



Nitric Acid-activated Nteje Clay: Structural and Bleaching Properties

R. O. Ajemba*, O. D. Onukwuli

Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Anambra, Nigeria

PAPER INFO

Paper history:

Received 02 July 2012

Received in revised form 08 November 2012

Accepted 13 December 2013

Keywords:

Activation

Bleaching

Surface Area

Characterization

Cation Exchange Capacity

Clay

ABSTRACT

The structural and bleaching properties of nitric acid-activated Nteje clay was studied to investigate its ability to serve as an alternative to the high cost imported bleaching earth. The clay was mined, sun-dried, grinded, and reacted with different concentrations of nitric acid, ranging from 2 mol.L⁻¹ to 15 mol.L⁻¹. The un-activated and activated samples were characterized to study the structural effects of the activation process. The activated samples were employed in bleaching palm oil under controlled conditions of the process variables. The characterization results showed that the surface area, cation exchange capacity (CEC), and oil retention properties of the activated samples were affected by the activation reaction. The surface area increased to about 4 times (288.8 m².g⁻¹) the initial value (68.5 m².g⁻¹), while the CEC decreased from 154 to 65 meg.100⁻¹.g⁻¹ with acid activation. The bleaching studies revealed that the activated clay samples adsorbed color pigments from palm oil more than the un-treated clay sample, with the bleaching efficiency of the sample activated using 13 mol.L⁻¹ HNO₃ increased from 37.82 % to 89.76 %. This study has shown that nitric acid can be employed favourably in activation of Nteje clay to improve its bleaching ability. It is also concluded that the activated samples can serve as an alternative to the imported bleaching earths.

doi: 10.5829/idosi.ije.2013.26.05b.05

1. INTRODUCTION

Clay minerals have acquired prominence as low-cost adsorbents in recent years as a result of their local and abundant availability and the ease with which they are modified to increase the surface area, adsorption capacity, and range of applicability [1]. The modified clay minerals have high potential of serving as an alternative to the most widely used high-cost activated carbon. To increase the adsorptive properties and other range of applications of these clay minerals, some physical and chemical modification methods are applied to them. Such modification methods have been investigated by several authors, which includes thermal treatment [2-6]; acid activation [7-13]; and polymer modification [14, 15]. These treatments modify the surfaces of the clay minerals by dis-aggregations of particles, possible elimination of mineral impurities, and removal of metal-exchange cations [10]. The common commercial use of acid-activated clay minerals is bleaching or de-colorations of oils [16] and in general in the field of adsorption and catalysis [17, 18].

Treatment of clay minerals with strong inorganic acids is called acid dissolution or acid activation. Depending on the extent of acid activation, the resulting solid product also contains unaltered layers and amorphous three-dimensional cross-linked silica, while the ambient acid solution contains ions according to the chemical composition of the clay and acid used [3], [19]. Early acid-dissolution studies of di-octahedral smectites in HCl by Osthaus [20, 21], based on solution analysis, indicated faster dissolution of octahedral than tetrahedral sheets. The extent of the dissolution reaction depends on both clay mineral type and reaction conditions, such as the acid/clay ratio, acid concentration, time and temperature of the reaction. The composition of the clay layers substantially affects their stability against acid attack. Tri-octahedral layers dissolve much faster than their di-octahedral counterparts [9, 10, 22, 23].

Nigeria is endowed with vast deposits of clay minerals that are unharnessed. The deposit located at Nteje has not been employed industrially, but, it is only used for local pottery work by the rural inhabitants. Palm oil is a major source of dietary for people in the western part of Africa and this oil has some storage and use difficulties. Palm oil congeals on storage at ambient

*Corresponding Author Email: ginaajemba@rocketmail.com (R. O. Ajemba)

temperature and has a very low smoke point, which makes it unsuitable for frying. These difficulties can be reduced if the oil can be bleached to remove the impurities. Impurities present in palm oil can be reduced appreciably by adsorption process or bleaching using clay mineral adsorbents [24].

In this study, the effects of nitric acid activation on the structural and bleaching properties of Nteje clay were investigated. More emphasis was laid on the effects of variation in acid concentrations and their subsequent behavior in palm oil bleaching.

