A STUDY OF IRON REMOVAL FROM SABAH MONTMORILLONITE BY EXTRACTING WITH ORGANIC ACID

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Abstract

The removal of iron from Sabah montmorillonite mineral with three organic acids (citric, gluconic and oxalic) has been studied under various experimental conditions in order to optimise the process parameters and reach a high degree of iron removal at minimum operating cost. The parameters studied were: temperature, pH of the solution, organic acid concentration, and time of leaching process. For the Sabah montmorillonite sample used, at temperature varying between 60 -80°C the maximum iron extraction especially with oxalic acid that can achieved is approximately 90%. Oxalic acid is capable of dissolving all the extracted iron in montmorillonite, thus making the montmorillonite suitable for its basic industrial application. Iron dissolution is significantly affected by the pH, while it is practically independent of the oxalate concentration. Iron extraction is optimized in high acid solution, best results are achieved at concentration 7 Kg m^{-3}, pH less than 2, 80°C in temperature and 2 hours in stirring time.

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

INTRODUCTION

Montmorillonite is by far the most abundant of the smectite clay minerals. It is the predominant mineral composing bentonite as well as fuller's earths throughout the world and is major component of soils formed in arid and semiarid areas. In industry, montmorillonite is generally classified as sodium (Na) or calcium (Ca) type, depending on which exchangeable ion is dominant. The major problems facing the utilization of Sabah montmorillonite are their low concentration of smectite, high level of iron content and inconsistent of composition.

The iron content of the industrial minerals can be reduced by a number of physical, physicochemical and chemical methods namely: attrition process, aiming at removing iron bearing minerals from the surface of the particles; separation processes (e.g. magnetic separation or floatation) for the separation of iron-rich minerals, and chemical treatment aiming at dissolving iron compounds bonded at the surface or existing as distinct mineral grains. The appropriate method for the removal of iron from montmorillonite mineral depends on the mineralogical forms and the distribution of iron in the montmorillonite.

Chemical methods involve extracting of the mineral with organic acid and inorganic acids. The most commonly used organic are oxalic[1,2,3], citric[4] and gluconic[5], and inorganic[6] are hydrofluoric, hydrochloric, sulphuric and perchloric acid. Studies on the dissolution of iron oxide, hematite and magnetite, in organic acid has shown that the dissolution mechanism comprises of three steps[4]:
1. Adsorption of organic ligands on system interface: activation of solid surface.

2. Reductive dissolution of active centers: generation of ferrous ions in the solution (induction period)
3. Autocatalytic dissolution of active centers.

The iron dissolution proceeds through a reductive process characterized by a well defined induction period, during which generation of ferrous ions in the solution takes place. The induction period is caused by the slow rate of ferrous ions generation in solution. When a sufficient amount of ferrous ions has been formed in solution, the dissolution process is accelerated. In organic acid solutions and in the presence of dissolves oxygen, bivalent iron is easily oxidized to trivalent. In order to avoid this oxidation and decrease the duration of the induction period, the dissolved oxygen has to be removed from the organic acid solution. This can be achieved by purging the solution with an inert gas (e.g., Ar).Moreover, the addition of ferrous ions in the initial organic acid solution has as a result elimination of the induction period and increase of the rate of the dissolution[6].

For the treatment with oxalic acid a kinetic model [7,8] was employed, the equation of which would be :

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

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

$$\ln \left[\frac{C_{Fe \, max}}{C_{Fe \, max} - C_{Fe}} \right] = kt \tag{2}$$

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

$$\ln k = \ln A - \frac{E_a}{R \, T} \tag{3}$$

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

The present work aims to study the removal of iron from Sabah montmorillonite with organic acid. Based on the above mechanistic observations, an attempt was made to optimize the process parameters and reach a high degree of iron removal at minimum operating cost. The parameters studied were temperature, pH .content, and organic acid concentration.
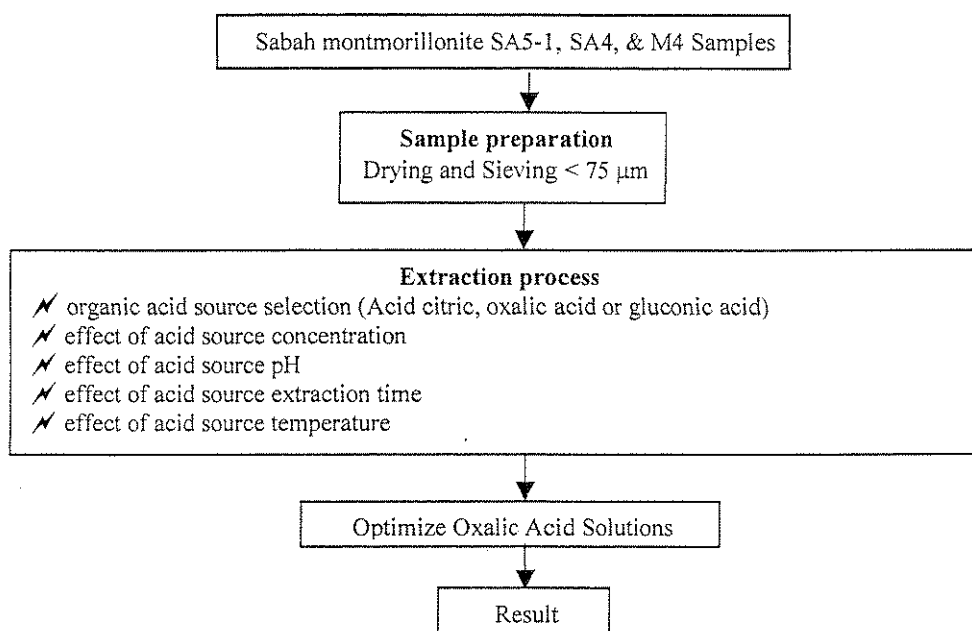
EXPERIMENTAL PROCEDURE

