PURIFICATION OF LOCAL CLAY FOR CERAMIC MEMBRANE SUPPORT

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ABSTRACT

PURIFICATION OF LOCAL CLAY FOR CERAMIC MEBRANE SUPPORT

This research is aimed towards purifying clay from Indah Permai for ceramic membrane use. Conventional methods produce larger than 5 µm kaolin which is not tailored for ceramic membrane use due to the presence of inconsistent particle size and agglomerates. On the other hand, the presence of iron oxides in the raw clay creates a barrier in the pore structure of ceramic membrane. Therefore, particle size reduction and chemical extraction were performed to refine the clay particles. Probe-type ultrasonic technique was found to give the best results. Approximately 90% of its particle size is less than 5 µm. Larger agglomerates were also not found. The ultrasonic treated clay particles were further processed using oxalic acid to remove iron oxides. The reaction parameters such as concentration, pH and temperature were optimized. The optimum conditions required were acid concentration 0.2M, pH 2.5 and temperature 55^0C. The corresponding iron oxides removal was 12.55%. 881 cm^{-1} was not observed in the FTIR spectrum, representing structural iron component was removed from Al-Fe-OH bond. The technological characterizations have shown that the purified clay is predominantly kaolinite, indicating that it can be used as a starting material for fabrication of ceramic membrane support.

ABSTRAK

Tujuan kajian ini adalah untuk menulenkan tanah liat dari Indah Permai bagi kegunaan membrane seramik. Kaedah konvesional menghasilkan size partikel kaolin > 5 µm yang lazimnya tidak sesuai digunakan untuk kegunaan membran seramik disebabkan oleh size partikel yang tidak sekata dan penggumpalan. Di samping itu, kehadiran besi oksida dalam tanah liat mentah membentuk halangan dalam struktur liang membran seramik. Oleh demikian, teknik pengasingan partikel dan pengekstrakan secara kimia telah dilakukan untuk merawat partikel tanah liat. Ultrasonik jenis probe didapati menunjukkan keputusan yang memuaskan. Lebih kurang 90% daripada size partikel adalah kurang daripada 5 µm. Gumpalan yang besar juga tidak dikesan. Partikel tanah liat yang telah dihaluskan seterusnya diproses dengan asid oxalic untuk menyingkirkan besi oksida. Proses parameter seperti kepekatan asid, pH dan suhu dioptimunkan. Keadaan optimal yang diperolehi adalah pada kepekatan asid 0.2M, pH 2.5 dan suhu 55^{0}C. Sebanyak 12.55% besi oksida telah disingkirkan pada keadaan optimal. 881 cm^{-1} tidak dikesan dalam analisis FTIR. Pemerhatian ini menunjukkan bahawa komponen besi berstruktur telah disingkirkan daripada ikatan Al-Fe-OH. Keputusan analisis juga menunjukkan bahawa tanah liat yang telah diltulenkan adalah terdiri daripada kaolinite. Keputusan ini menunjukkan bahawa tanah liat yang dihasilkan sesuai digunakan sebagai bahan mentah dalam penghasilan sokongan membran seramik.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
Al	Aluminium
Al_2O_3	Alumina
$Al_2Si_2O_5\ (OH)_4$	Kaolinite
$C_2O_4^{2-}$	Oxalate
EDTA	Ethylenediaminetetraacetic
Fe	Iron
Fe^{2+}	Iron (II)
Fe^{3+}	Iron (III)
FWHM	Full peak width at half maximum peak height
FTIR	Fourier Transform Infrared Spectrometer
HCl	Hydrochloric acid
H_2O_2	Hydrogen peroxide
$H_2C_2O_4$	Oxalic acid
IR	Infrared
LOI	Loss of ignition
M	Mole
Mg	Magnesium
NA	Not available
ml	Millilitre
OH	Hydroxide
p value	Probability value
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
SiO_2	Silica
SO_{2-}	Sulphate ion
SO_4^{2-}	Sulphate ions
St_{def}	Stokes deformation number
Stk	Stokes number
Stk^*	Critical value of the Stokes number
T	Tetrahedral
W	Watt
XRD	X ray diffraction

