Proceeding Paper

A Comparative Study of Acid-Activated Aluminium and Ferruginous Smectite in Oxalic Acid of Various Concentrations †

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Abstract: Acid activation is a chemical modification of minerals and mainly smectites, in order to enhance their surface properties and reinforce their adsorption capacity for specific ions. Acid-activated clays and, more specifically, inorganic acid-activated calcium montmorillonites are mainly used in the bleaching process of vegetable oils, which are holding third place in the world food consumption after cereals and rice, in order to remove chlorophyll and other undesirable substances from the oils. This study proposes the use of oxalic acid for the acid activation of smectites, in order to modify their surface characteristics and create high-quality bleaching earths. In particular, aluminium and ferruginous smectites are treated with oxalic acid concentrations of 0.5, 0.7 and 1 M, and the structural modifications in the materials after treatment are observed through FTIR analysis, combined with the determination of the main structural metals' extraction from the smectites. The results showed that ferruginous smectite is more susceptible to oxalic acid activation. The final product has developed vacant spaces in its structure to absorb other ions or molecules, although it retains the structure of smectite. Oxalic acid concentration of 0.5 M is sufficient for achieving this result. The materials produced through the oxalic acid activation are also compared with inorganic acid-activated smectites originating from the same deposits.

Keywords: acid activation; oxalic acid; smectites; bleaching earths; FTIR

1. Introduction

Smectites are a group of minerals with a 2:1 structure (two silicon tetrahedral sheets combined with one aluminium octahedral sheet). Many researchers are involved in their study because of their unique physical and chemical properties which can be enhanced by chemical treatment, such as acid activation. This process is usually carried out with inorganic acids such as HCl and H_2SO_4, targeting the surface characteristics modification, so as to mainly increase the specific surface area and to modify the porosity and surface acidity of the smectite [1]. Acid activation of smectites is of paramount importance for the vegetable oils industry since the materials produced constitute bleaching earths, which are being used in oil refining.

Vegetable oils, which occupy the third place in world food consumption after cereals and rice [2], need to be refined before consumption. Bleaching is an essential step of this process, during which chlorophyll and other substances are removed by using bleaching earth as an adsorbent. Inorganic acid-activated calcium montmorillonite is the main material used as bleaching earth in the industry of edible oils [3].

A number of researchers have investigated the influence of inorganic acids on smectites. Studies dealing with hydrochloric and sulphuric acid activation of smectites showed that octahedral sheets of the mineral are the first to be affected, and then, the tetrahedral sheets are dissolved as the process intensifies. Amorphous silica has been observed to be formed

in the final product, and when large quantities were produced, they were precipitated on the pores. The dissolution rate of smectite was increased with higher temperature and acid concentration. It was also observed that the trioctahedral smectite is more prone to acid activation, compared with the dioctahedral one, and that the dissolution rate of smectites was increased with higher content of Fe and Mg in the octahedral sheets (having substituted Al) [4–6].

In the presence of organic acid, the dissolution rate of silicate minerals is enhanced, due to the complexes formed between organic ligands and metals [7]. Oxalic acid has proven to be more efficient in the treatment of smectite among other organic acids [8]. As a study on the activation of montmorillonite with oxalic acid at 25 °C revealed, the dissolution is enhanced in the presence of oxalic acid, in comparison with ligand-free solutions (composed of nitric, acetic, and hydrochloric acids to control the pH) due to the formation of oxalate surface complexes and soluble chelates [9]. Based on the results of the above study, researchers modelled the complexation of oxalate on the edge surface of montmorillonite [10]. Materials which could be used as bleaching earths have been recently produced by oxalic acid activation of smectites. Moreover, the effluents from oxalic acid activation are more environmentally friendly than those from inorganic acids, due to their ability to be microbiologically and photochemically decomposed [11]. Taking into consideration the abovementioned points, oxalic acid could be an effective agent for smectite activation.