Montmorillonite sample preparation

In this study, two groups of local montmorillonite samples were collected, namely SA5-1 and SA5-4 (N4°18.97'- E 117°57.37') from Andrassy area in Tawau district and M4 (N5°7.35'- E118° 12.03') from Mansuli area in Lahad Datu district. The SA5-1 sample

were collected exactly at 0.5 m depths, SA5-4 sample was collected at 1.0 – 1.5 m depths and M4 at 0.3 m depths. The field sampling from Mansuli area were taken mainly in area underlain by the Ayer Formation, which collectively form the Segama Group and is interpreted to be Miocene in age The Andrassy area is underlain mainly by the high level of alluvium and volcanic rock, and occur in a bed underlying by Pleistocene to Holocene in age[9].

Experimental procedure

Experiments were carried out in 250 cm^3 Erlenmeyer flasks with 10 g montmorillonite and 95 cm^3 of extracting solution. The total operating volume was 100 cm^3. The treatment lasted for 5 hours, 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 variation amount of 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. Below the flow sheet of the experimental procedures.

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│   Sabah montmorillonite SA5-1, SA4, & M4 Samples    │
└─────────────────────────────────────────────────────┘
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            ┌──────────────────────────────┐
            │     Sample preparation       │
            │   Drying and Sieving < 75 μm │
            └──────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────────────────┐
│                      Extraction process                          │
│  ✗ organic acid source selection (Acid citric, oxalic acid or    │
│    gluconic acid)                                                 │
│  ✗ effect of acid source concentration                           │
│  ✗ effect of acid source pH                                      │
│  ✗ effect of acid source extraction time                         │
│  ✗ effect of acid source temperature                             │
└─────────────────────────────────────────────────────────────────┘
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            ┌──────────────────────────────┐
            │  Optimize Oxalic Acid Solutions │
            └──────────────────────────────┘
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                  ┌──────────────┐
                  │    Result    │
                  └──────────────┘
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EXPERIMENTAL RESULTS AND DISCUSSION

From laboratory investigation[10], it showed that Malaysian local montmorillonite has more impurity materials such as quartz, kaolinite, illite, muscovite and hematite as presented in **table 1**. Iron is present as magnetite and as amorphous oxides and hydroxides (analysis by XRD model D-500, Siemens).

Table 1

Chemical Analysis of Sabah Montmorillonite

Samples	SA51	SA54	M4
SiO_2 (%)	55.82	55.20	63.74
Al_2O_3 (%)	6.59	6.21	6.61
Fe_2O_3 (%)	22.68	18.35	17.15
TiO_2 (%)	0.71	0.71	0.71
K_2O (%)	0.51	0.47	0.83
MgO (%)	0.09	0.55	0.06
CaO (%)	1.10	0.53	0.16
Na_2O (%)	1.41	0.01	1.88
LOI (%)	11.09	17.97	8.86