LIST OF NOMENCLATURE

A	Concentration variable
A_m	Amplitude of vibration (m)
A_o, A_1 , A_2	Pre-exponential factor
a	Crystal unit cell vector in a axis
a ,a_1 ,a_2	Exponent of *a* is a measure for attractive force that need to be prevailed in the de-agglomeration process
a_H	Activity of protons in solution
B	pH variable
b	Crystal unit cell vector in b axis

b_1, b_2	Constant
C	Temperature variable
c_L	crack length
^{o}C	Celsius
$\mathbf{c}$	Crystal unit cell vector in c axis
E	Amount of energy dissipated
E	Power
E	Young's modulus
E_m	Energy density
E_o , E_1 , E_2	Activation energy
E_V	Specific energy for de-agglomeration process
D_b	Ball size
e	Exponent
e	Coefficient of restitution for the collision
F_1, F_2	Maximum surface coverage of protons
Hz	Hertz
h	Instantaneous height of the powder
h	Layer of liquid thickness
h_o	Initial height
h_o	Surface roughness of the particle
f	Frequency
I	Ultrasonic intensity
K	Constant
K	Stress concentration factor
L	Depth of the hardened layer
L	Ligand anion
L	Half the length of the crack
L	Particle diameter
Me	Metal cation
m_{Susp}	Mass of the suspension
$\dot{m}$	Mass flow rate
$\dot{N}$	Rate for a complete covering of the material surface
n	Number of values in a sample
n	Constant
P	Power output (W)
P_i	Fluid pressure
P_v	Power input per dispersion volume
P_v	vapour pressure of the fluid
P_∞	Sound pressure
R	Gas constant
R	Radius of crack tip or hole
R_{max}	Radius of the bubbles
r_d	Radius of the grinding cylinder
$\bar{S}$	Surface area
T	Temperature (K)
Th	Thoma number
t	Time
t_r	Residence time
U_c	Collision velocity
u_i	Fluid velocity

V	Volume of the suspension (ml)
v	flow velocity
v	Impact velocity
v_{app}	Velocity of the particle
v_g	velocity component it acquires during its subsequent fall
v_o	Threshold velocity of cavitation erosion
v_t	Tangential velocity of the ball when it leaves the internal wall
W_{cav}	Energy of cavitation
x	Diameter of the particle
x	Distance from the material surface
x_1	Concentration (M)
x_2	pH
x_3	Temperature (°C)
X_m	Maximum breakage of the particles
x_{mean}	Mean particle size
x_0	Mean particle size of the feed fraction
Y	Expected response
Y_d	Dynamic yield stress of the granule
y	Distance the ball falls prior to impact

LIST OF GREEK LETTERS

ρc	Acoustic impendence
γ	Amplitude of the ultrasonic
ξ	Amplitude of vibration
θ	Angle of reflection
ω	Angular frequency
ω	Angular velocity of the cylinder
ρ_g	Average granule density
v'	Ball velocity
α, β, γ	Corner angles
α	Constant parameter for a specific comminution process
β_o	Constant coefficient
ρr	Density of reactive surface sites on the mineral surface (mol m^{-2})
β_i	Estimated model coefficients or regression coefficient
$\bar{\sigma}$	Impact loads of mean amplitude
$\beta_i, \beta_j, \beta_{ij}$	Interaction coefficient of linear, quadratic and the second order terms, respectively
ε_{max}	Maximum strain
θ	Metallurgical parameter which measures the steepness of the hardening gradient
μ	Micro
ε_{min}	Minimum value of particle porosity
π	pi (3.142)
ρ	Population linear correlation coefficient
$\hat{Y}$	Predicted value of Y
ρ	Ultrasonic intensity

σ	Standard deviation of the population of all possible sample means
$\dot{\varepsilon}$	Strain rate
γ	surface energy
σ_B	Tensile stress
τ	Time interval
σ_U	Ultimate strength
ε	Velocity of sound
ϵ	Random error
μ	Viscosity