The present paper is a comparative study of the oxalic acid activation of two different types of smectites (aluminium smectite and ferruginous smectite) using various acid concentrations. The resulting structural modifications were observed via the FTIR method and the chemical analysis of the leachates and were also compared with the results of inorganic acid activation of smectites originating from the same deposits.

2. Materials and Methods

Two different raw smectite samples—aluminium smectite from the deposits of Milos island in Greece and ferruginous smectite from Gujarat in India—were provided by IMERYS S.A. and labelled as AlSm-G and FeSm-I, respectively. The chemical analysis of the raw materials was performed by the XRF method using the XEPOS apparatus of SPECTRO. FTIR spectra of solid samples were obtained in the 400–4000 cm^{-1} range, using a PerkinElmer, Spectrum 100, Fourier transform infrared (FTIR) spectrometer. The mineralogical composition was determined using a Bruker D8-Focus X-ray diffractometer with nickel-filtered CuKa radiation (l = 1.5406 Å), at 40 kV and 40 mA.

The leachates of the acid activation process were analysed regarding their Al, Si, Fe, and Mg content through Atomic absorption spectrometry, using a PerkinElmer PinAAcle 900T Atomic Absorption Spectrometer.

FTIR spectra were also obtained for the acid-activated samples, using the KBr pellet technique. This technique is a very sensitive one and can be used to observe the structural modifications occurring during the acid activation of the smectite samples.

3. Experimental Procedure

Batch oxalic acid activation experiments were carried out in a glass reactor with a heating jacket. Pulp density of 2% (*w/v*) was obtained by placing 8 g of solid in 400 mL of an oxalic acid solution of 0.5, 0.7, and 1 M concentrations. The temperature remained constant at 80 °C using a Teflon coated thermocouple, connected to the temperature controller. The reactor was sealed and a glass condenser was adjusted to it, in order to avoid vapor loss. The pulp was mechanically stirred at 400 rpm for 24 h, and samples of 5 mL were collected at 10 min, 20 min, and 30 min at the beginning of the process and then every hour. Finally, the pulp was filtrated, and the solid residue on the filter was washed with deionised water and dried at 100 °C for 24 h.

4. Materials Characterisation

4.1. Chemical Analysis

Table 1 presents the chemical composition of each raw smectite sample, determined by the XRF method. AlSm-G smectite has a lower content of Na_2O and higher content of CaO, compared with FeSm-I. The exchangeable cations (Ca, Na, Mg and K) were determined and the ratio Σ $(K^+ + Na^+)/\Sigma$ $(Ca^{2+} + Mg^{2+})$ was calculated at about 0.1 for AlSm-G and 0.5 for FeSm-I. Moreover, the swelling index of the AlSm-G sample is 7.97 cc/2 g, while that of the FeSm-I sample is 15.20 cc/2 g. The above observations lead to the assumption that FeSm-I falls within the classification of mixed Na/Ca smectite and AlSm-G within that of Ca smectite [12,13].

Table 1. Chemical analysis of raw materials.

	Oxides (wt. %)									
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	L.O.I.	Total
AlSm-G	48.28	17.25	3.68	5.28	9.01	0.40	0.30	0.71	15.10	100.00
FeSm-I	46.96	17.66	19.32	2.80	1.75	1.08	0.00	1.39	9.05	100.00

