

Extraction of Montmorillonite Mineral Iron-oxides With Organic Acids

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Abstract: Extraction of montmorillonite mineral with high content of iron oxide by means three organic acids (citric, gluconic and oxalic) was studied. The first two release small quantities of iron oxides from the montmorillonite, which means they will not be adequate for large-scale processes. Oxalic acid is capable of dissolving all the extracted iron in montmorillonite, thus making the montmorillonite suitable for its basic industrial application especially in oil and gas industry.

Key words: montmorillonite, extraction, organic acids, oxalic acid, iron oxides

INTRODUCTION

Montmorillonite is a mineral which appears in nature joined to other minerals such as feldspar, quartz, biotite, pyroxene, zircon and other mineral of volcanic igneous rocks, although it also combines with heavy metals, mainly iron oxides and hydroxides. Great parts of the montmorillonite are contaminated by iron oxides at concentrations of 7-8 %wt⁽¹⁾

Montmorillonite is a raw material for a lot of industrial process such as drilling mud and cement additives, paper manufacture, to decolorize oils, ceramic material, fat and greases, foundry molding and iron pellets.

The important consideration in the use of a premium montmorillonite in oil & gas industry are the properties that good montmorillonite gives good loss control, good rheological properties, good a lightweight cementing system and cost-effectiveness.

As many of montmorillonite beds with a potential economic interest are contaminated by iron, several chemical and physico-mechanical methods were developed for removing iron

oxides, so increasing the quality of it used in oil and gas industry⁽¹⁾. The efficiencies of the latter methods, ^(6,9) as well as those of magnetic separation, are highly dependent on the properties of the extracted material, which restricts their application.

Chemical methods, ^(5,8) the most used nowadays, are based on utilizing strong reducing agents (e.g. sodium dithionite) at low pH, attaining high levels of iron removal. However, they also have various drawbacks: recalcitrant effluents, extreme working conditions, and a high economic cost. The latter drawback can prevent the process being used when the iron content is high because of the quantity of the chemical reagent needed.

An alternative to the classical chemical methods is the use of organic acids, ^{7,3,10} which dissolve the iron oxides by direct attack of H⁺ ions over the mineral matrix, maintaining them in solution by forming soluble complexes and chelates. Organic acids can be

produced by fermentation with filamentous fungi such as *Aspergillus* and *Penicillium*, using as substrate residues with a high organic carbon content. The exhaust fermentation medium can be the extracting agent for dissolving the montmorillonite iron-oxides. This process is economically favorable, besides producing effluents which are easy to purify. This fact would allow the use of montmorillonite deposits which currently are not exploited because they are unprofitable.

In this study the extracting montmorillonite capacity of citric, gluconic and oxalic acids were analyzed.

MATERIALS AND METHODS

Montmorillonite

Sample from Malaysian local montmorillonite in Tawau district. This area is underlain mainly by high level of alluvium and volcanic rock, and occur in a bed underlying by Pleistocene to Holocene in Age (Yusairi & Yan, 1995).

From laboratory investigation, it showed that Malaysian local montmorillonite has more impurity materials such as quartz, kaolinite, illite, muscovite and hematite. Iron is present as magnetite and as amorphous oxides and hydroxides (analysis by XRD model D-500, Siemens).

Montmorillonite extraction process

Experiment were carried out in 250 cm³ Erlenmeyer flasks with 10 gr montmorillonite and 95 cm³ of extracting solution. The total operating volume was 100 cm³. The treatment lasted for 5 h, in a 3.3 Hz rotating shaker at 45°C.

The activity of three acids (citric, gluconic and oxalic) was studied at different concentration

(1-40 kg m⁻³) and pH values 1.3 – 9.7. the pH was modified by adding concentrated HCl or NaOH.

A more detailed study for oxalic acid was carried out at concentration of 0.7 – 7 kg m⁻³ (corresponding to 1-10 kg m⁻³ of dehydrated oxalic acid) and at the natural pH of the solution.

Kinetic study

For the treatment with oxalic acid a kinetic model^{20,21} was employed, the equation of which would be :

$$\frac{dC_{Fe}}{dt} = k (C_{Fe \max} - C_{Fe}) \dots\dots\dots (1)$$

Where: C_{Fe}, dissolved iron concentration; k, kinetic coefficient; C_{Fe max}, maximum attainable iron concentration. Its value can be limited by the medium extracting capacity or by the available iron in the solid; t, treatment time.

