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doi:10.4028/www.scientific.net/AMR.968.116

Orthogonal Experiments for Kaolin Bleaching by Using Sodium Dithionite and Sulfuric acid

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Keywords: Kaolin, bleaching, sodium dithionite, whiteness.

Abstract. The quality of the kaolin is always measured by iron contents since this element gives undesirable reddish color which limits the usage of this type of minerals. Reducing the iron contents to increase the value of kaolin by bleaching process is investigated. The effects of factors which can improve the whiteness of kaolin have been studied. The dosage of sodium dithionite, pH value, solid-to-liquid ratio and reaction time were chose as factors based on mono-factor experimental results. Orthogonal experiments were carried out and the optimum processing conditions of the reductive bleaching were obtained as the dosage of sodium dithionite 3%, pH 2, solid-to-liquid ratio 1:3 and reaction time 45min. After bleaching process described above, we obtained a great improvement in the whiteness from 69.93% to 81.31% and a decrease of Fe_2O_3 content from 0.52% to 0.40% of the kaolin.

Introduction

Kaolin is a kind of white clay which has wide application in many industries, such as paper making, ceramics and porcelain. It is usually accompanied by other minerals such as quartz, feldspars, micas, and iron and titanium oxides [1]. Iron is the main contaminant in kaolin minerals. Iron oxides cause yellow coloration, reduce the whiteness, impair the quality of kaolin and limit the use of kaolin in the industry [2-4].

Magnetic separation, flotation, chemical and biological leaching are some of the commonly techniques for the removal of irons [5-7]. In kaolin minerals, iron can form part or not of the kaolinite crystalline lattice. When iron atoms are in the crystalline lattice, low concentrations do not affect coloration. On the other hand, irons exist in secondary accompanying minerals such as hematite, goethite, pyrite and maghemite which can be removed by magnetic or leaching methods. Chemical methods are effective for iron removal involving the leaching of the kaolin with organic acids or inorganic acids [8]. Also there are reports of biological methods using microorganisms to reducing irons [9].

The present work aims to study the characterization of kaolin clay and the removal of iron in acid leaching conditions using sulfuric acid. In the bleaching studies the effect of parameters was investigated and orthogonal experiments were designed for the optimum processing conditions decision.

Experiments

Materials. The kaolin used in this work was supplied by LongYan Kaolin Clay Co. Ltd. and it was previously milled in the company. The chemical composition of the kaolin was analyzed by X-ray fluorescence (XRF) and listed in table 1. Its original whiteness was 69.93% determined by WSB-3 digital whiteness meter. All of other chemical reagents were commercial sources and were used without further purification.

Table 1 Chemical composition of kaolin sample

Composition/%	SiO_2	Al_2O_3	K_2O	Fe_2O_3	Ti_2O	MgO	Na_2O	CaO	LOI.
Kaolin	49.67	35.00	2.49	0.52	0.04	0.35	0.35	0.19	11.50

Experimental procedure. The kaolin was sieved at 100-mesh in order to prevent agglomeration and get a complete reducing reaction. Bleaching experiments were carried out in a glass flask with mechanical stirring. A certain quantity of clay was dispersed in distilled water in definite ratio and vigorously stirred, dilute sulfuric acid, sodium dithionite and oxalic acid were added in suspended solution in sequence. After reaction for a while, slurry was then filtered, repeatedly washed with distilled water, and dried at 105℃ for 24 hours at a dry oven. Resultant sample was determined by WSB-3 digital whiteness meter to measure the whiteness.

Results and discussion

Effect of sodium dithionite dosage. In order to study the effect of sodium dithionite dosage on resultant whiteness of kaolin, the experiment was carried out using dosage of sodium dithionite varying from 0.5 to 4.5%(mass). From Fig. 1, it can be observed that the whiteness of kaolin was increased stably with increment of sodium dithionite and reached to the maximum about 80.9% at the 3%(mass). As further increasing sodium dithionite usage, the whiteness of kaolin was decreased instead. This is because excessive sodium dithionite react to dilute sulfuric acid generating sulfuric dioxide and elemental sulfur which show light yellow color.

