Modification of Ntezi Bentonite Structure by Hydrochloric Acid: Process Kinetics and Structural Properties of the Modified Samples

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Abstract. Bentonite from Ntezi was modified by reacting it with different concentrations of hydrochloric acid solutions. The modified samples were analysed by x-ray fluorescence. The kinetics of the modification reaction was studied by performing the experiment at different temperatures and times. Results of the analysis of the modified samples showed that the octahedral cations were removed which altered the chemical composition of the bentonite. The surface area and adsorptive capacity of the bentonite were improved after the modification. The kinetic studies showed that the acid modification reaction is controlled by the product layer diffusion and can be represented by $[1-(1-X)^{1/3}]^2 = k\,t$; where, X is the fraction of the bentonite dissolved at time t. The activation energy was determined to be 24.98 kJ/mol.

Keywords: adsorption, bleaching, activation, kinetic model, chemical treatment, bentonite

Introduction

Natural clays are acquiring prominence as low-cost adsorbent over the past few decades due to their local and abundant availability and capability to undergo modification. The use of these natural clays is hampered by the presence of net negative charge on the surface and small surface area and these factors have led to the need for research and development in the field of modification of clay surfaces to enhance their adsorptive properties.

Clay minerals vary in their chemical composition and this leads to varying mineralogical properties that include: layer charge, cation exchange capacity, adsorption capacity and morphology (Steudel *et al*., 2009). Due to the large chemical composition variability, clay minerals are used in different industrial applications such as ceramics, food, chemical and paper industries. Sometimes, the clay minerals are used in their natural state and at other times after some specific modification (Komadel, 2003). One of such modification methods is acid treatment. Acid activation of clay mineral has been studied for years by many researchers (Steudel *et al*., 2009; Vicente-Rodriguez *et al*., 1994a; Suarez *et al*., 1992; Cetisli and Gedikbey, 1990; Bonilla *et al*., 1981; Rodriguez-Reinoso *et al*., 1981; Abdul-Latif and Weaver, 1969). Different types of acid treatment have been described in the literature, varying from each other by the nature of the acid used, temperature, and intensity

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and time of the attack. Acid treatment of clay minerals, namely fibrous clays (Myriam *et al*., 1998; Suarez-Barrios *et al*., 1995; Vincente Rodriguez *et al*., 1995, 1994a), smectites (Suarez *et al*., 2001; Prieto *et al*., 1999; Vincente Rodriguez *et al*., 1994b) and Kaolinite (Belver *et al*., 2002) is widely applied in order to optimise their physicochemical behaviour, aiming better industrial properties. Xianzhen and Chuyi (1990) have done acid treatments with sepiolite, concluding that the silica obtained could be competitive in different industrial ways, with that obtained by precipitation. The acid treatment of clay minerals is usually referred to as acid activation, because it increases the specific surface area and the number of active sites of the solids. This treatment modifies the surfaces of clays by disaggregations of particles, possible elimination of mineral impurities and removal of metal-exchange cations. The common commercial use of acid-treated clay minerals is bleaching or decolourations of oils (Christidis *et al*., 1997; Srasra *et al*., 1989; Taylor *et al*., 1989; Kheok and Lim, 1982) and in general in the fields of adsorption and catalysis (Mokaya and Jones, 1995; Fahn and Fenderl, 1983).

Two types of octahedral sheets occur in clay minerals: dioctahedral, where two-thirds of the octahedral sites are occupied by trivalent cations, such as Al^{3+} or Fe^{3+}; and the trioctahedral type, mostly occupied by divalent cations, such as Mg^{2+}; the negative charge of the layers is balanced by hydrated exchangeable cations in the

interlayers, mostly Ca^{2+}, Mg^{2+}, and Na^+ (Tomic *et al*., 2011; Tyagi *et al*., 2006). Acid modified natural bentonite are the subject of many researchers (Amari *et al*., 2010; Madejova *et al*., 2009; Steudel *et al*., 2009; Venaruzzo *et al*., 2002; Bergaya and Lagaly, 2001). The first step in modifying the clay mineral structure with acid is a separation of exchangeable cations from protons. The second step is flushing Al, Mg, and Fe from octahedral and tetrahedral sheets, in a way that SiO_4 groups of tetrahedral sheets remain mostly intact.

