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Physico-chemical and Morphological Changes of Sayong Kaolinite Clay Treated with Sulphuric Acid for Enzyme Immobilization

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Abstract. This study analyzed the effects of sulphuric acid (H_2SO_4) treatment on pysico-chemical properties and morphological changes of clay obtained from Sg. Sayong, Perak. The clay was ground and sieved to <150µm and treated with different concentrations of H_2SO_4. The treatment was completed by refluxing the clay with different concentration of H_2SO_4 (1M, 5M and 10M) at 100°C for 4 hours and followed by calcination at 500°C for 1 hour. The physic-chemical properties and morphological changes of the untreated and treated clay were compared using Surface Area Analyser, X-Ray Diffraction (XRD), Field Emission Scanning Electron Micrograph (FESEM), X-Ray Diffraction (XRD) and Fourier Transformed Infrared Spectroscopy (FTIR). The results showed that acid treatment of 5M increased the surface area from 25 m^2/g to 75 m^2/g and the pore volume increased from 0.1518 cc/g to 0.3546 cc/g. The nanopore size of the clay decreased from 24.8 nm to 19.4 nm after treated with acid. This can be explained due to the elimination of the exchangeable cations and generation of microporosity. The results of XRF showed SiO_2 increased from 58.34% to 74.52% and Al_2O_3 reduced from 34.6% to 18.31%. The mineral oxides such as Fe_2O_3, MgO, CaO, K_2O and TiO_2 also reduced. This concluded that H_2SO_4 treatment has led to significant removal of octahedral Al^{3+}, Fe^{3+} cations and other impurities. In conclusion, this study showed the physico-chemical properties and morphology of Sayong clay were improved once treated with H_2SO_4 and therefore suggests better supporting material for enzyme immobilization.

Introduction

Presently kaolin clay has many uses in different industries due to its unique physico-chemical properties. It is widely used in modern industry such as ceramics, paper coating, paper filling, paint extender, rubber filler, cracking catalysts, cements as well as traditional “Labu Sayong” cottage industry. In this type of clay, kaolinite is the major mineral component which usually contains quartz and mica, and some feldspar, illite, montmorillonite, ilmenite, anastase and others [1].

Worldwide there is an increasing interest of looking for a modern and higher value application of kaolinite clay. Enzyme immobilization supporting material is one of the promising applications for this clay. The use of kaolinite clay as a supporting material for immobilizing lipase, radioactive waste and application of NaY zeolite was reported by Ajayi et. al. (2012) [2][3][4]. According to Ajayi et. al. (2012), kaolinite clay are negatively charged aluminosilicate crystalline structures consisting of a three dimensional arrangement of SiO_2 and AlO_4^- tetrahedrally linked to each other by a shared oxygen atom. It is presence an inert, stable and relatively good pore aperture for immobilization purposes, aside the mechanical strength and thermostability. The silica and alumina content of kaolinite clay when upgraded, can serve as immobilization sites for various enzymes [3].

The industrial utilization of kaolinite is closely related to its reactivity and surface properties, which depend strongly on surface modification. Several methods have been suggested in literatures to improve the properties of clay materials which include among others mechanochemical activation [5], intercalation [6], thermo-chemical treatment [1][7] and chemical activation [7]. Acid activation has been widely studied as a chemical treatment method for the improvement of the surface and catalytic properties of fibrous clay (sepiolite and palygorskite), smectitic clays (saponite and montmorillonite) and amorphized (calcined/grounded) kaolin [1][7][8]. The method involves leaching of the clays with inorganic acids, causing disaggregation of clay particles, elimination of mineral impurities and dissolution of the external layers, thus altering the chemical composition and the structure of the clays [9].

The acid treatment is beneficial in terms of increased surface area, porosity and number of acid centers with respect to the natural clays. The acid treated clays are composed of a mixture of non-attacked clay layers and a hydrous, amorphous and partially protonated silica phase. These high surface area silica gels are competitive in different industrial uses and very promising as sorbents or as catalyst support [1]. Thus, the objective of this paper is to study the changes of Sayong kaolinite clay with sulfuric acid at different concentration. The physico-chemical and morphology changes of the clay were studied by different analytical instrument such as BET Surface Area Analyser, XRF, XRD, FTIR and FESEM.