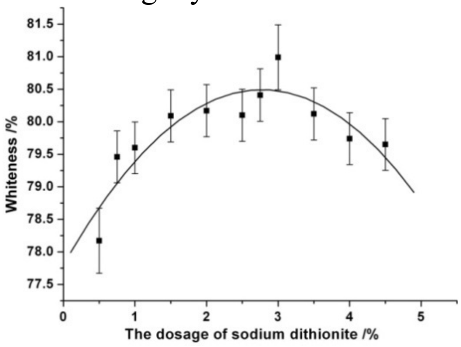

Fig. 1 Correlation between dosage of sodium dithionite and whiteness of kaolin

Effect of pH. The pH value of reaction mixture was adjusted by dilute sulfuric acid. The experiment was carried out as the pH value varying from 0.5 to 4.5. It was noticed from fig.2 that the whiteness of kaolin reached to highest value about 79.5% as pH equal to 2.5. Reduction speed of Fe^{3+} by sodium dithionite decreased clearly as pH value higher than 2.5 which result in lower whiteness of kaolin.

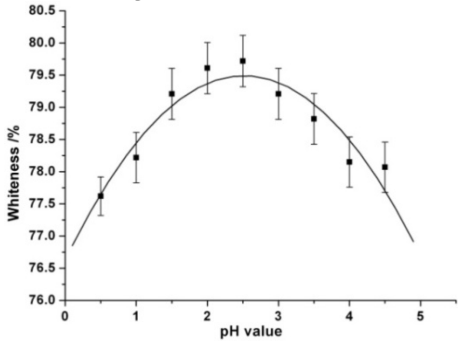

Fig. 2 Correlation between pH value and whiteness of kaolin

Effect of solid-liquid ratio. Solid-liquid ratio is an important parameter which relates to density and reaction effect of mixed solution. This experiment was conducted by varying the solid-liquid ratio from 1:2 to 1:8. The whiteness of kaolin increased and reached a maximum value about 80.1% at 1:4 solid-liquid ratios, and then declined as minifying the solid contents (fig.3). The suspension was well-distributed at suitable solid-liquid ratio and made the reaction effectively. Lower ratio (<1:4) of solution diluted the mixture and restricted the sodium dithionite effect on reduction of Fe^{3+} ions which made the decrease of the whiteness.

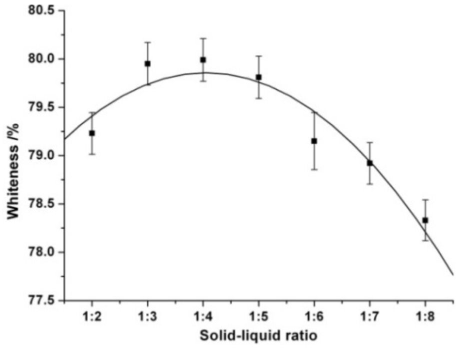

Fig. 3 Correlation between solid-liquid ratio and whiteness of kaolin

Effect of reaction time. From Fig. 4, whiteness exhibited a gradually rise tendency by the prolongation of reacting time. However, the effect of reaction time on the whiteness is not obvious. There was only 0.56 percent rate of increase from minimum time (30min) to maximum time (120min). Therefore, the reaction time was controlled in one and a half hour. It's not necessary to prolong reaction time infinitely.

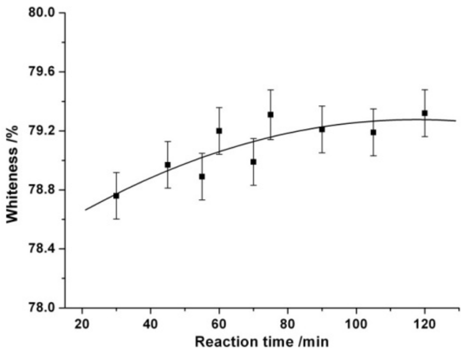

Fig. 4 Correlation between reaction time and whiteness of kaolin

Design of the orthogonal experiment. In order to evaluate the chemical bleaching effect on the whiteness of kaolin, orthogonal experiment was designed to decide the optimal experimental condition of bleaching which involved four factors and three levels. Four factors were the dosage of sodium dithionite (A), pH value (B), solid-liquid ratio (C) and reaction time (D) respectively. The selected three level values were: the dosage of sodium dithionite (A): 1%, 2% and 3%; pH value (B): 1.5, 2 and 3; solid-liquid ratio (C): 1:3, 1:4 and 1:5; and reaction time (D): 30, 45 and 60min which listed in table 2. Thus, a $L_{27}(3^{13})$ orthogonal experiment was carried out to determine the optimal condition and interaction of each factor. The table top design of the orthogonal experiment was shown in Table 3. The experimental results of chemical bleaching were shown in Table 4.

