

# REMOVAL OF IRON CONTAMINANT FROM SABAH MONTMORILLONITE USING GRAVITATIONAL AND EXTRACTION TECHNIQUES

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## ABSTRACT

The removal of iron contaminant from Sabah montmorillonite mineral by combination of gravitational method and organic extraction (oxalic acid) technique has been studied under various experimental conditions in order to optimize the process parameters at minimum operating cost. The degree of separation of light and heavy contaminant from Sabah montmorillonite mineral is not limited by one method (machine or chemically), but also by the particle size distribution of the contaminant. Therefore there is a need to combine the gravitational and organic acid extraction techniques in order to produce Sabah montmorillonite iron free with minimum need of chemical, which in return of operating cost. The parameters studied were pressure drop, airflow rate, temperature, pH of the solution, organic acid concentration, and time of extraction. For the Sabah montmorillonite sample studied, at airflow rate of 18 m<sup>3</sup>/hr the optimum pressure drop was 231 N/m<sup>2</sup>, has separated 60 percent by weight of iron contaminant from montmorillonite, and at temperature varying between 60-80°C, the maximum iron contaminant extraction with oxalic acid is approximately 30 percent. Oxalic acid is capable of dissolving all extracted iron in montmorillonite. Combination with gravitational and oxalic acid extraction techniques successfully removed 90 percent of iron contaminant from Sabah montmorillonite, thus making Sabah montmorillonite suitable for its basic industrial application.

Key words: montmorillonite, gravitational, airflow rate, extraction, oxalic acid, iron removal

## 1. INTRODUCTION

Montmorillonite  $\{[Al_{1.56}(Fe^{+3})_{0.03}Mg_{0.41}][Si_{3.74}Al_{0.26}]O_{10}(OH)_2\}(M^{+})_{0.67}$  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) types, depending on dominant exchangeable ion. The major problems facing the utilization of Sabah montmorillonite are their low concentration of smectite, high level of iron contaminant and inconsistent composition.

The iron contaminant of the industrial minerals can be reduced by a number of physical, physicochemical and chemical methods namely separation processes (e.g. aero cyclone, magnetic separation or floatation), attrition process, aiming at removing iron bearing minerals from the surface of the particles; 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.

Cyclone is commonly used as a collector and separation of particles in many mineral industries. They are relatively simple, inexpensive and have long trouble free service<sup>1</sup>. Current designs of industrial high-efficiency cyclones can provide collection efficiencies of 90 percent and higher for

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particles with diameters as small as 2  $\mu\text{m}$  (particulate specific gravity=1)<sup>2</sup>. The collection efficiency of a cyclone depends on various factors, which includes the characteristics of particle to be collected (particle density & size) and the configuration of the cyclone (body length, inlet duct area and smoothness of cyclone wall). In all cyclones, particulate is separated from the gas stream by centrifugal force. Particulate is thrown toward the outside of a spinning column of gas, while the relatively clean gas exhausts from the center of the spinning vortex.

Chemical methods involve extracting of the mineral with organic and inorganic acids. The most commonly used organic acids are oxalic<sup>3,4,5</sup>, citric<sup>6</sup> and gluconic<sup>7</sup> and inorganic<sup>8</sup> acids 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 three steps<sup>6</sup>:

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 duration of the induction period, the dissolved oxygen has to be removed from an organic acid solution. This can be achieved by purging the solution with an inert gas (e.g., Ar). Moreover, addition of ferrous ions in the initial organic acid solution has as a result elimination of the induction period and increase of the dissolution rate<sup>8</sup>. The present work aims to study removal of iron contaminant from Sabah montmorillonite using gravitational and extraction techniques. 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 parameter studied were pressure drop, airflow rate, temperature, pH of the solution, organic acid concentration, and time of extraction process.

