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CETEM

Série Tecnologia Mineral

Bleaching of Brazilian Kaolins by Using Organic Acids and Fermented Medium

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A **Série Tecnologia Mineral** publica trabalhos na área mínero-metalúrgica. Tem como objetivo principal difundir os resultados das investigações técnico-científicas decorrentes dos projetos desenvolvidos no CETEM.

Celso de O. Santos COORDENAÇÃO EDITORIAL E REVISÃO

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Indexado no *Chemical Abstracts* e no *Imm Abstracts*.

Mesquita, Luciana Maria S. de

Bleaching of Brazilian kaolins by using organic acids and fermented médium/Luciana Maria S. de Mesquita; Terezinha Rodrigues e Sandro de S. Gomes. – Rio de Janeiro: CETEM/CNPq, 1996.

16p. - (Série Tecnologia Mineral, 72)

1. Caulim – Branqueamento. 2. Ácidos orgânicos. I. Rodrigues, Terezinha. II. Gomes Sandro de Souza. III. Centro de Tecnologia Mineral. IV. Título. V. Série.

ISBN 85-7227-089-2
ISSN 0103-7382 CDD 622.361

PRESENTATION

The brightness of kaolin hás been receiving increasing attention from industry and the technical-scientific literature.

This paper, presented in an International Seminar in England and accepted for publication in a nearest edition of the "Minerals Engineering", reports some of the results achieved at the CETEM's laboratories for the bleaching of kaolins.

Rio de Janeiro, July, 1996.

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Director

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ABSTRACT

The use of kaolin for both coating and filler applications in the paper industry requires a high brightness grade and, consequently, treatment for the removal of iron that adds color to the mineral, decreasing its commercial value.

This paper presents a preliminar study of bleaching treatments with different samples of Brazilian kaolins by using organic acids and fermented medium from Aspergillus niger *cultivation as leaching agent. The brightness of a kaolin sample reached levels for filler clay (sample not submitted to magnetic separation) and coating clay (sample submitted to magnetic separation), not found for conventional methods, when fermented medium and oxalic acid were used as a bleaching agent.*

Key words: *Kaolin, bleaching, organic acid,* A. niger.

RESUMO

A aplicação do caulim como carga e cobertura na indústria do papel necessita de um elevado grau de alvura. Consequentemente, a remoção de ferro é requerida já que confere cor indesejável ao mineral, diminuindo seu valor comercial.

Este artigo apresenta um estudo preliminar do alvejamento de diferentes amostras de caulim brasileiro, tendo como agentes lixiviantes ácidos organicos e meio fermentado por Aspergillus niger. *Índices de alvura para aplicação como carga (amostra não submetida à separação magnética) e cobertura (amostra submetida à separação magnética), foram atingidos para uma determinada amostra, quando meio fermentado e ácido oxálico foram empregados como agentes de alvejamento.*

Palavras-chave: *Caulim, alvejamento, ácidos orgânicos,* A. niger.

1. INTRODUCTION

The term kaolin is used for near-white clay deposits which are dominantly comprised of kaolinite mineral, or for products refined from such deposits. Kaolin is mined and processed in many nations. Brazil is among the major exporting nations. In 1992, Brazil produced 790,000 ton of processed kaolin, being 495,000 ton exported. Kaolin is one of the most important industrial minerals in Brazil in terms of volume, quality and perspective of enlargement for export market. In large expansion of its productive capacity, Brazil could be the third world producer by 1996, with 1.3 million ton./year.[1]

For most modern industrial applications kaolin must be extensively refined and processed to enhance some important commercial characteristics. In the case of paper industry, the main consumer, one of the most important specifications for kaolin is the brightness. In general, a brightness of 79 - 83.5% is required for filler clay and 83.5-85.5% for coating clay.[2]

The presence of iron oxides in kaolin has detrimental effect on the colour of the clay, which declines in brightness with increasing iron content. The process employed for improving the brightness of the mineral product can be classified as physical and chemical ones, or both.

High intensity magnetic separation is a standard method used in the industry, which removes substantial quantities of iron and titanium as mineral impurities, consequently improving its brightness. The chemical methods consist of leaching with mineral acids and treatment with reducers, such as sodium dithionite plus aluminium sulphate, sulphur dioxide plus aluminium powder and sulphur dioxide plus zinc powder. These bleaching methods are usually suitable for achieving a higher extent of iron removal but, at the same time, they are more expensive, the operating conditions are very complicated, and the processes are environmentally dangerous.