2. MATERIALS AND METHODS

2. 1. Materials Ash-colored clay material from Nteje (N: 5° 54' 27.5"; E: 6° 56' 3.7"; A: 137m) in Aniocha, Anambra state, Nigeria was used as the primary raw material. Refined palm oil was obtained at oil mill located at Isuofia (N: 6° 1' 60"; E: 7° 2' 60"; A: 361m). All chemicals used were analytical grade, bought from Conraws Company Ltd, Enugu.

2. 2. Experimental Methods

2. 2. 1 Acid Activation of the Clay Sample The clay material was prepared for activation by air-drying and grinding to a particle size of 0.212 mm. 10 g of the prepared sample was weighed into flask (250 ml capacity) and 100 ml of nitric acid solution was added. The resulting suspension was heated on a magnetically stirred hot plate at temperature of 90 °C for 2 hrs 30 min. At the end of the experimental duration, the resulting slurry was poured into a Buchner funnel to separate the acid and clay. The residual clay was washed severally with distilled water until neutral point was obtained with pH indicator. The clay residue was dried in an oven at 80 °C for 4 hrs. The dried samples were crushed and sieved again to 0.212 mm particle size. The activation process was repeated with varying acid concentrations of 2 – 15 mol.L⁻¹ of HNO₃, varying time of 0.5 – 3 hrs, and varying temperatures of 70 – 120 °C. Thus, the clay samples prepared were labeled NT0, NT2, NT4, NT7, NT10, NT12, and NT15, where the numbers indicate the acid concentrations used in the activation step.

2. 2. 2. Characterization The chemical and mineralogical compositions of the natural and activated clay samples were determined. The chemical composition was determined using X-ray fluorescence (XRF), Philips PW 2400 XRF spectrometer; while the mineralogical composition was determined using Fourier transform infrared (FTIR), Shimadzu S8400 spectrophotometer, with samples prepared by the conventional KBr disc method.

2. 2. 3. Specific Surface Area The surface area was determined using ethylene glycol mono-ethyl-ether (EGME) described by Carter et al. [25, 26]. Clay samples were sun-dried and grinded to pass No. 40 sieve. A small amount of the sample was then placed in an oven at a temperature of 105 °C overnight to remove water and dried with P₂O₅. 1 g of the dried sample was spread into the bottom of aluminum tare and weighed (W_a) using an analytical balance with an accuracy of 0.001 g. Approximately, 3.0 ml of laboratory grade EGME was added to the sample using a pipette and mixed together with a gentle swirling motion to create uniform slurry. All clay samples were covered with the EGME in order to obtain an accurate surface area measurement. After that, the aluminum tare was placed inside a standard laboratory glass sealed vacuum desiccators and allowed to equilibrate for 20 min. The desiccators were evacuated using vacuum pump. The aluminum tare was removed from the desiccators and weighed (W_s) after a period of 12, 16, and 24 hrs. When the mass of the sample varied by more than 0.001 g between two measurements, the sample was placed back in the desiccators and evacuated again for an additional 2 hrs. The process was continued until the sample mass did not vary by more than 0.001 g. The surface area was expressed as follows:

$$A = \frac{W_a}{0.000286W_s} \quad (1)$$

A = surface area (m².g⁻¹), W_a = weight of EGME retained by the sample, W_s = weight of P₂O₅-dried sample, 0.000286 is the weight of EGME required to form uni-molecular layer on a square meter of the surface [27].

2. 2. 4. Cation Exchange Capacity (CEC) [28] 5 g of the clay sample was weighed into the 250 ml polythene bottle with a magnetic stirrer. The bottle and its contents were weighed (M_1). 100 ml of buffered barium chloride solution was added to the bottle and was placed on a magnetic stirring plate and agitated for 1 hr. At the end of the period, the bottle was centrifuged at 1500 rpm for 15 min and the supernatant was discarded. Furthermore, 200 ml of the buffered barium chloride solution was added and the mixture was agitated on a magnetic stirring plate for another 1 hr. The bottle and its contents were left overnight. The following day, the bottle and its contents were centrifuged at 1500 rpm for 15 min and the supernatant discarded. 200 ml of distilled water was added and agitated for few minutes on the magnetic stirring plate. It was centrifuged for further 15 min and the supernatant discarded. The bottle and its contents were weighed (M_2). 100 ml of MgSO₄ solution was pipette into the bottle and stirred well and was left to stand for 2 hrs with occasional agitation on the magnetic stirring plate. After 2 hrs, the contents were centrifuged at 1500