Citric Acid performance

Experiments at citric acid concentration of 1-40 kg m^{-3} and pH 1.3 – 9.7 were performed, and results for a 5 hours treatment are shown in **Figure 1**. In general, iron dissolution decrease at pH decreasing, especially when pH more than 3 but constant after pH reach the value of 7.
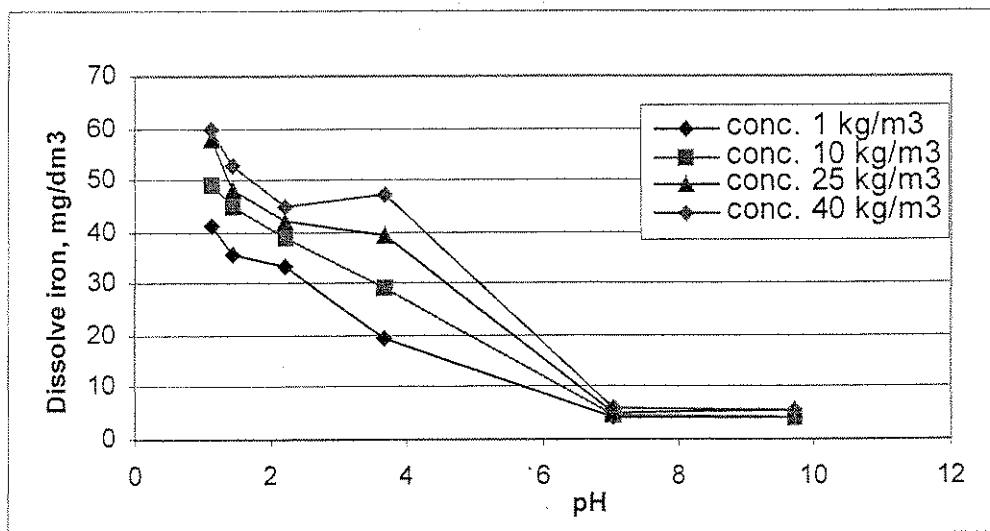
Fig. 1. Effect of citric acid as montmorillonite extracting agent
for a treatment time of 5 hours.

Gluconic Acid performance

The experiment was done in an analogous way to that shown for citric acid. **Figure 2** shows the results. In generally showed that, dissolution iron drastically decrease with increasing pH up to 2.23, after which decreasing in dissolved iron relatively small, which in every case gave values lower than those with citric acid.
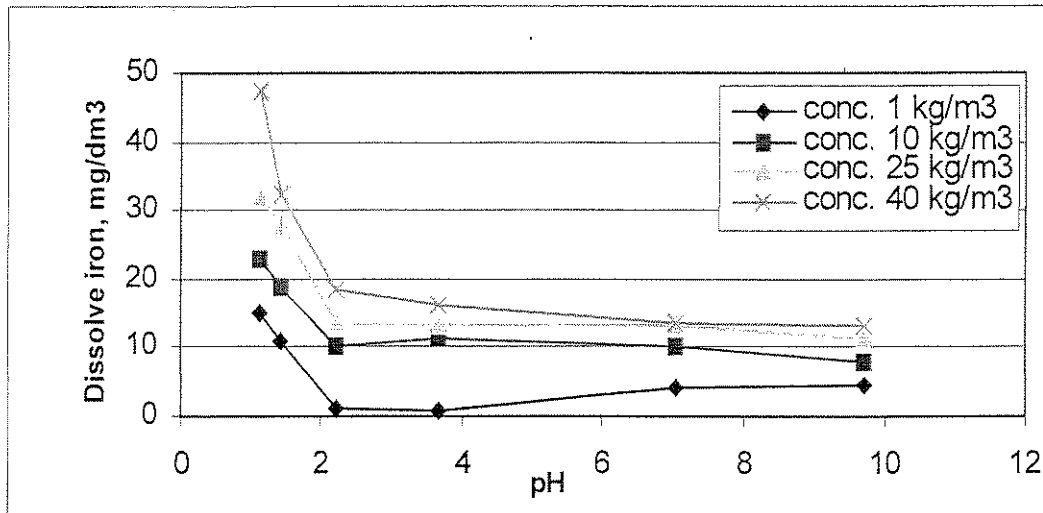
Fig. 2. Effect of gluconic acid as montmorillonite extracting agent for a treatment time of 5 hours.