Materials and Methods

Material Preparation: Clay Sample. Fresh local clay was obtained from Sg. Sayong in Kuala Kangsar, Perak, Malaysia. After collection, the sample was dried at 90˚C for 24 hours, ground by using grinder machine into fine powder and sieved through 150 μm mesh (Endecotts Octagon 2000 Digital Sieve Shaker, England) before further use as proposed in the literature [10]. **Acid Treatment of Clay.** The clay treatment was carried out by adding 50 g of the clay to 500 ml of acid solution (sulphuric and hydrochloric acid) of different concentrations (1M, 5M and 10 M) and refluxing at 100˚C under the atmospheric pressure in a round bottom flask equipped with a reflux condenser for 4 hours. The clay suspension was then rapidly quenched by adding 500 ml ice cold water. The content was then filtered, repeatedly washed with distilled water to remove any unspent acid, dried in an oven at 102˚C for 24 hours, calcined at 500˚C for 1 hour and ground in a mortar pastel to powder form as proposed in the literature [11].

Characterizations. The physico-chemical properties and morphological changes of untreated and treated Sayong kaolinite clay was characterized by using different analytical equipment such as BET Surface Area Analyser, X-Ray Flourescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Micrograph (FESEM). **BET Surface Area Analyser.** The surface area of untreated and treated Sayong kaolinite clay was performed by using nitrogen adsorption at liquid nitrogen temperature (77.35 K). The samples were out-gassed first at 110˚C and vacuumed for 10 hours. Analysis of the results involved the determination of specific surface area for treated and untreated samples using the BET equation. **X-Ray Fluorescence (XRF).** The chemical composition oxides of the samples were measured by using PANalytical's MiniPal (USA). **X-Ray Diffraction (XRD).** The XRD data was collected using Phillips analytical instrument (PANalytical X'Pert PRO, USA). The XRD patterns were recorded in the range of 10-70˚ with a scanning rate of 2˚/min. **Fourier Transform Infrared Spectroscopy (FTIR).** The clay sample was analyzed for its vibrational spectra with the aid of Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer 2000, USA) Spectrophotometer in the 400-4000 cm^{-1} range. The room temperature was 28˚C during the measurement. **Field Emission Scanning Electron Micrograph (FESEM).** Field Emission Scanning Electron Microscopy (FESEM) (Carl Zeiss, Supra 40VP, Germany) was used to observe the surface morphology and analyse the microstructure of the clay. The sample was initially dusted on a double sided carbon tape that was placed on a metal stub and coated with a layer of gold to minimize the charging effects.

Results and Discussion

BET Surface Area Measurement. The results for pore volume and BET specific surface area of untreated and acid treated Sayong kaolinite clay is summarized in Table 1. It can be clearly observed that the pore volume and BET surface area increase with the increase of H_2SO_4 concentration. The surface area of the Sayong clay increase to 72.78 m^2/g which is nearly three times than the untreated clay once the clay was treated with 5M H_2SO_4. The pore volume increase to 0.3546 cc/g which is more than 2 times than the untreated clay. The nanopore size of the clay decrease from 24.8 nm to 19.4 nm after treated with 5M H_2SO_4 acid. The increase of the surface area from natural to activated samples could be explained by the increase generation of silica as shown in the chemical data in Table 2, which related to the elimination of the exchangeable cations, delamination and the generation of micro-porosity during the processes as described in literatures [9][12]. It was also observed that the surface area decreased at higher acid concentration (10M), due to the polymerization of the generated free silica by the effect of excess acid concentration and deposited on the surface of the clay particle preventing it from further attack as described previously [13].