rpm for 15 min and the supernatant decanted into the stopper bottle. 5 ml aliquot of this solution was pipette into a 100 ml conical beaker and 5 ml of ammonia buffer and 6 drops of indicator were added to it. This mixture was titrated with standard EDTA (titer A_1 ml). Another titration was done with a 5 ml of aliquot of 0.05 M $MgSO_4$ solution (titer B ml). The end point was indicated by a blue to pink colour change. The Cation Exchange Capacity was calculated as follows:

$$CEC = 8 \left\{ B - \frac{(A_1 \times (100 + M_2 - M_1))}{100} \right\} \text{ meq}/100g \quad (2)$$

where, M_1 = weight of bottle plus dry content (g), M_2 = weight of bottle plus wet content (g), A_1 = titration end-point of sample (ml), and B = titration end-point of $MgSO_4$ solution (ml).

2. 2. 5. Bleaching Experiment The bleaching experiments were carried out in a batch process. 50 g of the refined palm oil were charged into a 250 ml beaker and 2 g of the activated clay samples were also added. The mixture of clay and oil were placed in a water bath and heated to a temperature of 80 °C for 30 min under continuous stirring. At the end of the reaction, the slurry formed was filtered through a dry filter paper. The bleaching capacity of the acid activated clays was then determined by measuring the colour of the bleached oils using a UV-Vis spectrophotometer (Shimadzu UV mini 1240) at wavelength of 450 nm. The bleaching efficiency of the acid activated clay was calculated in this study using the following equation:

$$\% \text{ Bleaching Efficiency} = \frac{(A_{\text{unbleached}} - A_{\text{bleached}})}{A_{\text{unbleached}}} \times 100 \quad (3)$$

where, $A_{\text{unbleached}}$ and A_{bleached} are the absorbencies of the unbleached and bleached oils, respectively.

3. RESULTS AND DISCUSSIONS

3. 1. Characterization The changes in the chemical composition of the natural and acid activated clay mineral at different acid concentrations are shown in Table 1. The content of SiO_2 was observed to increase as the acid concentration increased up to 13 mol.L⁻¹ and decreased with further increase in concentration. This could be due to "passivation" of the rest of the clay which protects the clay layers from further acid attack [31]. The contents of the octahedral cations (Al_2O_3 , Fe_2O_3 , and MgO) decreased intensely as the acid concentration increased and increased with further attack after 13 mol.L⁻¹ concentration (Table 1). The behavior 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

[29]. Pesquera et al. [30] suggest that this free silica generated by the initial destruction of the tetrahedral sheet, is polymerized by the effect of such high acid concentration. It is deposited on the undestroyed silicate fractions, thereby protecting it from further acid attack [9, 16] better and more valuable.

3. 2. Surface Area It was observed from the surface area analysis of the natural and treated samples that the surface area increased as the acid concentration used in the activation step increased. The increase in surface area from natural to activated samples is related to the elimination of the exchangeable cations, de-lamination, and the generation of micro-porosity during the processes [29]. This increase continued up to the sample activated with 13 mol.L⁻¹ of HNO_3 and dropped when the concentration was increased to 15 mol.L⁻¹ (Figure 3). This is attributed to the polymerization of the generated free silica by the effect of excess acid concentration and is deposited on the surface of the clay particle preventing it from further attack [30].

3. 3. Fourier Transforms Infrared (FTIR) Spectroscopy Analysis The FTIR spectra of the raw and nitric 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 Figures 4 and 5, 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.