LIST OF SYMBOL

≈	Approximately
=	Equal to
>	Greater than
<	Less than
≠	Not equal to
%	Percentage

CHAPTER 1

INTRODUCTION

1.1 Overview

A membrane is a thin film which serves as a selective barrier between two phases. In the action of a driving force (i.e. pressure, concentration, etc), it allows permeable particles in the permeate stream whilst accumulates impermeable particles in the retentate stream. Generally, membranes can be classified into three groups: ceramic, polymeric and biological type. These three types of membranes differ significantly in their structure and functionality. The use of membrane technology has been commonly applied in the existing filtration facilities such as wastewater treatment, food processing (Basso *et al.*, 2009), water purification (van Gestel *et al.*, 2002), gas separation and the like. Figure 1.1 depicts the schematic diagram of membrane function in the filtration process.

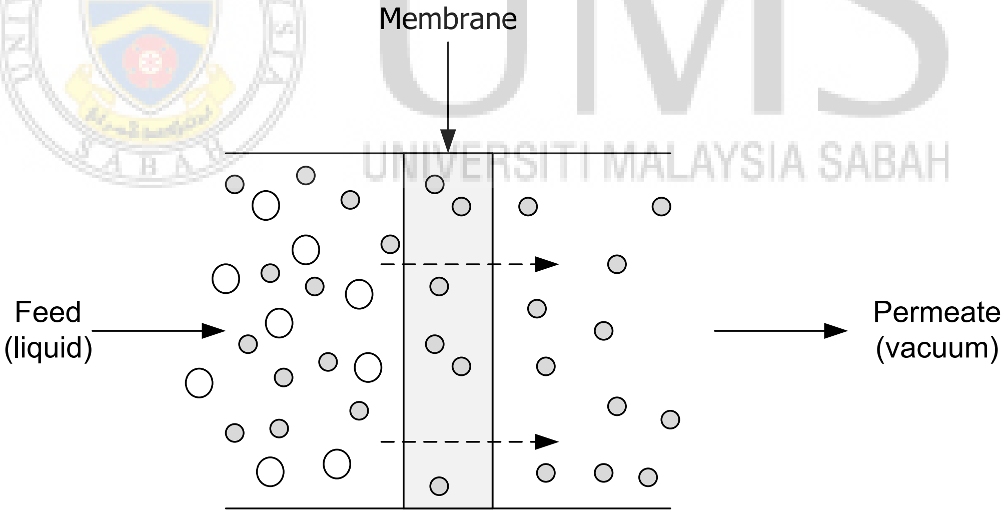

Figure 1.1: Schematic diagram of membrane function in the filtration process

In the separation technique, ceramic membrane has been recognized for years as it posseses several advantages like high thermal stability (Kirchner *et al.*, 2008), good selectivity and permeability (Wee *et al.*, 2008), high chemical resistance (Hao *et al.*, 2004)and well defined pore structure (Xomeritakis *et al.*, 1997 ; Li and Li, 2007).

The fabrication of ceramic membrane conventionally uses limited inorganic materials such as alumina, titania and zirconia, which have a relatively higher cost. Among inorganic materials, kaolin is an inexpensive material that can be utilized and its utilization is still investigated. In this study, kaolin is referred to as purified clay. The attractiveness of this research is the utilization of local clay to produce purified clay for membrane support use. Malaysia, particularly Sabah is endowed in abundance with clay soil, thus paving the way to develop the production of a potential industrial commodity. From the viewpoint of abundant local availability and technical feasibility it will become economical to establish such an industry in Sabah. Moreover, the purified clay on the market now is mostly used for industries such as paper making, paint manufacturing and so on. It is not tailored for ceramic membrane use. Against this current scenario, we took the initiative to produce purified clay from local clay, which can be used as raw material for ceramic membrane support.