4.2. X-ray Diffraction

The XRD spectra and the mineralogical compositions of the two raw materials are presented in Figure 1. The peaks of AlSm-G smectite are assigned to montmorillonite, calcite, dolomite, and illite, while the FeSm-I smectite contains montmorillonite, kaolinite, hematite, calcite, and calcium titanium oxide.
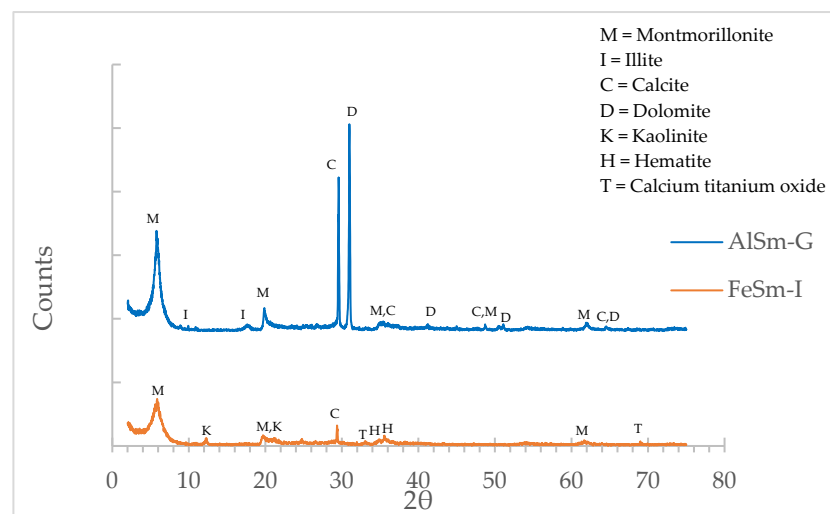

Figure 1. X-ray diffraction of raw materials.

4.3. Infrared Spectroscopy

The full FTIR spectra of AlSm-G and FeSm-I smectites are presented in comparison with the corresponding activated products in Figure 2, Figure 3 and Figure 4, respectively.