Table 1, BET surface area for acid-treated clay

H_2SO_4 concentration (M)	BET surface area (m^2/g)	Pore Volume (cc/g)	Nanopore Size (nm)
Untreated clay	24.46	0.1518	24.8
Treated clay H_2SO_4 1 M	36.30	0.1851	20.4
Treated clay H_2SO_4 5 M	72.78	0.3546	19.4
Treated clay H_2SO_4 10 M	57.32	0.2829	19.7

Chemical Composition Analysis (XRF Characterization). The XRF characterization was carried out to know the chemical compositions of the clay and the subsequent chemical changes that occurred due to acid treatment. Table 2 shows the results of chemical analysis of the untreated and acid treated Sayong kaolinite clay. From Table 2, the major compounds in the natural Sayong kaolinite clay is silica (SiO_2) and alumina (Al_2O_3) with minimal presence of some oxides such as potassium oxide, iron oxide, titanium oxide, magnesium oxide and others.

Due to the acid treatment, it is clearly observed that the oxides compositions of natural clay had changed significantly. The content of SiO_2 increased from 58.34% for the untreated clay to 74.52 % for the clay treated with 5M H_2SO_4. However it reduced to 70.77 % once the H_2SO_4 concentration was further increased to 10 M. This result can be explained due to the formation of mullite which protects the clay layers from further attack by the acid as reported in the other study [12]. From Table 2, it is clearly observed the reduction of Al_2O_3 contents at different concentrations of H_2SO_4. It can be concluded that the removal of Al^{3+} cations was highest at 5M H_2SO_4 compared to 1M and 10M concentrations. For the 1M H_2SO_4 concentration the percentage of Al_2O_3 remained was only 29.40% whereas at 5M H_2SO_4 the percentage was 18.31%. Once the H_2SO_4 concentration was increased to 10M the remained percentage was slightly higher at 22.03%.

The results of Al^{3+} removal with progressive H_2SO_4 concentrations (1M – 5M) can be related to the progressive dissolution of the clay mineral as described by the literature [14]. The other oxides such as Mg and Fe also decreased due to the leaching of the Mg^{2+} and Fe^{3+} as the acid concentration increased [11]. The octahedral sheet destruction passes the cations into the solution, while the silica generated by tetrahedral sheet remains in the solid phase due to its insolubility.

Table 2, Chemical compositions of untreated and treated Sayong kaolinite clay

Oxides compounds	Compositions (%)			
	Untreated clay	Treated clay (1M H_2SO_4)	Treated clay (5M H_2SO_4)	Treated clay (10M H_2SO_4)
SiO_2	58.34	60.32	74.52	70.77
Al_2O_3	34.60	29.40	18.31	22.03
K_2O	3.14	2.95	3.20	3.28
Fe_2O_3	2.58	0.92	1.09	0.63
CaO	0.11	0.03	0.02	0.02
Na_2O_3	0.23	0.20	0.20	0.21
TiO_2	0.44	0.45	0.47	0.50
MgO	0.19	0.12	0.13	0.14

Mineralogy Analysis. The mineralogical changes occurred in the clay due to H_2SO_4 acid treatment was studied by using X-Ray diffraction technique. Figure 1 shows the XRD patterns of the untreated and H_2SO_4 treated Sayong kaolinite clay at different concentrations. In general it was found that the peak intensity and the crystallinity of the kaolinite had decreased upon the increased of H_2SO_4 concentrations (in black circle). This can be explained due to the structural disorder that occurred owing to the acid treatment, which affects the crystalline character of the clay. The reduction of the peak may be related to the increase of crystallite size and/or the decrease of the mean lattice strain as previously discussed [11][15].