1.1.1 Ceramic Membrane Background

The synthesized membrane is a type of inorganic film which made up of three layers. As shown in Figure 1.2, the first layer of the membrane is called the top layer, followed by an intermediate layer and a porous support. The top layer ,the intermediate layer and the porous support has different thickness, typically 1-10 µm,10-100 µm and a few millimeters thick ,respectively. Their pore sizes are usually in the range of 2-50 nm, 0.05-0.5 µm and 1-10 µm, respectively (Lindqvist and Lidén, 1997).

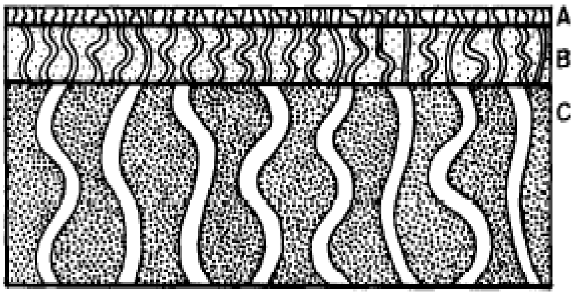

Figure 1.2: Schematic diagram of an inorganic membrane : (A) top layer, (B) intermediate layer and (C) porous support (Lindqvist and Lidén, 1997)

Among these layers, the porous support is an important layer as it governs the transport property as well as provides structural stability to the fabricated membrane (Wee *et al.*, 2008). In this study, the purified material that we prepared will be used to fabricate the porous support. Therefore, it is important to choose the suitable raw material from the viewpoint of purity and characteristics, in order to produce defect free porous support structure.

Several materials have been used for ceramic membrane support synthesis, as shown in Table 1.1. Basically, the preparation of ceramic membrane is based on the nature characteristics of a suitable starting material. For example, silica element has higher thermal stability and can withstand in the acidity condition whereas alumina element enhances mechanical strength to the ceramic membrane (Wee *et al.*, 2008). Besides that, kaolinite acts as a binder in the green state of ceramic membrane due to its good film forming ability (Dondi *et al.*, 2007). It is also evidenced that kaolinite shows plasticity behavior on the ceramic membrane by shaping homogenous surface (Bouzerara *et al.*, 2006).

Table 1.1: Different Materials for Ceramic Membrane Support Synthesis

Element	Reference
α- alumina/ corundum	Wee *et al.* (2008); Ganesh and Ferreira (2009) ;Martín-Ruiz *et al.*(2009)
γ- alumina	Lamber and Gonzalez (1999); Wee *et al.* (2008)
Kaolinite	Mohammadi and Pak (2003)
Silica	Kang *et al.* (1995);Dong *et al.* (2006)
Titania	van den Berg *et al.* (2003); Wee *et al.* (2008)

1.2 Clay Background

Basically, rocks that are rich in kaolinite are known as china clay or kaolin. In nature, kaolin is an aluminosilicate material enriched with kaolin group minerals such as kaolinite, halloysite, dickite and nacrite (Grim, 1962). Kaolinite is the dominant clay mineral in the kaolin. Its chemical formula is expressed as $Al_2Si_2O_5(OH)_4$. Kaolinite belongs to 1:1 clay minerals. Inside 1:1 clay minerals, the tetrahedral sheets are situated adjacent to the octahedral sheets in the clay minerals with hydrogen bonding. The coplanar tetrahedral sheets and the apical oxygen are bonded to an octahedral second layer containing cations such as Al (II), Fe (III) or Mg (II) (Pérez-Rodríguez *et al.*, 2006).

1.2.1 Characteristics of Kaolinite

A unit cell of kaolinite is a combination of tetrahedral and octahedral layers. It consists of primary elements such as silicate and alumina, with hydroxyl groups present between the layers, as shown in Figure 1.3.