## 2. EXPERIMENTAL WORK

### 2.1. MONTMORILLONITE SAMPLE

In this study, two groups of Sabah montmorillonite samples were collected, namely SA5-1, SA5-4 and SA5-7 (N4<sup>o</sup>18.97' - E 117<sup>o</sup>57.37') from Andrassy area in Tawau district and M4 (N5<sup>o</sup>7.35' - E118<sup>o</sup> 12.03') from Mansuli area in Lahad Datu district. The SA5-1 sample was collected exactly at 0.5 m depths, SA5-4 and SA5-7 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 occurs in a bed underlying by Pleistocene to Holocene in age. From laboratory investigation<sup>9</sup>, it showed that Malaysian local montmorillonite has more impurity materials such as quartz, kaolinite, illite, muscovite and hematite as presented in Table 1. Iron as magnetite and as amorphous oxides and hydroxides (analysis by XRD model D-500, Siemens).

### 2.2. LABORATORY WORK

All samples were dried at 55°C for 1 hour and then crushed using a 'Wedag' jaw crusher to 100% below 5 mm in size. A representative batch of each sample was further ground to 100% below 200 mesh (75  $\mu\text{m}$ ) using a porcelain mill to avoid contamination of samples. This was followed by dry cyclone<sup>13</sup>, to disintegrate the smectite from its associating gangue minerals. Both the dry cyclone underflow (coarser than 63  $\mu\text{m}$ ) and the overflow fractions (finer than 63  $\mu\text{m}$ ) were filtered dried at 55°C and weighed.

Table 1. Chemical Analysis of Sabah Montmorillonite<sup>9</sup>

Samples	SA5-1	SA5-4	SA5-7	M4
SiO <sub>2</sub> (%)	55.82	55.20	52.62	63.74
Al <sub>2</sub> O <sub>3</sub> (%)	6.59	6.21	23.35	6.61
Fe <sub>2</sub> O <sub>3</sub> (%)	22.68	18.35	7.37	17.15
TiO <sub>2</sub> (%)	0.71	0.71	0.63	0.71
K <sub>2</sub> O (%)	0.51	0.47	0.58	0.83
MgO (%)	0.09	0.55	2.08	0.06
CaO (%)	1.10	0.53	0.95	0.16
Na <sub>2</sub> O (%)	1.41	0.01	0.24	1.88
LOI (%)	11.09	17.97	11.77	8.86

The underflow fractions, which were heavily contaminated with iron and quartz impurities, were discarded. Meanwhile, the overflow fractions were used as montmorillonite pre-concentrates. The latter were further upgraded by extracting with organic acid solution. The extracting procedures were carried out in 250 cm<sup>3</sup> Erlenmeyer flasks with 10 g montmorillonite and 95 cm<sup>3</sup> of extracting solution. The total operating volume was 100 cm<sup>3</sup>. The treatment lasted for 5 hours, in a 3.3 Hz rotating shaker at 45°C. Three acids (citric, gluconic and oxalic) were studied at different concentration (1-40 kg m<sup>-3</sup>) and pH values of 1.3 – 9.7. The pH was modified by adding of concentrated HCl or NaOH. Fig. 1 shows a simplified flow sheet for the experimental scheme.

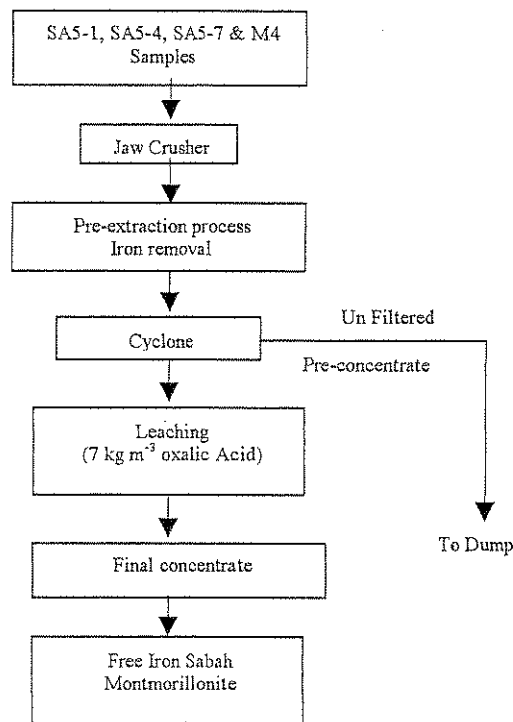


FIGURE 1. Flow sheet of the experimental procedures

### 3. RESULTS AND DISCUSSION

The experimental results showed that dry cyclone could be used for an associated iron content removal from Sabah montmorillonite. About 40 % by weight of iron content had been removed as an underflow fraction and 60% by weight of more pre-concentrate as an overflow fraction.