Heterotrophic microbial leaching have been studied for many industrial minerals. GROUDEV and GROUDEVA[3,4] demonstrated that iron could be removed from quartz sand by using microbial leaching to remove ferrugineous compounds. This group has also demonstrated microbial removal of iron from clays and improvement of kaolin and ceramic properties via the action of metabolic products.[5]

The ability of heterotrophic microorganisms to leach iron from oxide minerals can be used for the removal of this element from kaolin, improving its brightness. The solubilization of iron occurs through the action of organic acids and other excreted metabolites, acting as complexing agents, as well as enzymatic and non-enzymatic iron reduction.

Microbiologically produced organic acids of particular effectiveness are citric and oxalic acids, produced by many fungi in their metabolism of carbohydrate substrates. For low-grade hematitic laterites, TZEFERIS *et al.*[6] demonstrated that citric acid was the most effective organic acid for nickel extraction while oxalic acid displayed remarkable selectivity on iron extration.

The aim of the present study was to investigate the possibility of using fungal fermented medium for the removal of iron, and consequently to improve the brightness, of four different samples of Brazilian kaolins. Also, a chemical bleaching experiment was conducted with citric and oxalic commercial acids for the same purpose.

2. EXPERIMENTAL

2.1 Kaolin Samples

Four samples of kaolin from different regions of Brazil were used in this study. The mineralogical and chemical analyses are presented in Tables 1 and 2, respectively.

Table 1 - Mineralogical qualitative analysis of kaolin samples

Sample	Region	Major Minerals
MFE	Laranjal do Jari / AP	kaolinite, quartz, magnetite/ hematite
RCA	Rio Capim / PA	kaolinite, quartz, magnetite/ hematite
MPA	Monte Pascoal / BA	not available
MAC	Macacos / MG	kaolinite, muscovite, quartz

Table 2 - Chemical analysis - Fraction: -44 μm (% wt)

Sample	Chemical Composition						
	SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O
MFE	48.50	32.30	0.16	1.60	1.30	-	-
RCA	47.40	28.96	0.05	3.67	2.32	2.18	0.87
MPA	46.50	33.90	0.40	1.60	0.90	1.20	0.16
MAC-1*	-	-	-	0.35	0.34	-	-
MAC-2**	-	-	-	0.34	0.16	-	-

*Sample not submitted to magnetic separation.

**Sample submitted to magnetic separation.

The Ore Dressing Department from CETEM (Center for Mineral Technology) provided the samples as kaolin pulp, after dispersion and desanding operation, as well as the mineralogical composition and chemical analysis.

2.2 Microorganism and Media

The microorganism used in this work was a strain of *Aspergillus niger* isolated from a talc ore[7]. The strain was maintained in potato-gelose [8] in order to produce spores. For fermentation, it was used the medium with the following composition (g/L): Sucrose, 80.0; $(NH_4)_2SO_4$, 3.0; KH_2PO_4, 2.0; $MgSO_4.7H_2O$, 0.2 . The pH of the medium was adjusted to 7.0 with NaOH solution 0.1 M.

The surface process was used for conducting the fermentation at 23°C in Erlenmeyer flasks. At the end of the process, indicated by constant acidity, the fermented medium was filtered and the content of citric and oxalic acids were determined. The Marrie and Boulet method[9] was used for citric acid determination, and an enzymatic method was used for oxalic acid determination (Sigma Diagnostics).

2.3 Bleaching Experiments

The bleaching tests were carried out at 60°C in 250 ml flasks containing 50 ml of kaolin pulp and 50 ml of bleaching solution. As bleaching solutions citric and oxalic commercial acids, as well as fermented medium, were used. The final pulp density at the systems were around 10% for all the experiments. The systems were continuously agitated in rotatory shaker for 3 hours.

The ISO brightness was determined after filtration and drying the solid at 100°C, in a ELREPHO-ZEISS photometer. The dissolved iron was determined in the filtrate by atomic absorption spectrophotometry.

All the experiments were conducted in duplicate.