In this work, hydrochloric acid modification of bentonite from Ntezi was carried out to increase the surface area and adsorption capacity and also to investigate the structural changes that occurred in the modified samples. Special emphasis was paid to the kinetics of the modification process to study its mechanism.

Materials and Methods

Bentonite samples were mined from the site, dried and grinded to 0.212 mm particle size. These samples were reacted with different concentrations (2, 4, 6, 8, 10, and 12 mol/L) of hydrochloric acid solution. Ten grams of the sized fraction was reacted with already determined volume of the acid solution in a 250 mL bottomed flask and heated to a fixed temperature of 70 °C, while, on a magnetic stirring plate stirring was continued throughout the reaction duration. After completion of the reaction time, the suspension was immediately filtered to separate undissolved materials, washed three times with distilled water. The resulting solutions were analysed for aluminum, magnesium and iron ions using MS atomic absorption spectrophotometer (AAS 4000 Perkin Elmer). The residue was washed to neutrality with distilled water, air dried and oven dried at 80 °C and labeled as NZ0, NZ2, NZ4, NZ6, NZ8, NZ10, and NZ12, where, the numbers denote the acid concentration used in the activation process. To study the kinetics of the dissolution process of the octahedral ions-aluminum, magnesium and iron, the activation was repeated at different times (1 to 6 h) and at different temperatures (70 to 120 °C).

The chemical compositions and intensity change of absorption bands of the solid residues were determined by x-ray fluorescence (XRF, Philips PW 2400) and fourier transforms infrared (FTIR, Shimadzu S8400) spectroscopy, respectively. The surface area of the natural and treated samples were determined using the method of ethylene glycol monoethyl-ether (EGME) as developed by Carter *et al*. (1986; 1965), while, the cation exchange capacity (CEC) was determined using

the method of Inglethorpe *et al*. (1993) which involves centrifuging a mixture of few grams of clay with solution of buffered barium chloride for hours and discarding the supernatant, adding distilled water and solution of magnesium sulphate, then titrating the mixture with EDTA.

The bleaching capacity of the natural and acid activated clay samples was investigated by using them to bleach palm oil. About 5 g of each sample was reacted with refined palm oil and heated to 80 °C for 30 min. At the completion of the reaction time, the oil was filtered and the bleaching efficiency was determined by measuring the colour of the bleached oils using a uv-vis spectro-photometer (Shimadzu UV mini 1240) at wavelength of 450 nm.
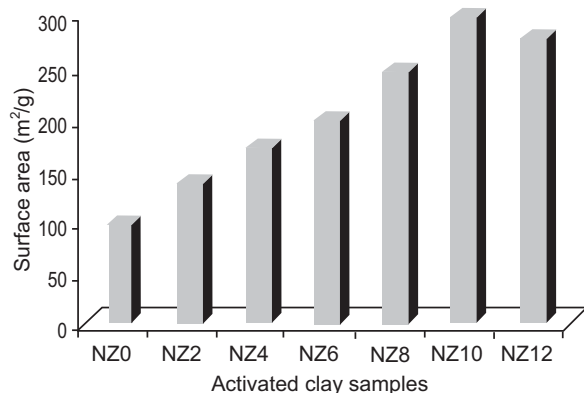
Results and Discussion