By integrating eqn (1) between the initial moment (t = 0, C_{Fe} = 0) and the conditions corresponding to a time t, eqn (2) is obtained, from which the value of the kinetic constant can be deduced:

$$\ln \left[\frac{C_{Fe \max}}{C_{Fe \max} - C_{Fe}} \right] = kt \dots\dots\dots(2)$$

Kinetic constants from the experiments at different temperature were used to estimate activation energy (E_a) using the eqn (3):

$$\ln k = \ln A - \frac{E_a}{R T} \dots\dots\dots (3)$$

where: A, arhenius constant; R, ideal gases universal constant; T temperature, E_a, activation energy.

analysis

The dissolved iron concentration was followed by atomic absorption spectrophotometry²² at 248.3 nm in a Perkin-Elmer ICP/5000 instrument (Germany). A commercial solution of Fe(III) of 1000 ppm (Merck, Darmstadt, Germany) was the standard, properly diluted for calibrating in a range of 1.3 – 5 mg dm⁻³.

RESULTS

Citric Acid

Experiments at citric acid concentration of 1-40 kg m⁻³ and pH 1.3 – 9.7 were performed, and results for a 5 h treatment are shown in figure 1

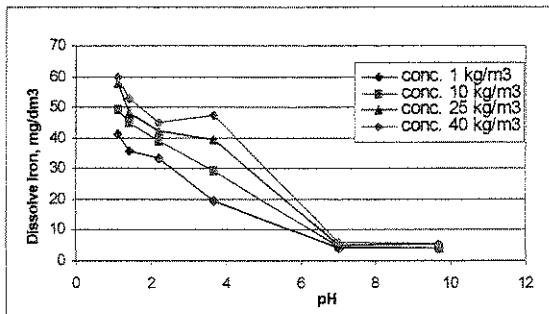


Fig. 1. Effect of citric acid as montmorillonite extracting agent for a treatment time of 5 h.

As can be seen, an increase in concentration favors the iron dissolution at all pH values. However, the experiments above pH 3 reduced the concentration of dissolved iron, down to a value of 4 mg dm⁻³. The solubilization of iron appears to be better as the pH decreased to 3 and then increased up to pH 1.3, when values of

41.17 mg dm⁻³ soluble iron are obtained for 25 – 40 kg m⁻³ citric acid. This fact suggested trying a lower pH; hence at pH 1.3 a solubilization of 59.84 mg dm⁻³ iron was achieved for 40 kg m⁻³

citric acid. To determine if the HCl added to reduce the pH 1.3 was responsible for this fact, a series of four experiments with 1, 10, 25, 40 kg m⁻³ citric acid at pH 1.3 were carry out, comparing the results with the ones from four solutions of HCl in water (prepared with the same quantity of HCl as the one employed for modifying the pH of citric acid solutions). Table 1 clearly shows that the high quantity of dissolved iron is basically due to the added HCl and not to the citric acid solution.

Gluconic Acid

Te experiment was done in an analogous way to that shown for citric acid. Figure 2 shows the results, which in every case gave values lower than those with citric acid. The trend is the same, but from pH 9.71 to 7.03, the value for each concentration are relatively stable. They undergo an increase until pH 2.23,

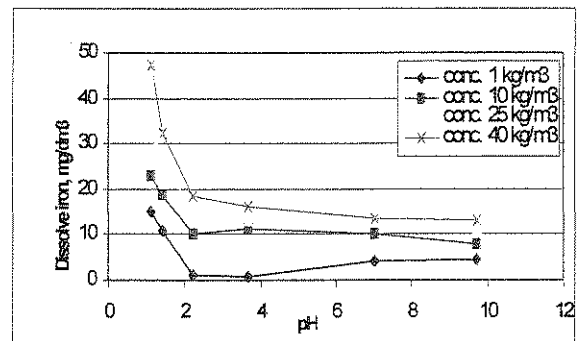


Fig. 2. Effect of gluconic acid as montmorillonite extracting agent for a treatment time of 5 h.

reaching the highest value of 47.50 mg dm⁻³ for pH 1.3 at 40 kg m⁻³. the conclusion is also that gluconic acid does not act as a good extracting agent.