At airflow rate  $18 \text{ m}^3/\text{hr}$ , the optimum pressure drop was  $231 \text{ N/m}^2$ , respectively has separated 60 percent by weight of iron contaminant from montmorillonite. Table 2 showed that the iron contents is significantly decreased in comparison with the original sample. Meanwhile, leaching of the montmorillonite pre-concentrate with  $7 \text{ kgm}^{-3}$  oxalic acid showed that such technique was successful in removing the majority of the remaining iron where the  $\text{Fe}_2\text{O}_3$  content decreased 0.74% to 2.68% by weight.

TABLE 2. Chemical analysis of Sabah montmorillonite sample

Sample	$\text{SiO}_2$ (%)	$\text{Al}_2\text{O}_3$ (%)	$\text{Fe}_2\text{O}_3$ (%)	$\text{TiO}_2$ (%)	$\text{K}_2\text{O}$ (%)	$\text{MgO}$ (%)	$\text{CaO}$ (%)	$\text{Na}_2\text{O}$ (%)
Montmo	57.58	11.60	6.97	0.43	0.66	2.22	1.65	2.22
SA5-1	55.82	6.59	22.68	0.71	0.51	0.09	1.10	1.41
Pre-c*	60.25	5.64	9.072	7.65	0.48	3.35	1.36	1.18
Final c*	66.65	2.25	6.68	8.65	0.34	6.85	1.25	1.02
SA5-4	55.20	6.21	18.35	0.71	0.47	0.55	0.01	1.41
Pre-c*	65.75	2.48	7.34	8.25	0.52	0.84	0.53	1.54
Final c*	66.51	0.62	6.84	9.45	0.22	1.39	0.35	1.34
SA5-7	52.62	23.35	7.37	0.63	0.58	2.08	0.95	0.24
Pre-c*	54.32	19.24	2.96	6.38	0.52	2.25	0.65	0.22
Final c*	65.05	12.45	0.74	7.25	0.32	2.75	0.62	0.2
M4	63.74	6.61	17.15	0.71	0.83	0.06	0.16	1.88
Pre-c*	62.65	5.65	6.86	5.25	0.78	1.06	0.15	1.75
Final c*	64.85	4.25	6.72	8.23	0.75	1.15	0.12	1.2

c\* = concentrate

#### 4. EFFECT OF ORGANIC ACID

##### *Citric Acid*

With citric acid concentration of  $1\text{--}40 \text{ kg m}^{-3}$  and pH 1.3 – 9.7 the results for a 5 hours treatment are shown in Figure 2. In general, iron dissolution decrease with pH decreased, especially when pH more than 3 but constant after pH reach the value of 7.

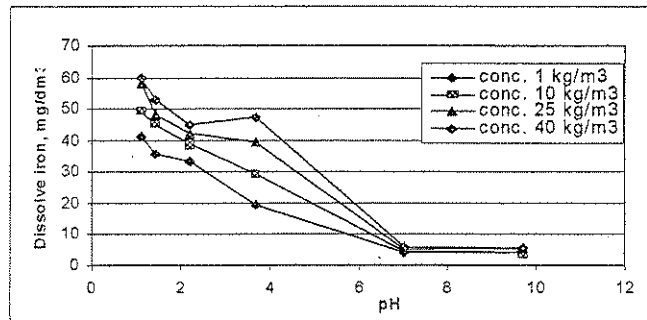


FIGURE 2. Effect of citric acid as montmorillonite extracting agent after 5 hours treatment

*Gluconic Acid*

Figure 3 showed the results of experiment with gluconic acid. In generally the dissolution iron drastically decrease with increased pH up to 2.23, after which the dissolved iron decreased relatively small, which in every case gave values lower than those with citric acid.