Chemical composition of bentonite samples. The chemical composition of the natural and treated bentonite samples are shown in Table 1. The content of SiO_2 was observed to increase as the acid concentration increased up to 10 mol/L and decreased with further increase in acid concentration. This could be due to the formation of mullite which protects the clay layers from further acid attack. The contents of the octahedral cations (Al_2O_3, Fe_2O_3 and MgO) decreased intensely as the acid concentration increased and they were increased with further attack after 10 mol/L concentration (Table 1). The behaviour shown by the Al_2O_3, Fe_2O_3, and MgO contents with progressive acid treatment is related to the progressive dissolution of the clay mineral. The octahedral sheet destruction passes the cations into the solution, while, the silica generated by the tetrahedral sheet remains in the solid phase due to its insolubility (Dias *et al*., 2003). Pesquera *et al*. (1992) suggest that this free silica generated by the initial destruction of the tetrahedral sheet, is polymerised by the effect of such high acid concentration and is deposited on the undestroyed silicate fractions, thereby protecting it from further acid attack (Vicente-Rodriguez *et al*., 1994a; Srasra *et al*., 1989).

Surface area of the activated bentonite. The acid activation was carried out with hydrochloric acid concen-tration range from 2 mol/L to 12 mol/L. Pushpaletha *et al*. (2005) reported that the surface area of acid activated bentonite generally increases with increase in acid concentration until a maximum surface area is reached after which it gradually decreases. In this study, the surface area was observed to increase with increase

**Table 1.** Chemical composition and Si/(Al + Fe + Mg) of natural and HCl modified bentonite from Ntezi

Chemical composition	Clay samples						
	NZ0	NZ2	NZ4	NZ6	NZ8	NZ10	NZ12
Al_2O_3	16.54	13.87	10.23	7.09	5.94	2.41	2.88
SiO_2	54.72	59.93	65.84	69.75	72.53	75.61	75.09
Fe_2O_3	13.23	10.14	8.06	5.04	3.78	2.17	2.23
CaO	0.41	0.35	0.21	0.12	0.04	0.01	0.01
MgO	7.10	5.36	3.19	2.16	1.49	0.52	0.54
K_2O	0.35	0.16	0.09	0.03	0.01	0.01	0.01
TiO_2	1.24	0.93	0.68	0.48	0.27	0.14	0.06
Na_2O	0.04	0.02	0.01	0.01	0.01	0.001	0.001
ZnO	0.89	0.57	0.38	0.19	0.11	0.04	0.02
LOI	5.28	3.85	3.16	2.42	1.94	1.65	1.11
Total	99.80	95.18	91.85	87.29	86.12	82.561	81.951
Si/(Al + Fe + Mg)	1.48	2.04	3.07	4.88	6.47	14.83	13.29
Bleaching efficiency (%)	38.9	54.97	62.87	69.82	77.45	91.64	84.06
Surface area (m^2/g)	97	136	169	197	245	297	275

in acid concentration from 2 mol/L to 10 mol/L. A maximum surface area was obtained with 10 mol/L HCl as shown in Fig. 1. This increase in surface area with rise in acid concentration is attributed to the removal of impurities, replacement of exchangeable cations such as K^+, Na^+ and Ca^{2+}, with hydrogen ions and leaching out of Al^{3+}, Fe^{3+} and Mg^{2+} from the octahedral and tetrahedral sheets which expose the edges of the platelets (Tsai *et al*., 2007). The decrease in the surface area with further increase in acid concentration could be attributed to the deeper penetration of the acid into the voids and excessive leaching of Al^{3+}, Fe^{3+} and Mg^{2+}, resulting in the collapse of the crystalline structure (Pesquera *et al*., 1992).

Cation exchange capacity of the activated samples. The results of the cation exchange capacity of the activated samples showed that the exchange ability of the activated samples decreased as the concentration of the acid used in the activation increased (Fig. 2). With the increase of concentration of hydrochloric acid, the bentonite showed a gradual decrease of the CEC until dissolving with 10 mol/L acid. In treatment with 12 mol/L HCl acid, as the SiO_2 content decreased, an increase of CEC was observed in comparison with the CEC observed with the sample treated with 10 mol/L. This is due to the removal of the exchangeable ions from the lattice of the clay samples by the acid hydrogen ion which occupies the vacant sites.