Table 1
Dissolved iron for a treatment time of 5 h with citric acid and hydrochloric acid solutions

Citric Acid (kg m ⁻³)	Hydrochloric acid (kg m ⁻³)	Dissolved iron (mg dm ⁻³)	
		With citric Acid	With hydrochloric acid
1	17.5	41.17	31.5
10	18.3	49.18	41.3
25	19.0	58.16	43.5
40	19.3	59.84	52.7

Oxalic Acid

Figure 3 shows the dissolved iron after 5 h, for concentration of 1-40 kg m⁻³. For the highest value, 40 kg m⁻³, the solubilized iron only appears at pH 1.3, because pH values higher than its natural pH, the solubility of oxalic acid is less than this value.

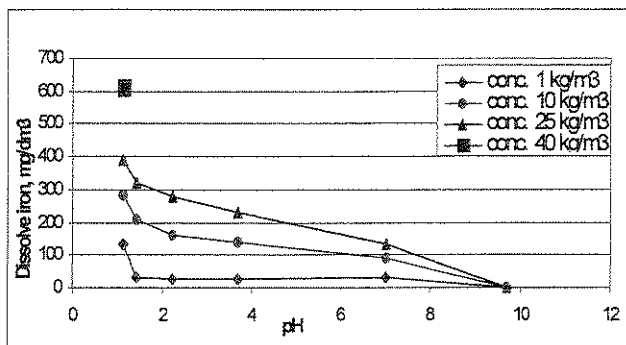


Fig. 3. Effect of oxalic acid as montmorillonite extracting agent for a treatment time of 5 h.

The results are different from those of the other acids. With oxalic acid, solubilized iron reaches 131.7 – 613 mg dm⁻³ for several concentrations at low pH (1.3 – 1.44) values, and quickly decreases when the pH rises, coming near to zero for pH 9.71 or higher.

This great extracting capacity of oxalic acid is intrinsic and not due to HCl as in the previous cases. Its greater acidity implies that it is necessary to add less HCl to reach low pH value. Besides, when experiments are carried out at 10 and 25 kg m⁻³.

Because of the results obtained with oxalic acid, it is convenient to do a more detailed study to determine its maximum extracting capacity for the iron in the montmorillonite, as well as the kinetic parameters defining the process velocity. Table 2 shows the experiments performed in a range of 0.7 – 7 kg m⁻³ oxalic acid at its natural pH. The temperature varied between

Table 2
Dissolved iron concentration after oxalic acid extraction

Oxalic acid (kg m^{-3})	pH	Dissolved iron (mg dm^{-3})
7	1.12	985
5.5	1.09	735
4.5	1.20	620
2.5	1.35	313
1.5	1.68	295
0.7	2.02	30

30 and 80°C and the experiments were continued for long enough to enable the highest iron concentration for each solution of oxalic acid to be achieved. The maximum iron concentration reached in each experiment depended on the concentration, but not on the operating temperature. Nevertheless, high

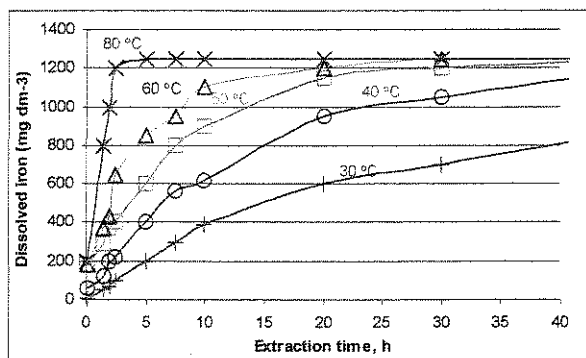


Fig. 5 Kinetic modeling to eqn. (1) of oxalic acid extracting at different temperature

Temperatures greatly reduce the extraction time needed to reach a maximum dissolved iron concentration. For instance, with 7 kg m^{-3} oxalic acid a maximum concentration of 985 mg dm^{-3} in 200 h at 30°C was achieved, at 80°C the extraction time needed to reach the same concentration of iron was only 2 h. Temperature only accelerates the dissolution

process, thus temperature selection will be a compromise between the energy demands and the extraction time. Figure 4 shows the fitting to this model of the results from experiments at different temperatures with 7 kg m^{-3} oxalic acid.