From the XRD and FTIR spectra, it is deduced that AlSm-G smectite is aluminium smectite and FeSm-I is ferruginous smectite [14,15].
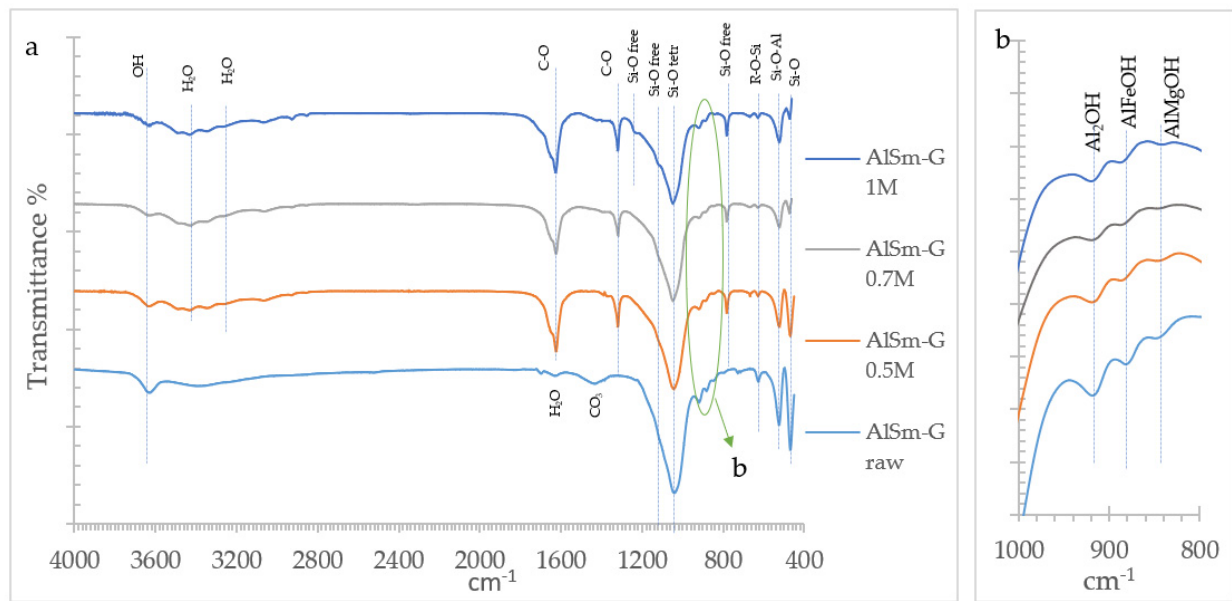
Figure 2. (**a**) FTIR spectra of AlSm-G smectite (raw and activated with 0.5, 0.7, and 1 M oxalic acid); (**b**) FTIR spectra (Section 1000–800 cm^{-1}) of raw and treated AlSm-G smectites.
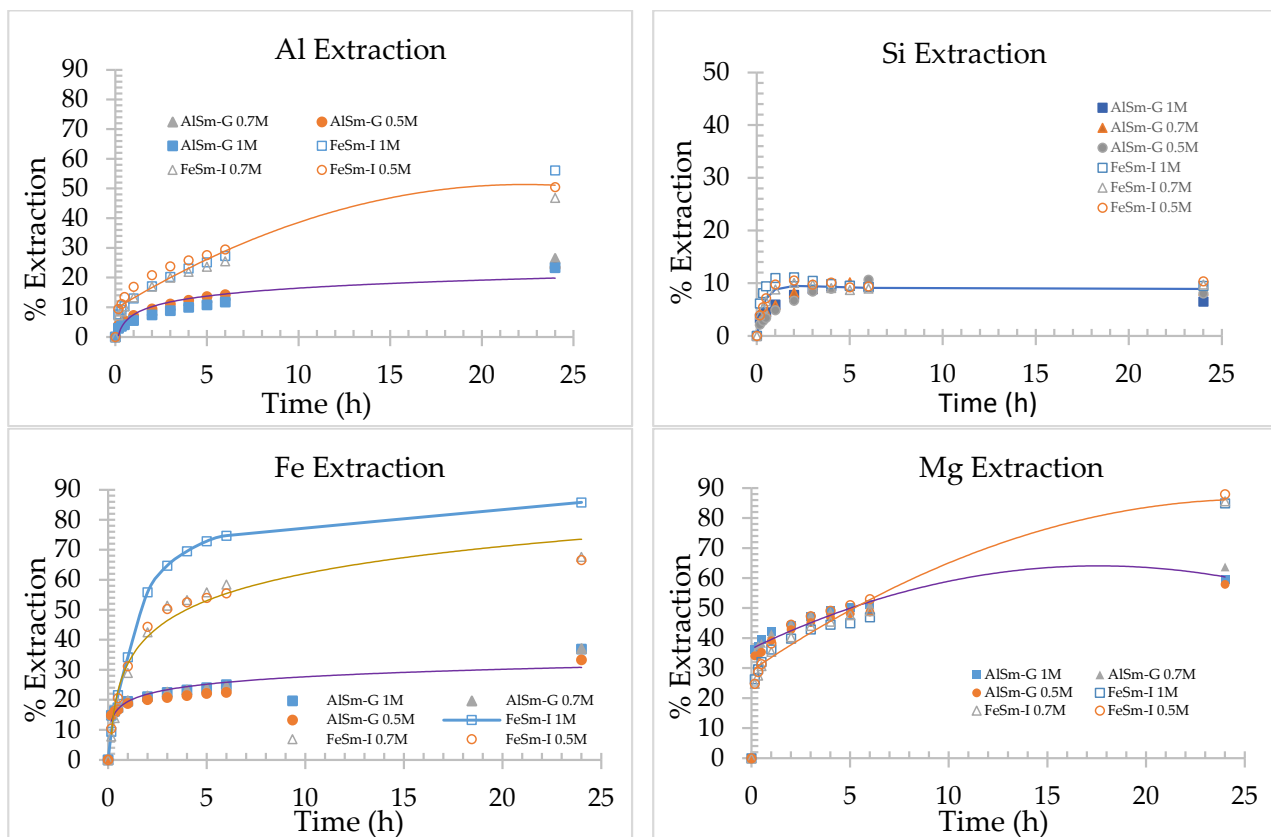