3. RESULTS AND DISCUSSION

This study is part of an Industrial Mineral Program in progress at CETEM (Center for Mineral Technology). From previous studies, not described in this paper, it was verified the susceptibility of bleaching kaolin with organic acids. It was observed a greater effectiveness of oxalic and citric acids on kaolin bleaching, when compared with other organic acids such as acetic, lactic and ascorbic. Another important observation was the influence of the temperature on the bleaching process. The use of high temperatures instead of raising the concentration was more effective in order to enhance the bleaching process of kaolin when oxalic commercial acid was used. These previous results indicated that these two acids, citric and oxalic, would be more promising to investigate than other organic acids microbiologically produced.

The use of bioleaching as a bleaching process requires, in this case, a two-stage process in which leaching is carried out with acids and metabolites produced in a first stage, as schematized in Figure 1.

These two stages (fermentation and bleaching) were required due to the mineral granulometric characteristics (very small particles) which rendered difficult the further separation, besides the necessity of adapting the atrain to the mineral at a high iron concentration.

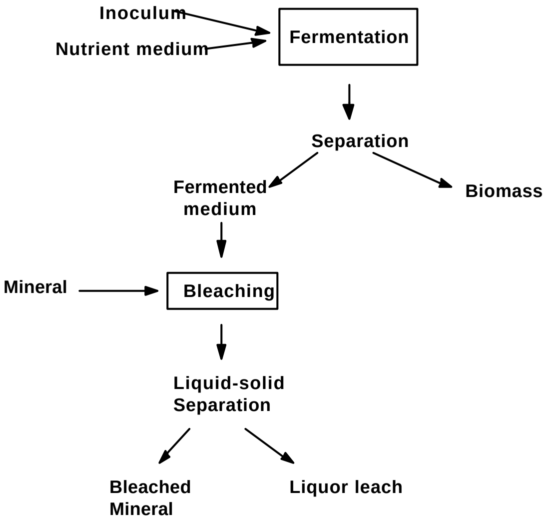

Figure 1 - Steps involved in minerals bioleaching by heterotrophic microorganisms

Table 3 summarizes the characterization of the filtered fermented medium used for the experiments of bleaching, after 40 days of fermentation, in terms of citric acid, oxalic acid, pH and final acidity.

Table 3 - Characterization of the filtered fermented medium from *A. niger*

pH	Final acidity (H^+ eq./L)	Citric acid (M)	Oxalic acid (mM)
1.62	1.16	0.28	60

Tables 4, 5, and 6 show the results of the bleaching tests carried out with citric acid, oxalic acid and fermented medium, respectively.

Table 4 - Bleaching of samples kaolin with citric acid. Final concentration at the bleaching system: 0.25M

Samples	Initial Brightness (ISO)	Final Brightness (ISO)	Brightness Increase
MFE	79.2	80.3	1.1
RCA	83.5	84.1	0.6
MPA	82.7	83.2	0.5
MAC-1	62.9	64.4	1.5
MAC-2	76.7	77.1	0.4

Table 5 - Bleaching of samples kaolin with oxalic acid. Final concentration at the bleaching system: 0.25M

Samples	Initial Brightness (ISO)	Final Brightness (ISO)	Brightness Increase
MFE	79.2	80.4	1.2
RCA	83.5	85.5	2.0
MPA	82.7	84.7	2.0
MAC-1	62.9	67.8	**4.9**
MAC-2	76.7	80.3	**3.6**

Table 6 - Bleaching of samples kaolin with filtered fermented medium. Final concentrations at the bleaching system: Citric acid 0.14M, Oxalic acid 30 mM.

Samples	Initial Brightness (ISO)	Final Brightness (ISO)	Brightness Increase
MFE	79.2	80.8	1.1
RCA	83.5	85.0	1.5
MPA	82.7	84.0	1.3
MAC-1	62.9	66.2	**3.3**
MAC-2	76.7	81.4	**4.7**

For better evaluation of the action of organic acids and fermented medium, it was interesting to compare the increase of the sample brightness. These values were obtained by the difference between the final and initial brightness of each sample.

The first aspect that should be detached from the previous results is the effectiveness of both commercial acids and fermented medium on the bleaching of kaolin samples. In the case of RCA, MPA, MAC-1 and MAC-2 samples, could be observed that the brightness increases were very different among the bleaching agents used, while for MFE sample the levels were very similar (Tables 4, 5 and 6). These results recommends additional studies about the mechanisms involved in the bleaching process by using organic acids and fermented medium as well as its relation to the iron form occurring in the mineral sample, providing the best evaluation of the method.