Fig. 1. Surface area of bentonite modified with different acid concentrations.
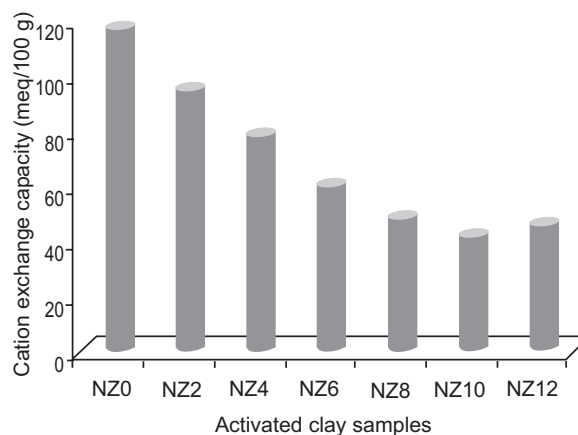
**Fig. 2.** Cation exchange capacity of the clay samples modified with different acid concentrations.

Effect of time on the modification of bentonites.
Results of the activation process at different times
showed that there is a linear relationship between the
fraction of the octahedral ions removed and time. This
is shown in Figs. 3-5 for the removal of Al^{3+}, Fe^{3+} and
Mg^{2+} ions, respectively. Comparison of the rate of
removal of these three cations, showed that the removal
is in the following order, $Mg^{2+} > Fe^{3+} > Al^{3+}$ as shown
in Figs. 3-5.

**Effect of temperature on the modification of
bentonite.** The effect of temperature on the bentonite

modification was studied in the range of 70-120 °C.
The experimental results are presented in Fig. 6. Data
in the figure shows that the dissolution rate of the
cations in the acid medium increased as the leaching
temperature increases up to the maximum temperature
used in this study. The increase in removal rate of the
cations could be as a result of high kinetic energy in
the system which speeds up the rate of reaction on the
surface of the clay. The same trend was reported by
others (Numluk and Chaisena, 2012; Xu *et al.*, 2012;
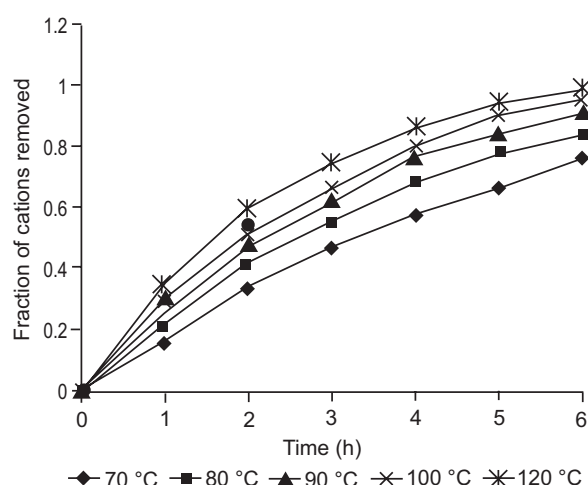Philips and Wills, 1982).
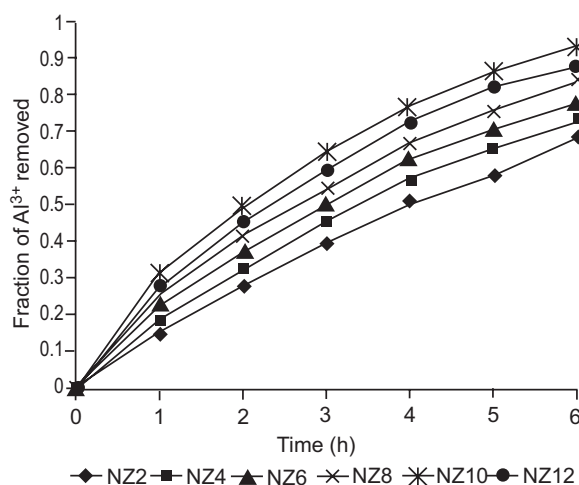
Fig. 3. Plot of fraction of Al^{3+} removed *vs* time
for samples activated at different acid
concentrations.
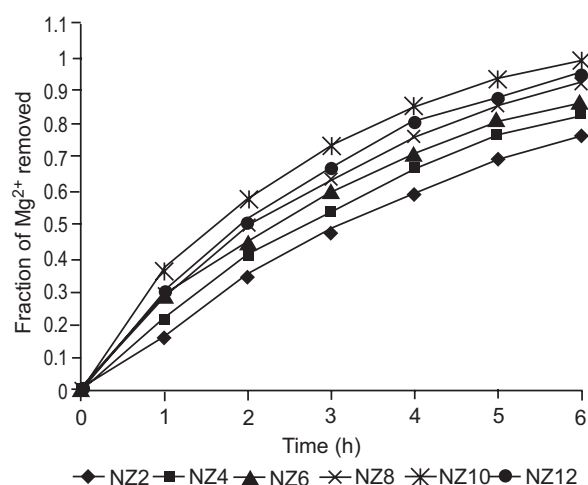
Fig. 5. Plot of fraction of Mg^{2+} removed *vs* time
for samples activated at different acid
concentrations.
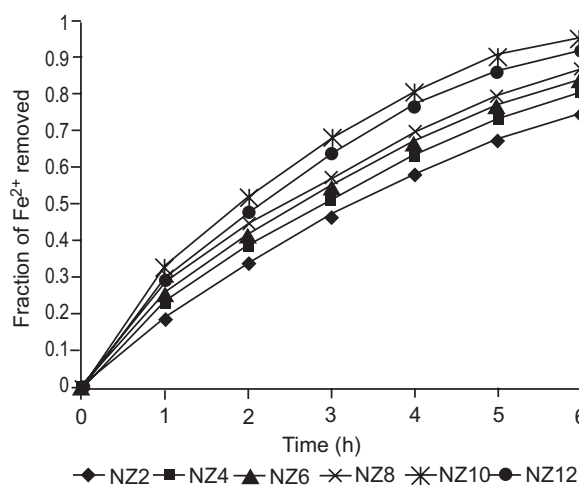
Fig. 4. Plot of fraction of Fe^{3+} removed *vs* time for
samples activated at different acid
concentrations.