Figure 3. Extraction of metals versus time for AlSm-G and FeSm-I smectites in oxalic acid (80 °C; acid concentrations of 0.5 M, 0.7 M, and 1 M; 2% of pulp density).
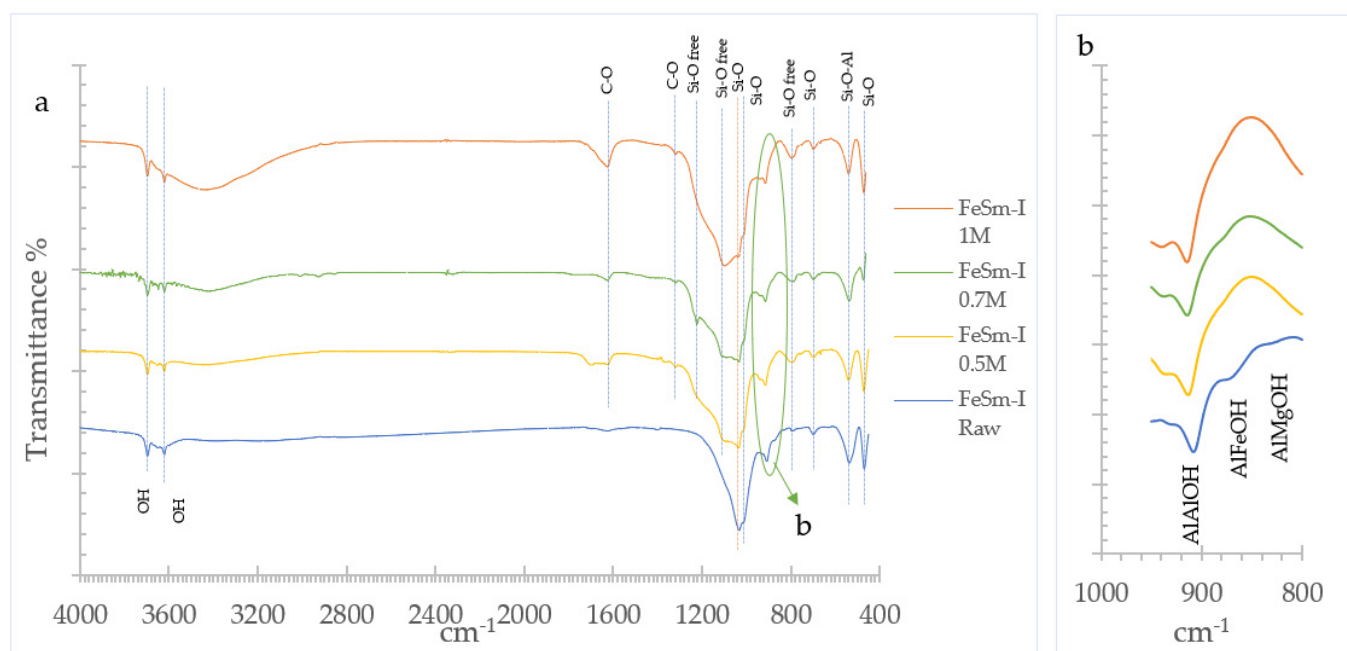
Figure 4. (**a**) FTIR spectra of FeSm-I smectite (raw and activated with 0.5, 0.7, and 1 M oxalic acid); (**b**) FTIR spectra (section $1000-800$ cm^{-1}) of raw and treated FeSm-I smectite.

5. Results and Discussion

5.1. Oxalic Acid Activated Aluminium Smectite

Figure 2 presents the FTIR spectra of the raw and activated AlSm-G smectite samples. The characteristic bands of smectite structure are observed: The most intensive one attributed to Si-O stretching vibrations of the tetrahedral layer, the Si-O-Al and Si-O-Si bending vibrations at 524 and 468 cm^{-1}, respectively, and also the peaks assigned to AlAlOH, AlFeOH, and AlMgOH, which indicate the presence of iron and magnesium in the octahedral sheets. A band appears at 627 cm^{-1}, due to perpendicular vibration of the octahedral atoms (R-O-Si) [16]. In addition, the bands at 1382–1430 cm^{-1} in the raw sample are related to CO$_3$ stretches of calcite and dolomite, and the one detected at 710–715 cm^{-1} is assigned to Si-O stretching and the in-plane bending of calcite and dolomite [17].