Due to its great application in the food industry, the majority of the studies found in the literature showed information about the citric acid production. However, for removal of iron from minerals, the best results are provided by oxalic acid[10,11], which is an undesirable by-product of commercial citric acid fermentation. According to ALIBHAI *et al.*[10], citric acid and oxalic acid act on the oxidized mineral through an initial acid-base reaction, carried on by chelation and complexation of metal ions. In the case of iron, a reduction from Fe^{+3} to Fe^{+2} could occur by the action of oxalic acid. This could explain the best results reached with oxalic acid when compared to citric acid.

The results obtained with filtered fermented medium should be emphasized, considering the final concentrations of citric and oxalic acids on the bleaching system (0.14 M and 30 mM, respectively), that were inferior to those employed when synthetic solutions were used (0.2 5 M). The increases of brightness were similar to that of oxalic acid one (0.25 M), that provided the best results. This behavior could be explained due to the possible action of others metabolites present in the fermented medium as well as an enzymatic action. By now, it is not still possible to attribute enzymatic activity of the fermented medium, as no tests were conducted to evaluate this mechanism on the removal of contaminants from the mineral. However, a possible enzymatic involvement can not be neglected as the fermented medium was not subject to harmful conditions that could inactive possible excreted enzymes.

From Table 7 it could be observed the marked action of the oxalic acid and fermented medium on the iron leaching. Despite the negligible removal, the increases in the associate brightness were significant, see Tables 4, 5 and 6.

Table 7- Iron leaching % during the bleaching tests

Bleaching agent	Samples				
	MFE	RCA	MPA	MAC-1	MAC-2
Citric acid	0.04	0.06	1.48	-	0.02
Oxalic acid	1.01	0.87	7.54	-	9.33
Fermented medium	0.22	0.18	5.11	14.3	5.83

Table 8 shows the best results obtained with conventional treatments conducted at CETEM for the same samples. A comparison among these results and those obtained with oxalic acid and fermented medium demonstrate an inferior increase in brightness for the MFE, RCA and MPA samples. Nevertheless, the results obtained with oxalic acid and fermented medium were not conducted in optimal conditions leading up to a possibility of achieving even better results. In the case of the MAC-1 and MAC-2 samples the brightness levels reached were satisfactory, providing better results than the conventional process, with its optimal conditions well defined.

Table 8 - Results obtained with conventional treatments realized at DTM/CETEM.

Sample	Initial brightness (ISO)	Final brightness (ISO)			
		Sodium ditionite	Aluminium powder	Zinc powder	Ozone
MFE	79.9	82.3	84.5	83.9	-
RCA	83.3	87.9	88.4	88.2	-
MPA	83.0	87.8	-	-	86.7
MAC-1	62.9	65.4	65.0	67.8	-
MAC-2	72.8	74.9	74.4	74.6	-

A particular test was carried out with MAC samples (both submitted and not submitted to magnetic separation). In this test the sample was consecutively bleached (three times) with filtered fermented medium and oxalic acid as bleaching agent. The results are presented at Table 9.

Table 9 - Consecutive bleaching of MAC samples with filtered fermented medium and oxalic acid*.

Sample	Initial Brightness (ISO)	Final Brightness (ISO)		Brightness Increase	
		Oxalic Acid	Fermented Medium	Oxalic Acid	Fermented Medium
MAC-1	62.9	81.2	73.6	18.3	10.7
MAC-2	76.7	87.2	83.8	10.5	7.1

* The final concentrations of organic acids at the bleaching system were the same used on the previous tests.

The results showed a great increase of brightness on the MAC samples. These increases overcome the results reached with the conventional methods, with the additional advantage of producing less-aggressive effluent to the environment.

4. CONCLUSIONS

The results obtained in the bleaching experiments with fermented medium and oxalic commercial acid showed the possibility of using these solutions as bleaching agents.

The consecutive bleaching test carried out with MAC samples (both submited and not submitted to magnetic separation), showed the potential possibility to improve the brightness. The brightness of the MAC-1 sample reached levels for filler clay and the MAC-2 sample reached levels for coating clay, after three cycles of bleaching, indicating that more satisfactory results could be taken with an optimization of the bleaching conditions.

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