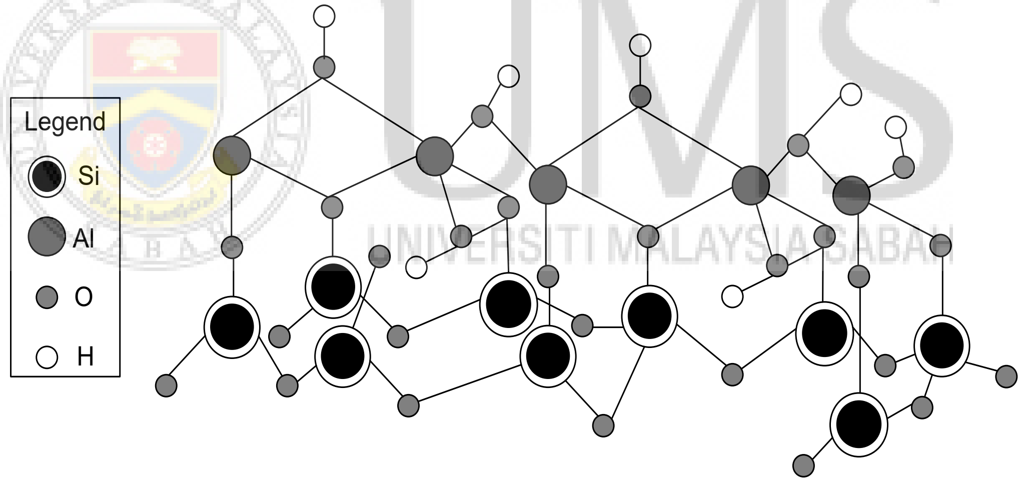

Figure 1.3: Model of kaolinite structure (Alkan *et al.*, 2005)

Typically, two significant hydroxyl groups exist in the kaolinite structure, namely inner surface hydroxyl groups and inner hydroxyl groups (Frost *et al.*, 2002; Pérez-Maqueda *et al.*, 2005). The first one is commonly distributed around the outer of the octahedral layer whereas the latter is situated in the inner plane of the octahedral layer. 3 of 4 hydroxyl elements in kaolinite are situated in the outer layer whilst the remaining one is entrapped inside layers.

Different lattice has different corner angles (α, β, γ) and crystal unit cell vectors (a,b,c) . Figure 1.4 shows the geometry of a basic unit cell of kaolinite. The silica (tetrahedral-bonded) and alumina (octahedral-bonded) inside kaolinite are in the **a** and **b** axis, in the arrangement of atoms in unit cell. They stacked one above along direction of **c**, resulting formation of triclinic frame.

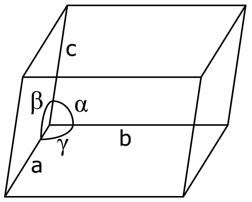

Figure 1.4: Geometry of a common unit cell

Figure 1.5 shows planes in a unit cell of kaolinite clay. The planes in a unit cell of kaolinite are categorized in two groups, namely basal plane and prism plane. The basal plane (i.e. 001,002) refers to the orientation of the particle is perpendicular to Z direction whereas the prism plane (i.e. 020,110) is not oriented in the tangent axis (Sachan and Penumadu, 2007).