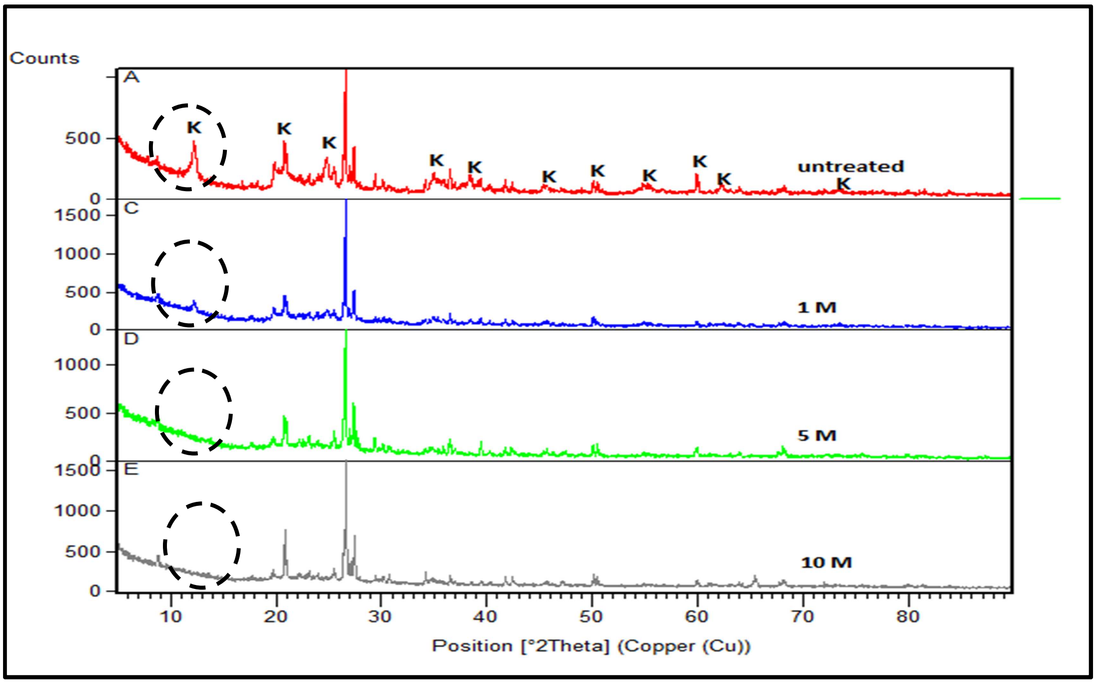

Fig 1. The XRD patterns of the untreated and treated Sayong kaolinite clay

FTIR. The FTIR spectrum of the untreated clay and H_2SO_4 treated Sayong kaolinite clay at different concentrations is shown in Figure 2. The sample was carried out in the range from 400-4000 cm^{-1} to study the effect of H_2SO_4 acid treatment on the clay mineralogical changes. The FTIR spectra of the untreated and treated clay samples reflect the structural modification which takes place due to acid activation. The intensity of the hydroxyl stretching band at 3694 cm^{-1} and 3620 cm^{-1} clearly show significant decrease after acid activation. This can be explained due to the removal of octahedral cations, causing the loss of water and hydroxyl groups coordinated to them [16]. In the O-H stretching region, the untreated and treated clay shows two predominant bands at 3694 cm-1 and 3620 cm^{-1} correspond to Al-OH stretching. Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets gives the absorption at 3620 cm^{-1}. A strong band at 3694 cm^{-1} is related to the in phase symmetric stretching.

When the clay was treated with acid, the peak intensity was found to decrease progressively as the acid strength increase from 1M to 10M. The structural hydroxyl vibration band is extremely weak indicating penetration of protons into the clay mineral layers and attack to the structural hydroxyl groups resulted in the dehydroxylation and a successive leaching of the Al^{3+} ions from the octahedral layer [17]. Leaching causes the intensity of the absorption bands at 913 and 749 to decrease. This result suggests the partial reduction of Al^{3+} and Fe^{2+} from the clay structure, in accordance with the changes in chemical composition as previously discussed in Table 2 and in agreement with the literature [16].

Strong bands in the range 1120-1000 cm^{-1} region are due to Si-O stretching in the untreated clay which changed in shape and position and finally diminished after treated with acid due to structural changes in the tetrahedral cations. The new peak was observed at 802 cm^{-1} for the 10 M H_2SO_4 acid treated sample, which gained intensity with the increased in the acid strength. This peak is due to the formation of free amorphous silica as reported in the literature [18]. The FTIR result is in clear agreement with the previous XRF result which indicated sequential degradation of the clay sheet upon acid treatment.