Kinetic Study

From the results of extraction experiments at different temperatures, the kinetics of the process with oxalic acid was studied. The highest dissolved rates were obtained at the beginning of the experiment, after which the rate decreased, and the dissolved iron concentration rose until the maximum iron concentration was attained. In our case, the process consists of a reaction between a solid (montmorillonite iron-oxide) and a liquid (extracting solution), and the model (eqn (1)) was employed to describe the kinetics of the extracting of iron oxides.

DISCUSSION

Among the tree acids, only oxalic acid is suitable for use on a large-scale. It is capable of removing the iron from montmorillonite at the tested operating conditions. The soluble iron from effluent can be precipitated in a

environmental problems. Organic acid concentration, temperature and extraction time are the parameter to be optimized. In this study oxalic acid removed 100% of the iron from montmorillonite higher than obtained with ascorbic acid, only 80% iron was removed. Bonney³ Indicates that a mixture 2:1 citric : oxalic is adequate for reducing the iron oxides content for a quartz sand 37%, if extraction is carried out at 90°C. In our case, oxalic acid is the only active agent for dissolving iron oxides, but mixture of citric : oxalic did not improve the results (data not shown). The extraction in the present study was carried out at lower temperatures, so offering a considerable energy saving in relation to the study of Bonney.

CONCLUSIONS

Oxalic acid is capable of dissolving iron oxides from montmorillonite, but extraction is effective only in a strongly acid medium (pH < 2). At this condition, oxalic acid dissolves a great quantity of iron, forming a soluble complex. The effluent from extracting process is easier to manage than that from chemical process. For petroleum industrial application oxalic acid would be available at a low price.

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REFERENCES

1. A. Samsuri, R. Junin, and A.M. Osman, 2001, The Utilization of Malaysian Local Bentonite as Extender and Free Water Controller in Oil-Well cement Technology, paper SPE 68674.
2. Blancarte-Zurita, M.A., Branion, R.M.R. & Lawrence, R.W., 1987, Application of Shrinking particle model to the kinetics of microbiological leaching. In *Fundamental and Applied Biohydrometallurgy*, eds R.W. Lawrence R.M.R., Branion & H.G. Ebner. Elsevier Science Publishers, Amsterdam, pp. 243-53.
3. Bonney, C.F., 1993, Removal of iron from industrial minerals. *Mines Carriers : Tech.*, (4-5), pp. 21-3
4. Cameselle, C., *et.al*, 1995, Leaching of iron by a spent fermentation liquor: influence of temperature, pH, agitation and citric acid concentration, *J.Ind.Microbiol.*, 14, 288-92.
5. Froment, G.F. & Bischoff, K.B., 1979, *Chemical reactor analysis and design*, J.Wiley and Sons, NY.
6. Gou, M.X., Zheng, J., Zeng, M., Qu, H. Q. & Jia, G.R., 1993, The magnetic circuit calculation and technical properties of a newly designed commercial sized metal-belt-type high gradient magnetic separator, *Coal Sci.Min. Technol.*, 21, pp. 603-14.
7. Marabini, A.M., Falbo, A., Passariello, B., Esposito, M.A. & Barbaro, M., 1993, Chemical leaching of iron from industrial mineral, *Publ.Australia Inst.Min. Metal. Ind. (XVIII International Mineral Processing Congress)*, Vol.5, pp.1253-9.
8. Mukherji, S.K., Machhoya, B.B., Chakraborty, A.K. & Dan, T.K., 1993, A Study on The beneficiation of some crude chine clays of Gujarat, *Res.Ind.*, 38, pp. 254-9.

9. Watson, J.H.P., 1994, Status of superconducting magnetic separation in the mineral industry, *Miner.Eng.*, 7, pp. 737-46.
10. Ubaldini, S. Piga, L., Fornari, P. & Massidda, R., 1996, Removal of iron from quartz sands : a study by column leaching using a complete factorial design, *Hydrometallurgy*, 40, pp.369-79.
11. Yusairi Hi. Basiran & Yan, A.S.W., 1995, Investigation of bentonite (montmorillonite clay) resources in The Andrassy area, Tawau, Sabah, Jabatan Penyiasatan Kajibumi Malaysia.