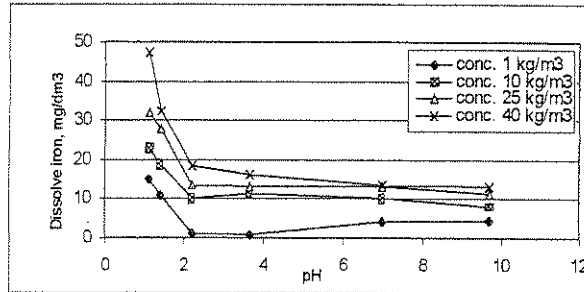


FIGURE. 3. Effect of gluconic acid as montmorillonite extracting agent after 5 hours treatment.

*Oxalic Acid*

Figure 4 showed the dissolved iron after 5 hours, for oxalic acid concentration of 1-40 kg m<sup>-3</sup>. The results are different from those of the other acids. With oxalic acid, solubilized iron reaches 131.7 – 613 mg/dm<sup>3</sup> for several concentrations at low pH (1.3 – 1.44), and quickly decreases when the pH

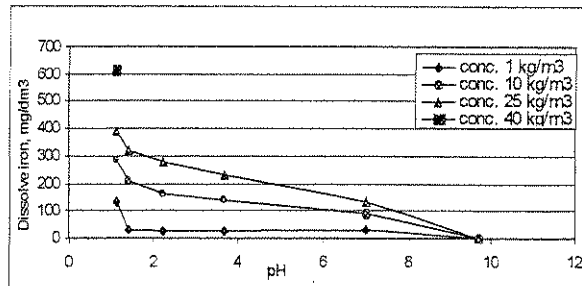


Figure 4.. Effect of oxalic acid as montmorillonite extracting agent after 5 hours treatment

increased, coming near to zero for pH 9.71 or higher. This great extracting capacity of oxalic acid is intrinsic particularly at lower pH. The dissolution iron already relatively high compared with others 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 showed the results of treatment with oxalic acid at its natural pH. The temperature were varied between 30 and 80°C and the experiments were continued for long enough to enable the highest iron concentration to be achieved. The maximum iron concentration dissolved reached in each experiment depending on the concentration of oxalic acid used, 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<sup>-3</sup> oxalic acid a maximum concentration of 985 mg/dm<sup>3</sup> was achieved in 200 hours at 30°C, 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 5 showed the results from experiments at different temperatures with 7 kg m<sup>-3</sup> oxalic acid.

Table 3  
Dissolved iron concentration after oxalic acid extraction

Concentration of Oxalic acid (kg m <sup>-3</sup> )	pH	Dissolved iron (mg dm <sup>-3</sup> )
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

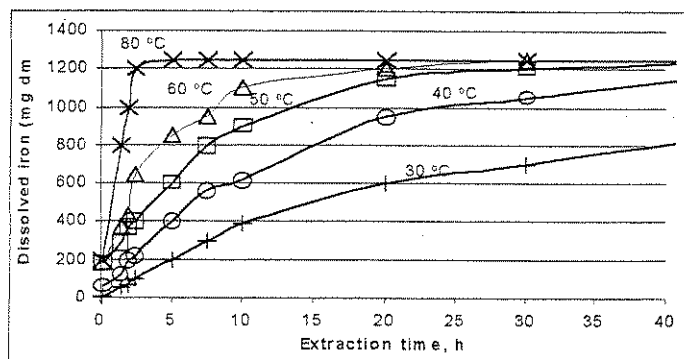


FIGURE 5. Effect of extraction time at various temperature

From experimental results 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 increased 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). Among three acids, only oxalic acid is suitable for used in 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 spontaneously precipitated, 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<sup>10</sup>.

## 5. CONCLUSIONS

1. Dry cyclone can be used to separate 60 percent by weight of iron contaminant from Sabah Montmorillonite.
2. Oxalic acid is the best acid type for leaching 30 percent by weight of iron contaminant from Sabah montmorillonite, thus making Sabah montmorillonite suitable for its basic industrial application
3. Combination with gravitational and oxalic acid extraction techniques successfully removed 90 percent of iron contaminant from Sabah montmorillonite.

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