The leaching caused by the oxalic acid treatment affects the bands concerning the octahedral atoms (Figure 2a,b), confirming their depletion. The band at 3625 cm^{-1}, which is assigned to hydroxyl groups joined together with octahedral Al, decreases when the sample is treated with oxalic acid [6]. Furthermore, the three peaks in the hydroxyl bending region for Al$_2$OH, AlFeOH, and AlMgOH also decrease (with the AlMgOH peak becoming the smoothest), while the octahedral structure is preserved, as the IR curves denote (Figure 2b). Two peaks assigned to calcium oxalate appear in the IR spectra of activated samples at 1624 cm^{-1} and at 1320 cm^{-1} (Figure 2a) [18]. Moreover, the band at 524 cm^{-1} (indicative of the extent of smectite dissolution) is still visible and, along with the bands of octahedral atoms and tetrahedral Si, reveals that the smectite structure still exists even after activation at 1M concentration. The metals' extraction diagrams in Figure 3 (the extraction percent for each metal is calculated as a fraction of mass of metal extracted in the oxalic acid solution $\times$ 100/mass of metal in the initial sample) confirm the abovementioned observations and also reveal that there is no significant effect on the dissolution of the aluminium smectite, as the acid concentration changes from 0.5 M to 1 M. Oxalic acid concentration between 0.5 M and 1 M leads to precipitation of free silica and calcium oxalate, which apparently passivates the surface of the mineral and inhibits the continuation of its dissolution [4]. The metals extraction diagram reveals also that oxalic acid leaches out of the structure selectively the Fe and Mg, compared with Al and Si, whose extraction percentage is lower.

Precipitation of Si is confirmed by the presence of amorphous silica bands at 1200 cm^{-1} and 1100 cm^{-1}, prominent at 1 M concentration, and near 800 cm^{-1} in every studied concentration (Figure 2a) [5].

5.2. Oxalic Acid Activated Ferruginous Smectite

In the FTIR spectra of the FeSm-I raw smectite and activated samples (Figure 4a), the bands at 1030 cm^{-1} and 1012 cm^{-1} are assigned to Si-O stretching band [5]. There are also the two bands for calcium oxalate at 1627 cm^{-1} and 1318 cm^{-1}. The bands at 3623 cm^{-1} and 3696 cm^{-1} are assigned to hydroxyl groups joined together with octahedral atoms. The intensity of the latter bands reduces with acid treatment, due to the removal of the hydroxyl groups connected to the octahedral atoms that are leached out from the smectite structure [6]. The peaks of Al$_2$OH, AlFeOH, and AlMgOH gradually decrease as the acid concentration increases, which is confirmed by the metals' extraction diagrams (Figure 3).

In the FeSm-I sample, the structure alteration is observed through the increasing bands of amorphous silica (rising with increasing acid concentration) and a small decrease in the octahedral bands. The band at 1030 cm^{-1}, observed in all acid concentrations, indicates the presence of Si in the tetrahedral structure; thus, the crystal structure of the mineral did not completely collapse [5].

In this sample, similar to that of the AlSm-G, the characteristic band at 535 cm^{-1} and the bands referring to octahedral atoms, as well as the principal bands of the smectite structure, still exist; thus, the crystal structure seems to be preserved even at 1 M concentration. Figure 3 shows that the extraction of metals in ferruginous smectite is higher than that in aluminium smectite. This is attributed to the much lower calcium content of FeSm-I, compared with AlSm-G (Table 1) and, consequently, to the lower amount of calcium oxalate produced; thus, the inhibition of dissolution caused by precipitation is much reduced, leading to higher metal extraction. Ferruginous smectite seems to be more prone to dissolution in oxalic acid, as it can be indicated by the pronounced presence of amorphous silica and by the higher extraction of metals (Fe, Al, Mg), compared with the aluminium one (Figure 3). The selective extraction of Fe and Mg in comparison with Al and Si by oxalic acid is observed again, as in the AlSm-G sample.