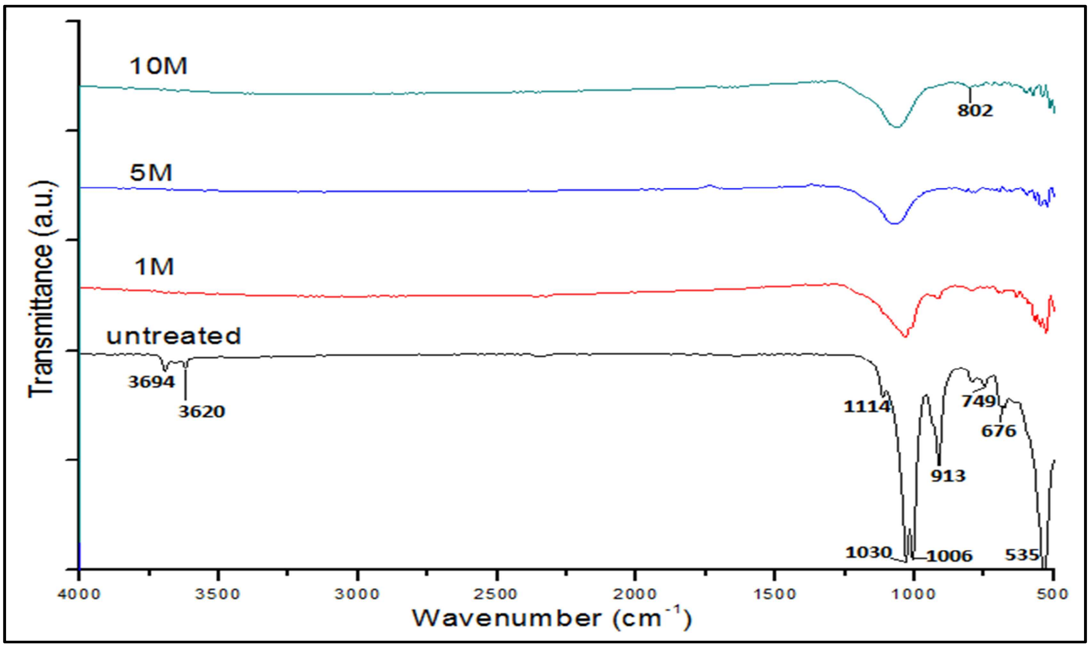

Fig 2, FTIR of untreated and H_2SO_4 treated Sayong kaolinite clay

FESEM. The scanning electron micrographs of the different Sayong kaolinite clay samples are presented in Figure 3 (a-f). Figure 3 (a,c,e) shows the morphological features of untreated clay, 1M and 5M H_2SO_4 treated clay at 5000x magnification, and Figure 3 (b,d,f) shows the morphological features of untreated clay, 1M and 5M H_2SO_4 treated clay at 10000x magnification. The SEM micrograph of untreated clay shows the presence of large particles that appeared to have been formed by several flaky particles stacked together in form of agglomerates. The SEM images of 1M and 5M H_2SO_4 treated clay show different particle morphology. The micrographs of 1M and 5M treated clay indicate the disaggregation and decrease in size of clay structure on acid treatment and in agreement with the previous study [11].