Fig. 6. Plot of fraction of cations removed after
modification at different temperatures
(using 10 mol/L HCl activated sample).

Fourier transforms infrared (FTIR) spectroscopy analysis. The FTIR spectra of the natural and hydrochloric acid-leached samples were carried out in the range from 400-4000 cm^{-1} to study the effect of acid-leaching on the clay mineral. The FTIR spectra of the raw and acid-leached samples are shown in Fig. 7-8, respectively. The changes in the functional groups provide the indication of the modifications that occurred during the activation process. During the acid-leaching of the clay samples the protons from the acid medium penetrate into the clay structures attacking the OH groups thereby causing the alteration in the adsorption bands attributed to the OH vibrations and octahedral cations. The intensities of the stretching bands observed at 3623, 3432, 1641, and 920 cm^{-1} (associated with O-H, along with Al-OH stretch) decreased after acid-activation. The increase in the severity of acid caused the disappearance of the stretching bands at 4660, 3694, 2376, and 998 cm^{-1} assigned to the H-O-H stretching. The peak assigned to Si-O-Si stretch at 788 and 1066 cm^{-1} remained after acid leaching, similar result was reported by others (Christidis *et al*., 1997; Komadel *et al*., 1990). The bands at 525, 690, and 998 cm^{-1} disappeared after the acid treatment of the clay sample. The transformation of the tetrahedral occurred at 788 cm^{-1} which was increased after the acid treatment.
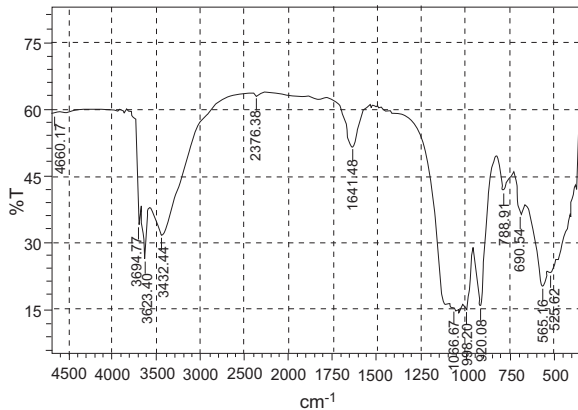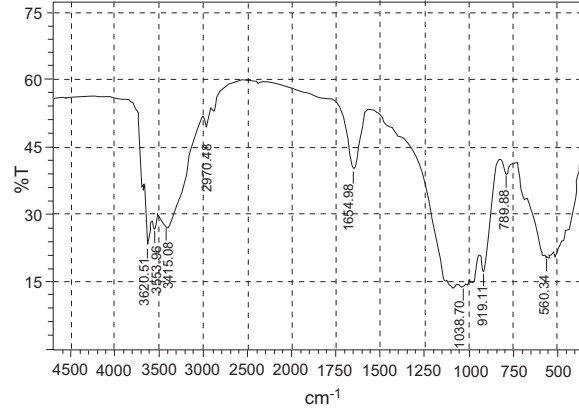