Oxalic Acid performance

Figure 3 shows the dissolved iron after 5 hours, for oxalic acid concentration of 1-40 kg m^{-3}. 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
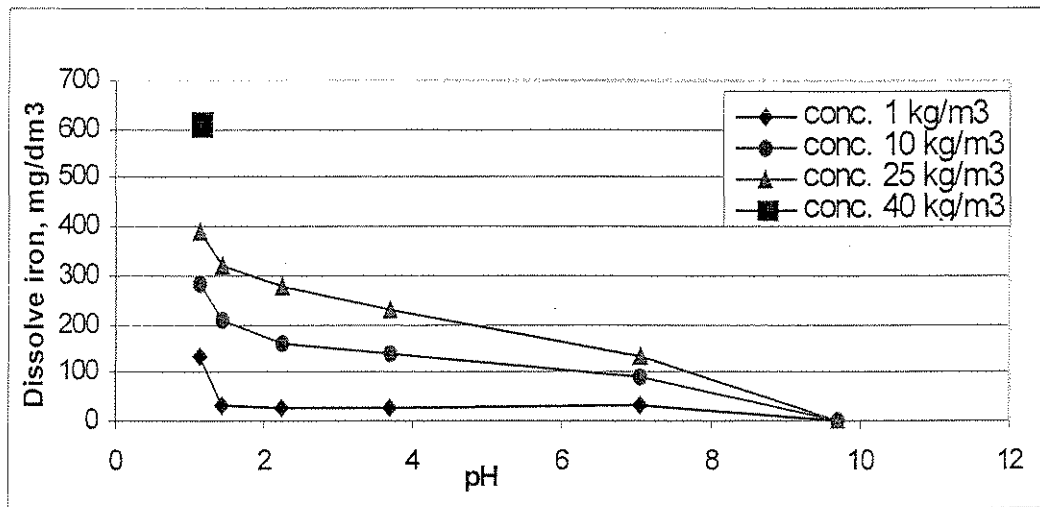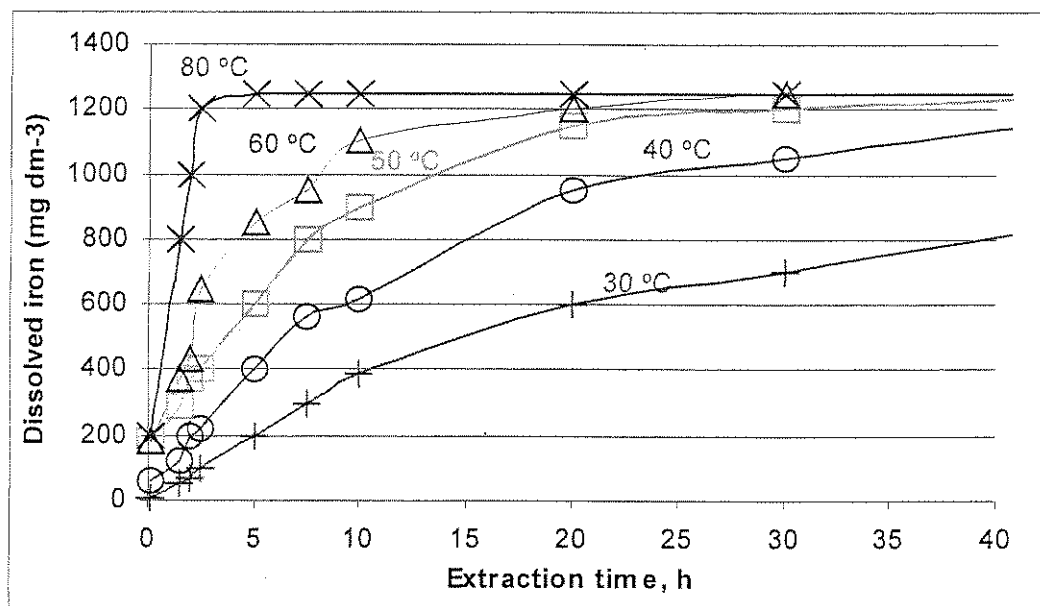

Fig. 3. Effect of oxalic acid as montmorillonite extracting agent for a treatment time of 5 hours

pH (1.3 – 1.44), and quickly decreases when the pH increase, coming near to zero for pH 9.71 or higher. This great extracting capacity of oxalic acid is intrinsic since at lower pH. The dissolution iron already relatively high compare with other organic acid. Therefore, 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 3** shows the experiments performanced in a range of 0.7 – 7 kg m^{-3} oxalic acid at its natural pH. The temperature varied between 30 and 80^{0}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 depending on the concentration, but not the operating temperature. Nevertheless, high 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 hours at 30°C was achieved, at 80°C the extraction time needed to reach the same concentration of iron was only 2 hours. 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 results from experiments at different temperatures with 7 kg m^{-3} oxalic acid.

Table 3

Dissolved iron concentration after oxalic acid extraction

Concentration of 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

Fig. 4 Kinetic modeling to eq.(1) of oxalic acid extracting at different temperature

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 increase 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 (eq (1)) was employed to describe the kinetics of the extracting of iron oxides.

DISCUSSION

This study has shown that the most important parameter effecting the dissolution iron from montmorillonite mineral in organic acid solutions are organic acid concentration, extraction time and temperature There are , two different temperature regions can be observed. In the first one, ranging greater than 80°C, the maximum iron extraction that can be achieved is 80%. In the second region , comprising temperature lower than 60°C the maximum percentage of iron that can be dissolved decreases to approximately 20%.This extraction is obtained either at low (ambient or even lower) temperatures which longer extracting time or at higher temperatures and shorter retention time. From the above phenomena, it is deduced that thermodynamic and kinetic inhibitions are taking place during extracting of montmorillonite mineral in organic acid solutions.

Among the tree acids, only oxalic acid is suitable for use on a large-scale. It is capable of removing the iron content from montmorillonite at the tested operating conditions. The soluble iron from effluent can be precipitated in a spontaneous process, thus avoiding environmental problems. 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[9].

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.

ACKNOWLEDGEMENT

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