Table 2 Factors and levels investigated in bleaching experiments

code	Factor	Level		
		-1	0	1
A	dosage of sodium dithionite	1%	2%	3%
B	pH value	1.5	2	3
C	solid-liquid ratio	1:3	1:4	1:5
D	reaction time	30	45	60

Table 3 Table top design of the orthogonal experiment $L_{27}(3^{13})$

Column number	1	2	3	4	5	6	7	8	9	10	11	12	13
Factor	A	B	A×B		C	A×C		B×C	D		B×C		

Note: A, the dosage of sodium dithionite; B, pH value; C, solid-liquid ratio; D, reaction time

Table 4 The orthogonal experiment $L_{27}(3^{13})$ of chemical bleaching

	1	2	5	9	whiteness/%
	A/%	B	C	D/min	
1	1(1)	1(1.5)	1(1:3)	1(30)	76.77
2	1	1	2(1:4)	2(45)	76.10
3	1	1	3(1:5)	3(60)	78.25
4	1	2(2)	1	2	79.21
5	1	2	2	3	79.21
6	1	2	3	1	79.21
7	1	3	1	3	78.17
8	1	3(3)	2	1	78.29
9	1	3	3	2	79.57
10	2(2)	1	1	2	80.03
11	2	1	2	3	78.78
12	2	1	3	1	79.35
13	2	2	1	3	79.36
14	2	2	2	1	78.15
15	2	2	3	2	78.71
16	2	3	1	1	79.31
17	2	3	2	2	79.36
18	2	3	3	3	79.36
19	3(3)	1	1	1	80.41
20	3	1	2	3	79.59
21	3	1	3	2	79.45
22	3	2	1	1	80.28
23	3	2	2	2	79.36
24	3	2	3	3	80.48
25	3	3	1	2	81.31
26	3	3	2	3	80.90
27	3	3	3	1	80.10

Note: A, the dosage of sodium dithionite; B, pH value; C, solid-liquid ratio; D, reaction time

Table 5 Range analysis of orthogonal experiment

	A	B	A×B		C	A×C	
	1	2	3	4	5	6	7
K1	78.30	78.74	78.80	78.85	79.42	79.04	78.94
K2	79.16	79.33	79.78	79.46	78.86	79.14	79.22
K3	80.20	79.60	79.08	79.36	79.38	79.48	79.50
R	1.90	0.84	0.98	0.60	0.56	0.43	0.56

Continued:

	B×C	D		B×C		
	8	9	10	11	12	13
K1	79.35	79.00	79.10	79.22	79.44	79.22
K2	79.15	79.23	79.28	79.07	79.07	79.04
K3	79.19	79.43	79.30	79.38	79.16	79.40
R	0.20	0.43	0.20	0.31	0.37	0.36

From Table 4, the results of range analysis suggest that the whiteness of kaolin is influenced by the following factors in descending order: the dosage of sodium dithionite (A) > interaction of sodium dithionite dosage and pH (A×B) > pH (B) > interaction of sodium dithionite dosage and solid-liquid ratio (A×C) > solid-liquid ratio (C) > interaction of pH and solid-liquid ratio (B×C). It shows that the dosage of sodium dithionite, pH and solid-liquid ratio have decisive influence on the whiteness of the final product in the bleaching process. As for reaction time (D), it has no interaction with other factors and its third level is the best from mean value.

As the most important factor affecting the bleaching process, the third level of sodium dithionite dosage (A) is the best. However, considering its interaction with both pH (B) and solid-liquid ratio (C) and interaction between (B) and (C), Fig. 5 was given to get the optimum level of these factors. From Fig. 5(a), it is evident that the optimum factor combination is A_3B_3(the third level of sodium dithionite dosage and the third level of pH), from Fig. 5(b), the optimum one is A_3C_1 (the third level of sodium dithionite dosage and the first level of solid-liquid ratio) From Fig. 5(c), the whiteness of B_3 is higher than another two groups and the whiteness of B_3C_1, B_3C_2 and B_3C_3 almost the same, due to the result of A_3C_1 of Figure 5(b), it should adopt B_3C_1 (the third level of pH and the first level of solid-liquid ratio) here. Therefore, the optimum factor combination for whiteness of kaolin from the result above is $A_3B_3C_1D_3$: 3% of sodium dithionite, slurry pH of 3, solid-liquid ratio of 1:3, and a reaction time of 60min. From Table 2, considering reaction time has little effect on the whiteness, the proximal one is the 25^{th} $A_3B_3C_1D_2$: sodium dithionite 3%, pH 2, solid-liquid ratio 1:3 and reaction time 45min. In this condition, the result showed a significant improvement in the whiteness of kaolin from 69.93 to 81.31%, increased about 11 percentage points. The decrease of Fe_2O_3 content is high from 0.52% to 0.28%. This can be attributed to the greater presence of iron in the kaolinite net, which hinders sodium dithionite access because it exhibits greater crystalline. The concentration of Al_2O_3 showed little change in bleached kaolin.

