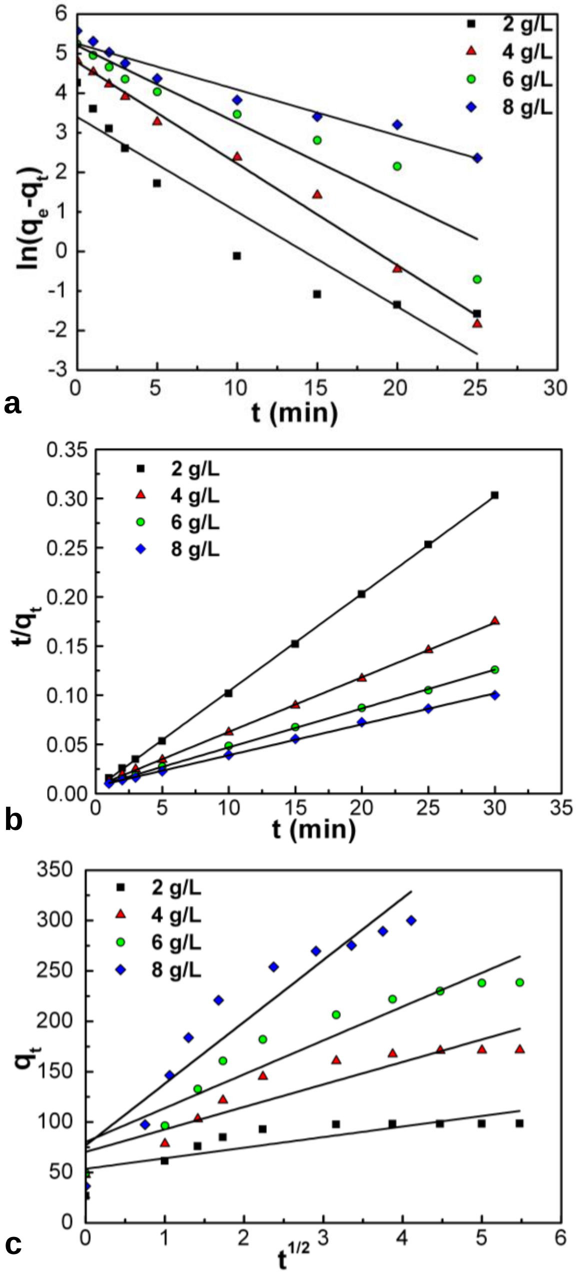

Fig. 5. Linear fit of (a) pseudo-first-order kinetic model, (b) pseudo-second-order kinetic model, and (c) intra-particle diffusion model for different concentrations

Table 3 was deduced from Fig. 5, which shows the relevant parameters of the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, and intra-particle diffusion model. As can be seen in the fitted figures, the pseudo-first-order kinetic model (Fig. 5a) fit poorly except at the lowest concentrations. The intra-particle diffusion model (Fig. 5b) had better goodness of fit at high concentrations. This indicates that with the increase of concentration, molecular polarity started to affect the adsorption. As seen in Table 3, the pseudo-second-order kinetic model described the adsorption process well. The R^2 all reached 0.999. The silicate adsorption process of AlMB corresponds to the pseudo-second-order kinetic model; this model represents the whole process of adsorption, such as the external liquid film diffusion, the surface adsorption, and intra-particle diffusion. Generally speaking, the pseudo-second-order kinetic model provides a more comprehensive description, accounting for the fact that the silicate adsorption of AlMB was affected by both physical and chemical adsorption.

Table 3. Parameters for Kinetic Models for Adsorption of Silicate on AlMB

Concentration g/L	Pseudo-first-order kinetic equation		Pseudo-second-order kinetic equation		Intra-particle diffusion equation	
	k_1	R^2	k_2	R^2	k_p	R^2
2	0.2397	0.8836	0.0196	0.9984	10.5032	0.6435
4	0.2566	0.9901	0.0021	0.9998	22.3126	0.8378
6	0.1956	0.9062	0.0042	0.9995	33.5635	0.8882
8	0.1161	0.9505	0.0013	0.9987	45.9955	0.8879

According to the kinetic parameters and equations of 3, 4, and 5, the equations of the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, and intra-particle diffusion model were calculated (Table 4).

Table 4. Fitted Equations of Adsorption Models

Concentration g/L	Model	Linear fit of equation $y = ax + b$	R^2
2	Pseudo-first-order kinetic model	$\ln(98.18156-q_t)=3.4067-0.23974t$	0.8836
	Pseudo-second-order kinetic model	$t/q_t=0.00503+0.00992t$	0.9984
	Intra-particle diffusion model	$q_t=53.78475+10.50322\ t^{1/2}$	0.6435
4	Pseudo-first-order kinetic model	$\ln(171.4403-qt)=5.2004-0.19556t$	0.9901
	Pseudo-second-order kinetic model	$t/q_t=0.00727+0.00555t$	0.9998
	Intra-particle diffusion model	$q_t=70.42761+22.31261t^{1/2}$	0.8378
6	Pseudo-first-order kinetic model	$\ln(238.4411-q_t)=4.7819-0.25655t$	0.9602
	Pseudo-second-order kinetic model	$t/q_t=0.00739+0.00396t$	0.9995
	Intra-particle diffusion model	$q_t=80.35984+33.56351\ t^{1/2}$	0.8882
8	Pseudo-first-order kinetic model	$\ln(299.9840-qt)=5.2497-0.11605t$	0.9505
	Pseudo-second-order kinetic model	$t/q_t=0.00746+0.00315t$	0.9987
	Intra-particle diffusion model	$q_t=76.87206+45.99547t^{1/2}$	0.8879

The equations with the highest R^2 values in each model were selected from Table 3, and the largest values of R^2 were almost 4 g/L. In addition, the calculated result was

252.5252 mg/g, which agrees well with the test result of 238.4411 mg/g. Hence, the equation of the whole adsorption process is:

$$t/q_t = 0.00727 + 0.00555t \qquad (6)$$

Desorption of AlMB

Desorption of adsorbents is an important practice in industrial production. The results showed that the desorbed rate was 17.01% when HCl solution was used. However, the desorbed rate was 56.78% when NaOH solution was used.

CONCLUSIONS

1. Aluminum salt-modified bentonite is an efficient and novel adsorbent for desilication. The maximum adsorption in green liquor reached 96.37%.
2. The optimum conditions for desilication were as follows: adsorbent dose 20 g/L, reaction time 10 min, and pH value ranging from 4.0 to 10.0. To save resources, the adsorption reaction can be carried out in an alkaline environment with an adsorption rate beyond 70%.
3. The adsorption process of different initial concentrations fit well to the pseudo-second-order kinetic model.
4. The kinetic model equation is $t/q_t = 0.00727 + 0.00555t$, with an R^2 of 0.999. The maximum adsorption capacity was 252.5252 mg/g in green liquor containing 4 g/L silicate, and the adsorption process was affected by both physical and chemical adsorption.
5. The desorption rate of AlMB regenerated in 2 M NaOH solution was 56.78% for silicate.

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