Fig. 7. FTIR spectra of natural Ntezi clay.

Activation kinetics studies. The kinetic studies showed that the acid modification reaction is controlled by the product layer diffusion and can be represented by
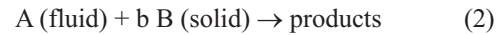
$$[1-(1-X)^{1/3}]^2 = k\,t \tag{1}$$

where:

X = fraction of the bentonite dissolved at time t. The activation energy was determined to be 24.98 kJ/mol.

Fig. 8. FTIR spectra of 10 mol/L HCl acid-activated Ntezi clay.

The reaction between a solid and a fluid may be represented by

$$A\,(fluid) + b\,B\,(solid) \rightarrow products \tag{2}$$

The rate of reaction between a solid and a fluid can be expressed by heterogeneous and homogeneous reaction models. According to the shrinking-core model, the reaction is considered to take place at the outer surface of the unreacted particle. When no ash forms, the reacting particle shrinks during reaction and finally disappears. For a reaction of this kind, the following three steps are considered to occur in succession during reaction (Levenspiel, 1972).

1. Diffusion of fluid reactant through the fluid layer to the surface of the solid.

2. Reaction of the fluid reactant and solid on the surface of the solid.

3. Diffusion of the products through the film layer to the bulk fluid.

The slowest of these sequenced steps is the rate-determining step. If the reaction is controlled by film diffusion, it becomes

$$X = [3bk_c C_A / \tilde{n}_B R]\,t = k_f\,t \tag{3}$$

if it is controlled by chemical reaction, it becomes

$$1 - (1 - X)^{1/3} = [bk_s C_A / \tilde{n}_B R]\,t = k_r\,t \tag{4}$$

the product layer diffusion control is given by

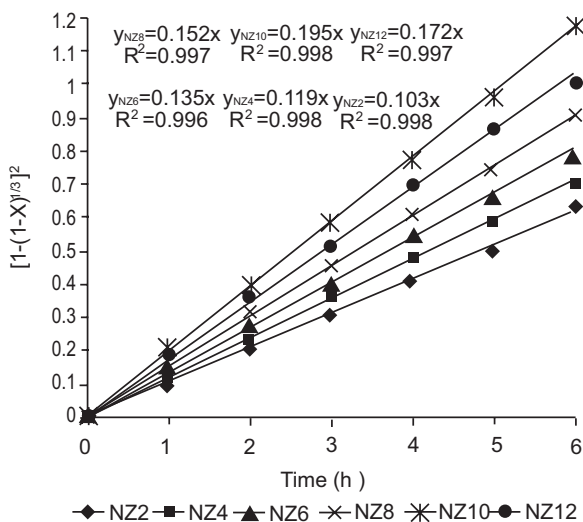$$1 + 2(1 - X) - 3(1 - X)^{2/3} = [2M_B DC_A / \tilde{n}_B bR^2]$$
$$t = k_d\,t \tag{5}$$

where:

X = fraction of B dissolved in A, $ñ_B$ is the molar density of solid reactant (mol/m^3), R is the radius of a sphere (m), b is the stoichiometric coefficient of the solid, k_c, k_f, k_s, k_r, and k_d are rate constants, D is the effective diffusion coefficient (m^2/s), M_B is the molecular weight of B, and C_A is the concentration of A in the bulk solution (mol/m^3).