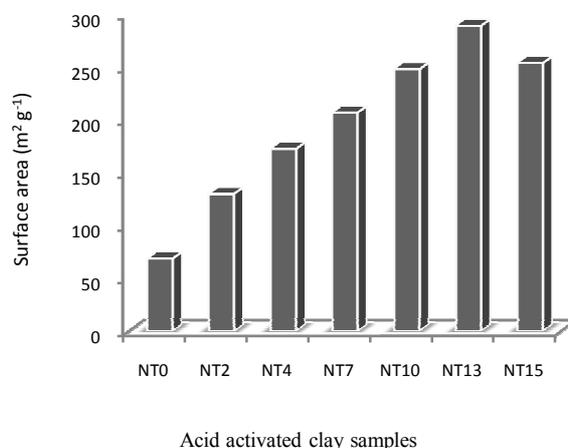


Figure 1. Variation of the surface area with acid activated samples at different concentrations.

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 [31, 32]. 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.

3. 4. Cation Exchange Capacity (CEC) The results of the cation exchange capacity of the activated samples show that the exchange ability of the activated samples decreased as the concentration of the acid used in the activation increased (Figure 4). 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 created by the removal of the octahedral and tetrahedral ions.

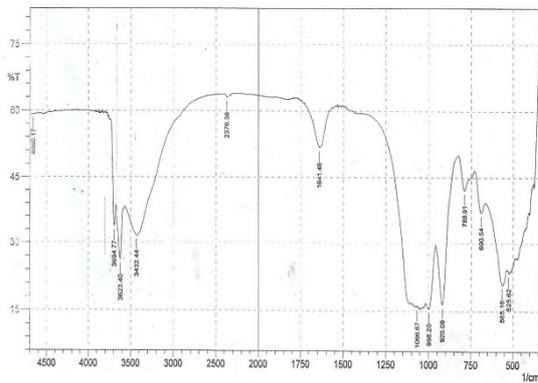


Figure 2. FT-IR spectra of natural Nteje clay

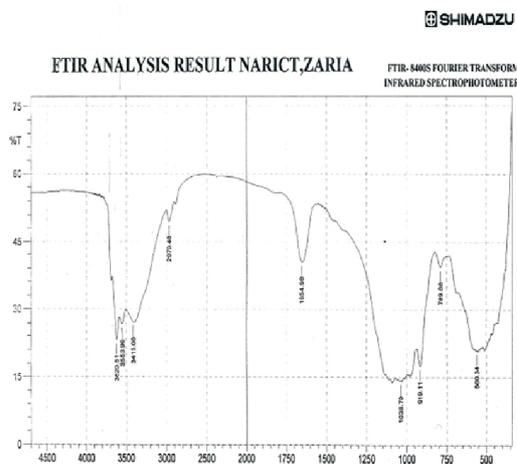


Figure 3. FT-IR spectra of acid-activated Nteje clay

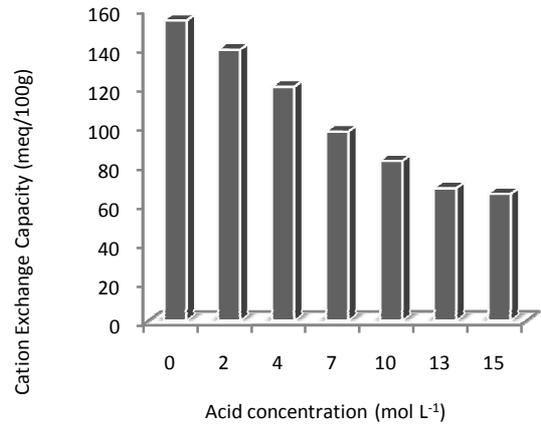


Figure 4. Plot of the variation of the cation exchange capacity with acid concentration

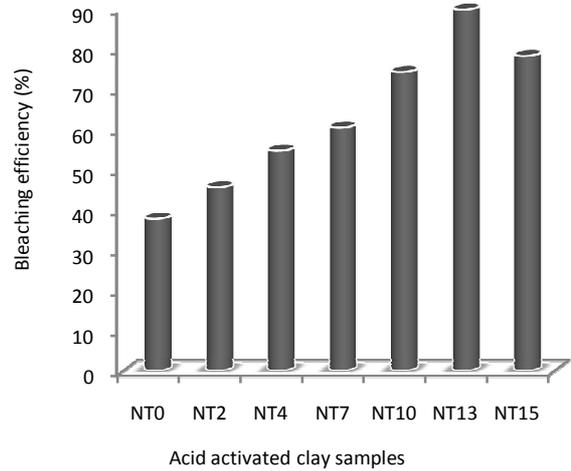


Figure 5. Plot of the bleaching efficiency values for the different acid activated samples