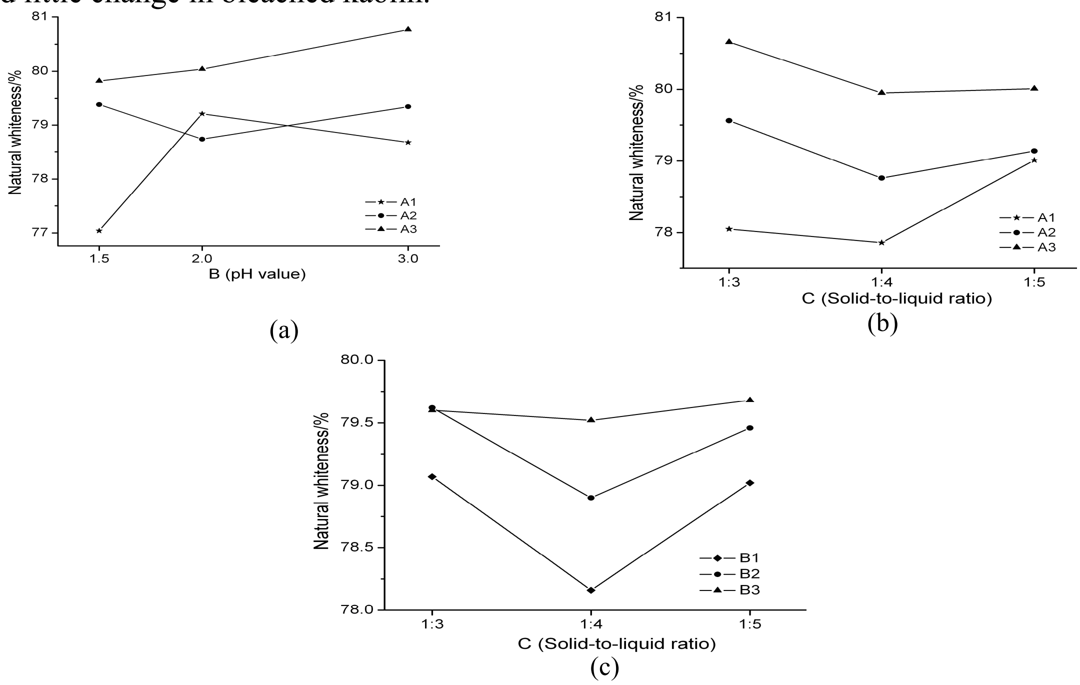

Fig. 5 Interaction between any two factors: (a) interaction of sodium dithionite dosage and pH (A×B), (b) interaction of sodium dithionite dosage and solid-liquid ratio (A×C) and (c) interaction of pH and solid-liquid ratio (B×C)