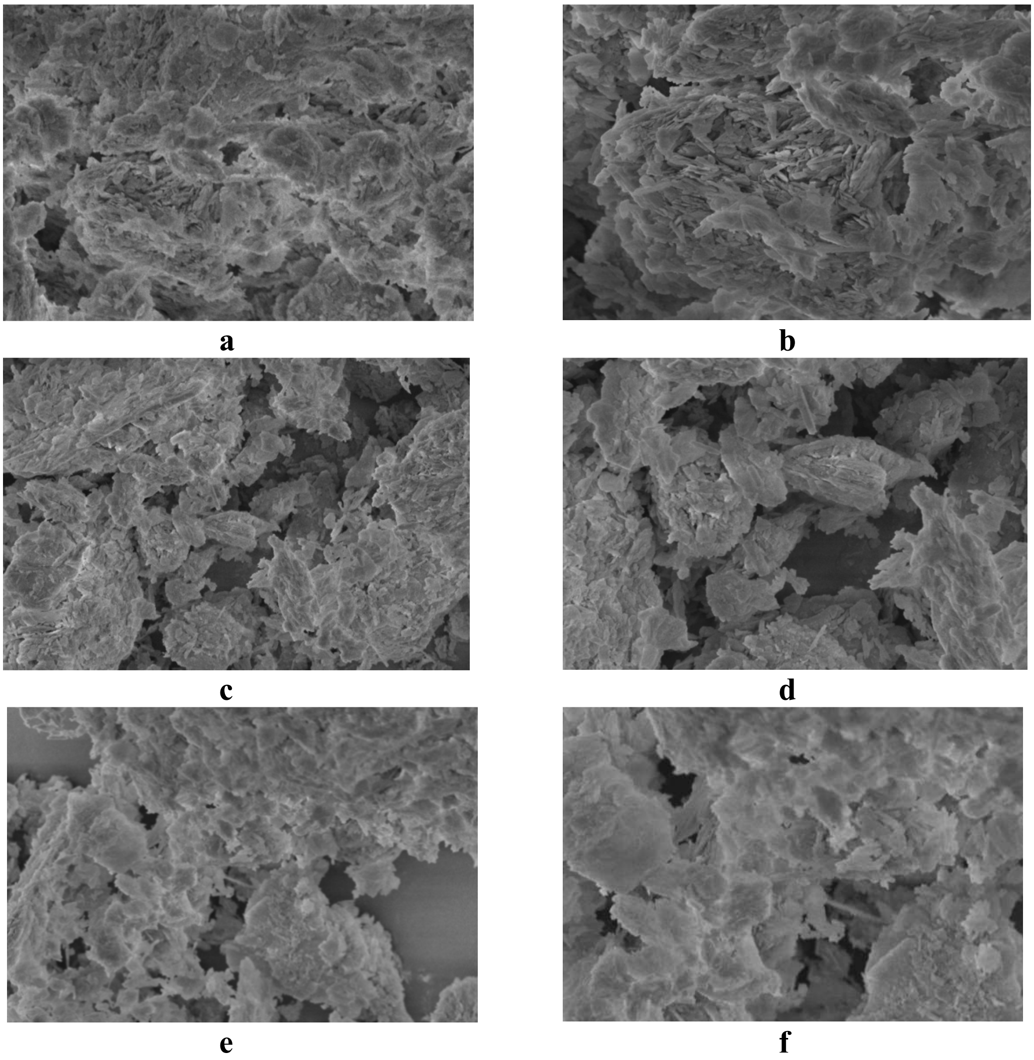

Fig 3, SEM pictures of untreated (a,b) and treated (1M-c,d; 5M-e,f) Sayong kaolinite clay for 5000x (a,c,e) and 10000x (b,d,f) magnification

Conclusions

The physico-chemical properties and morphological changes of Sayong kaolinite clay by H_2SO_4 was investigated. Analyses of the results showed that acid concentrations affect the physico-chemical and morphology of the clay. The BET Surface Area result clearly indicated the increase in surface area (from 25 m^2/g to 75 m^2/g) and pore volume (from 0.1518 cc/g to 0.3546 cc/g) once treated with 5M H_2SO_4. The XRF result showed the leaching and disintegration of the clay sheet after H_2SO_4 treatment at different concentration. As the acid concentration was increased from 1M to 5M and 10M, SiO_2 content increased and other oxides such as Al_2O_3, MgO, CaO, Fe_2O_3, TiO and K_2O decreased progressively. In conclusion this study showed improvement in the physico-chemical properties and morphology of Sayong clay after treated with H_2SO_4.

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