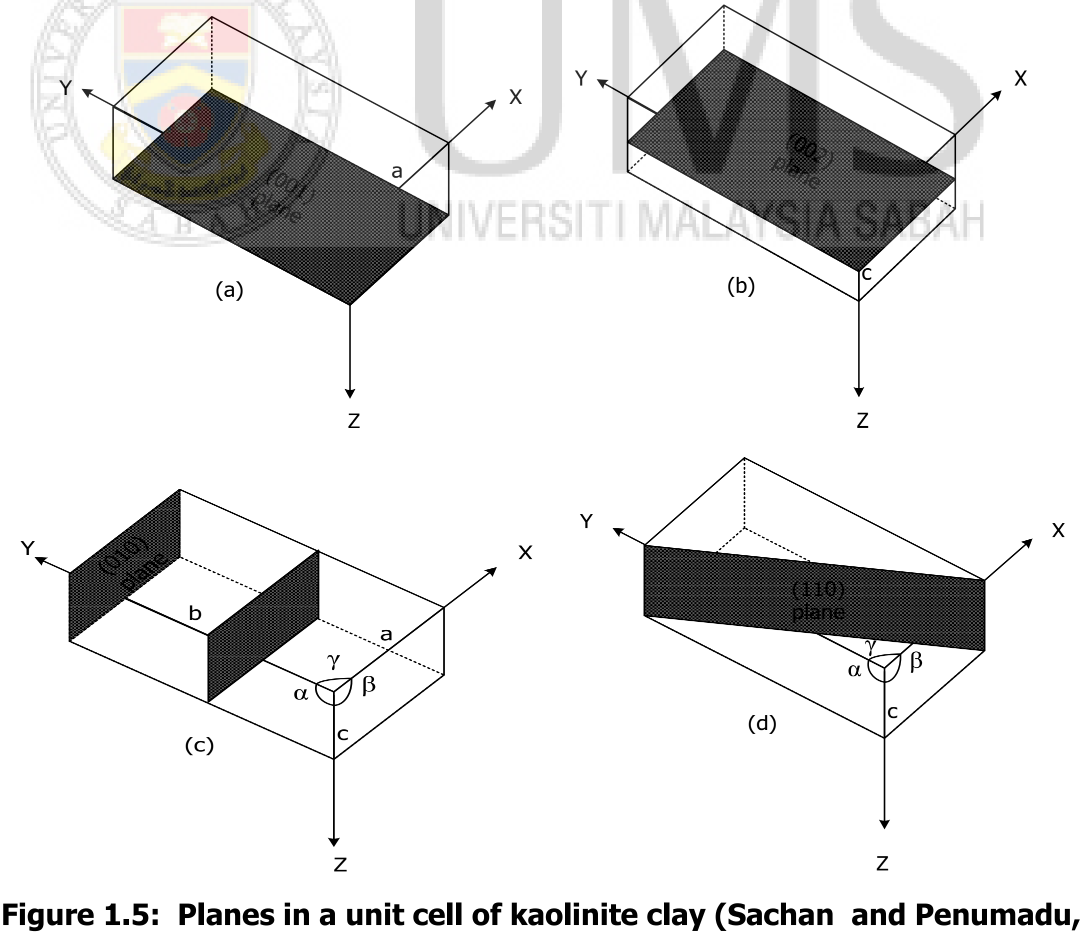

Figure 1.5: Planes in a unit cell of kaolinite clay (Sachan and Penumadu, 2007)

1.3 Demand Overview

Kaolin has been and continues to be of the vital industrial material. It can be seen that kaolin has a range of manufacturing applications, which are classified in three significant market areas, namely paper , ceramics and 'performance minerals'. According to British Geological Survey (2006), major kaolin demand is dominated by the paper industry which report for about 70% of total sales. Kaolin performs two different functions in the paper processing. 37% of kaolin is incorporated into the paper body as filler to reduce treatment cost and also to improve the printing characteristics of the paper. In the meantime, 33% of kaolin is used as a coating medium, boosting the surface properties of the paper such as brightness, smoothness, gloss and ink receptivity and the like. The ceramics industry is the second most essential sector, reporting for about 22% of total sales (British Geological Survey, 2006). Main market areas included United Kingdom, France, Italy, Spain, Germany and Asia. Its key function is to confer whiteness to the ceramic body. For this reason, kaolin is mostly used in the manufacturing of vitreous china sanitary ware, tableware, wall tiles, electrical porcelain and glazes. Other uses include act as 'performance mineral'. In the application of 'performance mineral', kaolin performs as fillers in paint, rubber, plastics, adhesives and pharmaceutical.

Similarly, Abdel-Khalek (1999) has reported that important market sectors were found related to the manufacturing of paper, sanitary and ceramic products. Figure 1.6 shows the percentage usage of both local and imported kaolin per year (Abdel-Khalek, 1999). The production of kaolin used in ceramic products in 1990 was 441,020 tonnes per year. Out of the total, the kaolin consumption in the cement and aluminosilicate sectors accounted 75%, followed by tiles and ceramics with 18%.