5.3. Comparison between Activation with Oxalic Acid and H$_2$SO$_4$

The smectite samples used in this study (AlSm-G and FeSm-I) were also treated with a conventional acid (H$_2$SO$_4$ 1 M) under the same experimental conditions. Figure 5a,b show the extraction curve of the main octahedral atom of AlSm-G and FeSm-I samples, respectively. In the FeSm-I sample, the extraction of iron, which predominates in octahedral sites, is more intense in oxalic than in sulphuric acid (Figure 5b). This result denotes that oxalic acid treated ferruginous smectite has probably obtained higher porosity and, therefore, higher possibility of adsorbing undesirable substances, than sulphuric acid treated one.

Focusing on the extraction curve of AlSm-G's main octahedral cation, aluminium, it is observed that until 6 h of treatment, aluminium is extracted at the same percentage in oxalic and sulphuric acid. Between 6 h and 24 h of treatment, the extraction curve of sulphuric acid activated smectite surpasses that of the oxalic acid activated sample, denoting a slight difference between the vacant space in the structure of the two products.
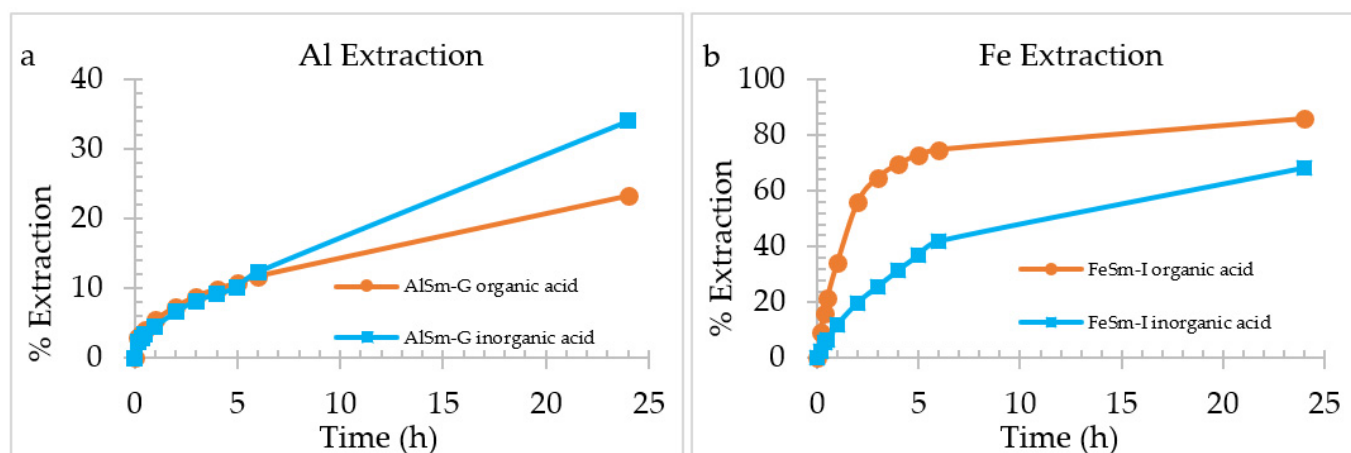
Figure 5. (**a**) Extraction of aluminium versus time for AlSm-G smectite and (**b**) extraction of iron versus time for FeSm-I smectite, in oxalic and sulphuric acid (80 °C; acid concentration 1 M; 2% pulp density).

6. Conclusions

It was observed that smectites with different substitutions in their octahedral sheets show different behaviour in oxalic acid dissolution. The FeSm-I sample, which contains larger amount of Fe in its octahedral sites than AlSm-G, proved to be more susceptible to oxalic acid activation. The amorphous silica peaks of the FeSm-I sample appear to be stronger, and its octahedral atoms are more easily leached during oxalic acid activation, compared with AlSm-G smectite in the same experimental conditions.

The oxalic acid activated product retains the structure of smectite, while the octahedral atoms are leached out. Oxalic acid concentration as low as 0.5 M is sufficient for achieving this result. The materials produced after this process could eventually adsorb other ions or molecules in their lattice.

The comparison between activation with oxalic and sulphuric acid leads to the conclusion that oxalic acid has almost the same or even better effect on creating pores within the mineral without destroying the structure of smectite.

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