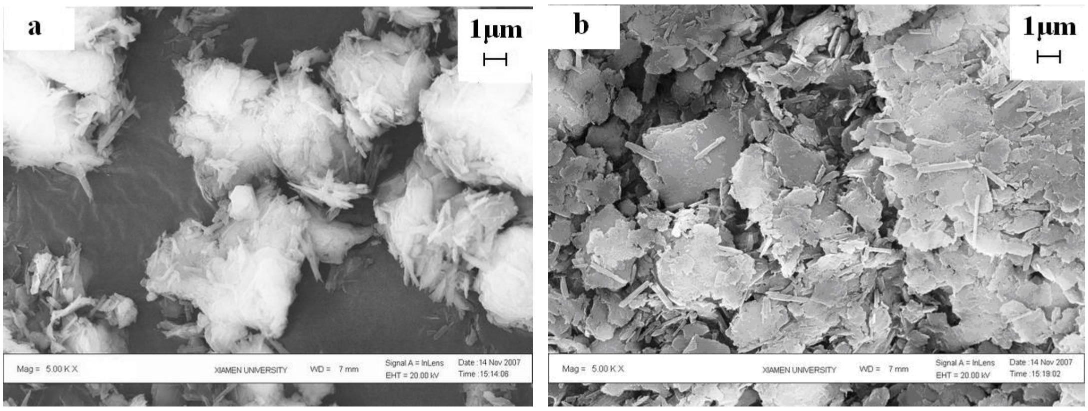

Fig. 6 Scanning electron micrograph of kaolin before (a) and after (b) bleaching with sodium dithionite

Conclusions

This study was conducted with a kaolin sample from which 0.52% of irons had to be removed to increase its whiteness and make it suitable for the production of ceramics. It is shown in this study that the optimum condition of the reductive bleaching of kaolin is: sodium dithionite 3%, pH 2, solid-liquid ratio 1:3 and reaction time 45min. In these factors, the whiteness of kaolin was improved significantly from 69.93% to 81.31%, increased approximately 11 percentage points. The decrease of Fe_2O_3 content is high from 0.52% to 0.28%. Electron micrographs of the kaolin indicated laminated structure has become more clear in the treated sample (Fig. 6a) compared to the untreated one (Fig. 6b). It may thus be concluded that the high whiteness of kaolin can be achieved using sodium dithionite. In addition, the interaction among the dosage of sodium dithionite, pH and solid-liquid ratio is not negligible.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (NNSFC) (Grant No. 51204143).

References

[1] J. Gonzalez, M. Delcruiz, Appl Clay Sci, 33 (2006), 219-229.

[2] S.Chandrasekhar, S.Ramaswamy, Appl. Clay Sci. 33(2006), 269-277

[3] N.Malengreau,, A. Bedidi, J.P.Muller, A.J. Herbillions, Eur. J. Soil Sci. 47 (1996), 13-20.

[4] A. Tuncuk, S. Ciftlik, A. Akcil, Hydrometallurgy, 134(2013), 80-86.

[5] G.D.T.Calderon, J.I.Rodriguez, U.Ortiz-Mendez, L.M.Torres-Martinez, J. Mater. Online 1 (2005),1-8.

[6] F.Larroyd, C.O.Petter, C.H.Sampaio, Miner. Eng. 15(2002), 1191-1192.

[7] G. H. Xia, M. Lu, X. L. Su, X. D. Zhao, Ultrason Sonochem 19(2012), 38-42.

[8] M.Taxiarchou, D.Panias, I.Douni, I.Paspaliaris, A.Kontopoulos, Hydrometallurgy 46(1997), 215-227.

[9] E. Aghaie, M. Pazouki, M. R. Hosseini, M. Ranjbar, Appl Clay Sci. 65 (2012), 43-47.

Metallurgy Technology and Materials III
10.4028/www.scientific.net/AMR.968

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DOI References
[1] J. Gonzalez, M. Delcruiz, Appl Clay Sci, 33 (2006), 219-229.
http://dx.doi.org/10.1016/j.clay.2006.05.001
[2] S. Chandrasekhar, S. Ramaswamy, Appl. Clay Sci. 33(2006), 269-277.
http://dx.doi.org/10.1016/j.clay.2006.06.008
[4] A. Tuncuk, S. Ciftlik, A. Akcil, Hydrometallurgy, 134(2013), 80-86.
http://dx.doi.org/10.1016/j.hydromet.2013.02.006
[6] F. Larroyd, C.O. Petter, C.H. Sampaio, Miner. Eng. 15(2002), 1191-1192.
http://dx.doi.org/10.1016/S0892-6875(02)00181-4
[7] G. H. Xia, M. Lu, X. L. Su, X. D. Zhao, Ultrason Sonochem 19(2012), 38-42.
http://dx.doi.org/10.1016/j.ultsonch.2011.05.008
[8] M. Taxiarchou, D. Panias, I. Douni, I. Paspaliaris, A. Kontopoulos, Hydrometallurgy 46(1997), 215-227.
http://dx.doi.org/10.1016/S0304-386X(97)00015-7
[9] E. Aghaie, M. Pazouki, M. R. Hosseini, M. Ranjbar, Appl Clay Sci. 65 (2012), 43-47.
http://dx.doi.org/10.1016/j.clay.2012.04.011