The experimental data of Figs. 3-5 were tested with the above kinetic models, but it was determined statistically that the dissolution reaction did not fit the models. The data were then analysed using the kinetic model as developed by Jander (1927) given by:
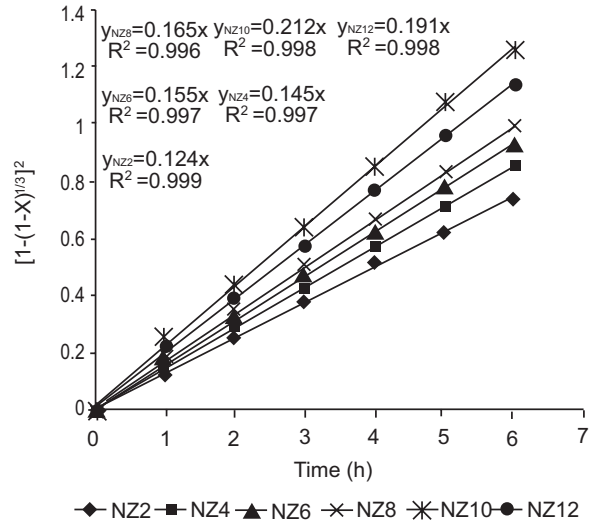
$$[1 - (1 - X)^{1/3}]^2 = k_q t \qquad (6)$$

Using this equation, the plot of $[1 - (1 - X)^{1/3}]^2$ versus time gave straight lines passing through the origin as shown in Figs. 9-11 for Al^{3+}, Fe^{3+} and Mg^{2+}, respectively. The coefficient of determination (R^2) values was used to determine the fitness of the data to the equation. As can be observed from the values of R^2, it is evident that the fitness is close to unity for all the data.

The experimental data of Fig. 6 was tested with the kinetic equation and straight lines passing through the origin were obtained as shown in Fig. 12. The apparent reaction rate constants calculated from the slopes of Fig. 12, were plotted against the reciprocal of the temperature according to the Arrhenius equation to

Fig. 10. Plot of $[1\text{-}(1\text{-}X)^{1/3}]^2$ vs time for Fe^{3+} removal at different acid concentrations.
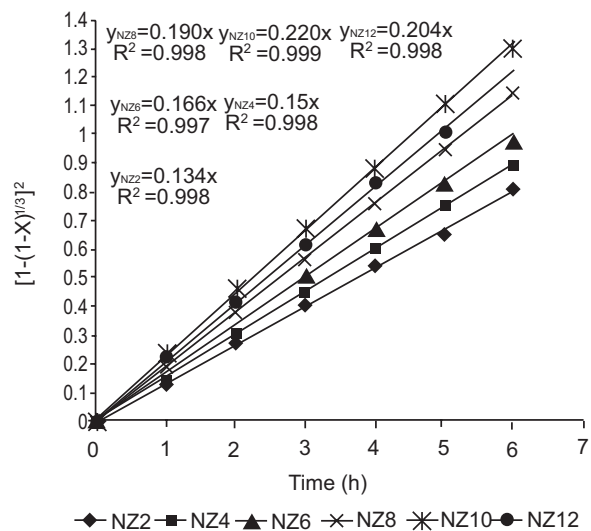

Fig. 11. Plot of $[1\text{-}(1\text{-}X)^{1/3}]^2$ vs time for Mg^{2+} removal at different acid concentrations.

determine the activation energy of the processes. The activation energy was determined to be 24.98 kJ/mol with a correlation coefficient of 0.963, which is in close agreement with the value calculated by Uzun and Gulfen (2007) of 21.42 kJ/mol for the dissolution of red mud in sulphuric acid solution.