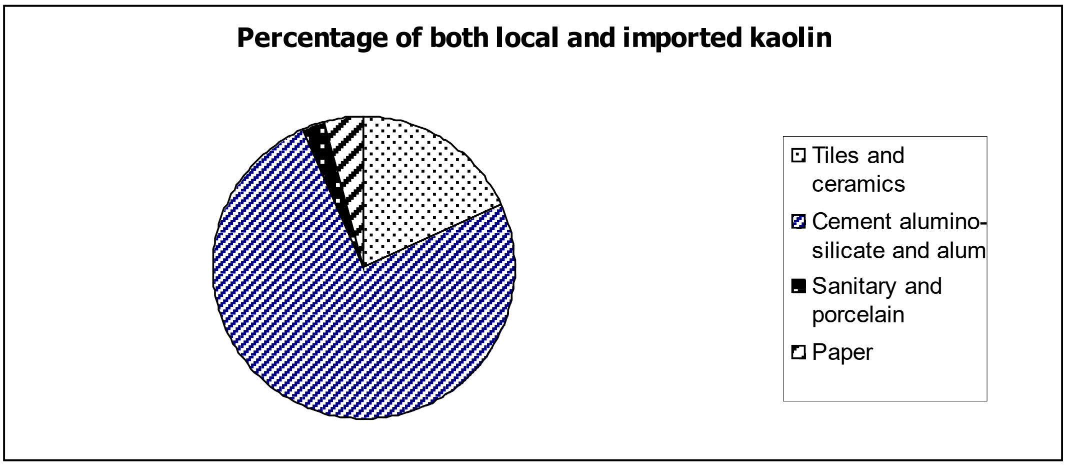

Figure 1.6: Percentage usage of both local and imported kaolin (Abdel-Khalek, 1999)

Figure 1.7 shows annual forecast of the demand of kaolin in ceramics and paper industries (British Geological Survey, 2006). From a total of about 166,345 tonnes in 1997, a total of 146,000 tonnes was utilized in ceramics production. The total demand on kaolin consumption in the year 2000 was reported at about 184,000 tonnes of which 155,000 tonnes was used in ceramics manufacturing and the remaining in paper processing. The increment of kaolin demand indicates the importance of kaolin as a raw material in the paper and ceramic industries.

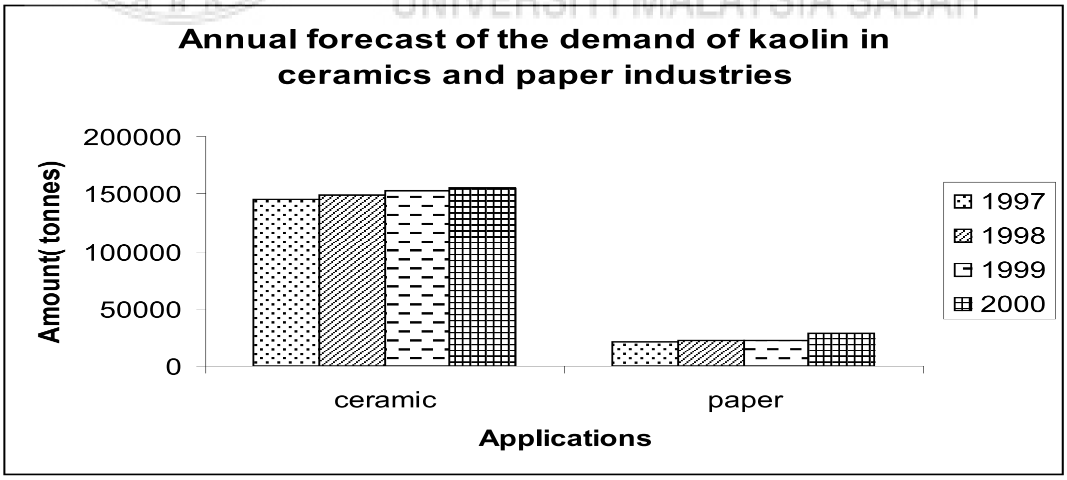

Figure 1.7: Annual forecast of the demand of kaolin in ceramics and paper industries (British Geological Survey, 2006)