Adsorption performance of the activated bentonite. Oils and fats are bleached in order to remove undesired colourants because these colourants can negatively affect the taste of the oil and in part because the colour

Fig. 9. Plot of $[1\text{-}(1\text{-}X)^{1/3}]^2$ vs time for Al^{3+} removal at different acid concentrations.
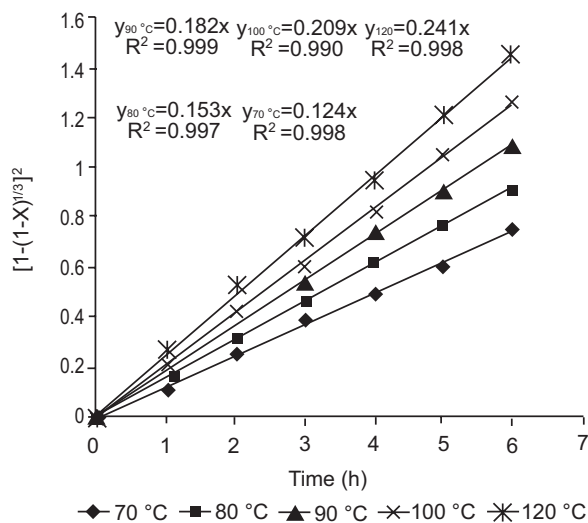
Fig. 12. Plot of $[1-(1-X)^{1/3}]^2$ *vs* time at different temperatures.

would disturb the consumers, therefore, on the whole, these colourants limit use and marketability. In addition to that, some particles or pigments that promote deterioration to oil quality is also being removed during bleaching process mainly due to their pro-oxidative properties that promotes oxidation. As a result, these undesirable pigments are removed using appropriate adsorbents, such as activated clays. To investigate the adsorptive performance of the acid treated samples, the samples were used to adsorb colour pigments from palm oil and the results are presented in Fig. 13. The figure shows that the adsorption power increased gradually as the intensity of the acid treatment increased and reached a maximum with 10 mol/L treated sample.
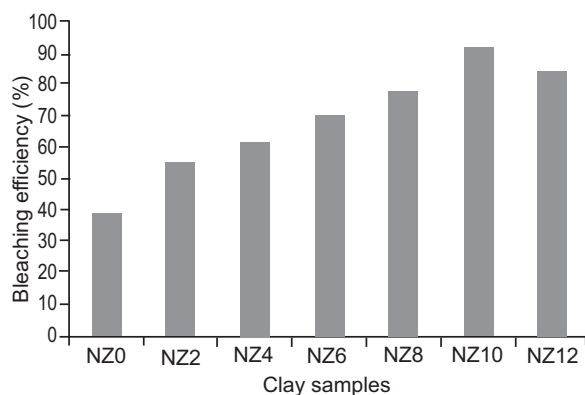
Fig. 13. Plot of the bleaching efficiency of the natural and acid activated Ntezi bentonite.

Further increase in the intensity of treatment caused a reduction in the adsorption capacity and this could be as a result of reduced surface area (Fig. 1) and Si/[Al + Fe + Mg] ratio (Table 1).

Conclusion

The structural modifications of Ntezi bentonite after hydrochloric acid activation and kinetics of the process have been investigated in this work. The acid activation caused reorganisation of the clay structures by the removal of the di- and trioctahedral cations and subsequent modifications of the tetrahedral arrangement. These resulted to samples with increased surface area, adsorption capacity, and reduced cation exchange capacity. The activation process could be described by the product layer diffusion kinetic model with activation energy of 24.98 kJ/mol. The results reveal that acid activation of bentonite with 10 mol/l HCl acid can be employed as an economical technique for modification of bentonite to enhance its surface properties and adsorption capacity.

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