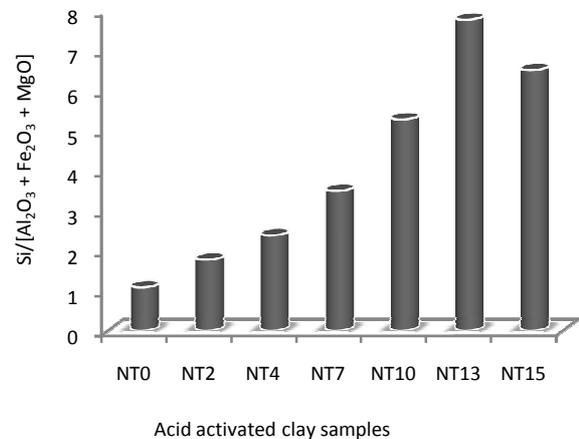


Figure 6. Plot of the Si/[Al₂O₃ + Fe₂O₃ + MgO] ratio for the different acid activated samples.

3. 5. Bleaching Studies The results of the bleaching studies performed using the un-activated and acid-activated samples are depicted in Figure 5. The figure shows that the bleaching efficiency increased as the concentration of the acid used in the activation step increased. This increase reached to a maximum with the sample activated with 13 mol.L⁻¹ of nitric acid and decreased as the concentration was increased to 15 mol.L⁻¹. This could be attributed to the fact that excess of the acid destroyed the crystalline structure of the clay and led to the decrease in surface area (Figure 1) and the ratio of SiO₂ to [Al₂O₃ + Fe₂O₃ + MgO] as shown in Figure 6 [13, 16, 22, 31] .

4. CONCLUSIONS

The nitric acid-activation of Nteje clay has successfully been studied. This study shows that the acid activation alters the structural properties of the clay mineral. The properties affected are the cation exchange capacity, surface area and bleaching efficiency. The surface area was observed to increase with an increase in the acid concentration while the cation exchange capacity decreased with an increase in acid concentration. The bleaching efficiency of the activated clay sample was observed to increase to about three times. The bleaching efficiency of the natural clay sample indicating that acid activation is an important process that improves the adsorptive performance of the clay sample. This study has revealed that Nteje clay is a viable source of adsorbent for palm oil bleaching when activated with nitric acid.

5. REFERENCES

1. Monvisade, P. and Siriphannon, P., "Chitosan intercalated montmorillonite: Preparation, characterization and cationic dye adsorption", *Applied Clay Science*, Vol. 42, No. 3, (2009), 427-431.
2. Al-Asheh, S., Banat, F. and Abu-Aitah, L., "Adsorption of phenol using different types of activated bentonites", *Separation and Purification Technology*, Vol. 33, No. 1, (2003), 1-10.
3. Bergaya, F., Theng, B. K. and Lagaly, G., "Handbook of clay science", Elsevier Science, Vol. 1, (2006).
4. Steudel, A., Batenburg, L., Fischer, H., Weidler, P. and Emmerich, K., "Alteration of swelling clay minerals by acid activation", *Applied Clay Science*, Vol. 44, No. 1, (2009), 105-115.
5. Sennour, R., Mimane, G., Benghalem, A. and Taleb, S., "Removal of the persistent pollutant chlorobenzene by adsorption onto activated montmorillonite", *Applied Clay Science*, Vol. 43, No. 3, (2009), 503-506.
6. Vimonses, V., Lei, S., Jin, B., Chow, C. W. and Saint, C., "Kinetic study and equilibrium isotherm analysis of congo red adsorption by clay materials", *Chemical Engineering Journal*, Vol. 148, No. 2, (2009), 354-364.
7. Prieto, O., Vicente, M. A. and Banares-Munoz, M. A., "Study of the porous solids obtained by acid treatment of a high surface area saponite", *Journal of Porous Materials*, Vol. 6, No. 4, (1999), 335-344.
8. Barrios, M. S., González, L., Rodríguez, M. and Pozas, J., "Acid activation of a palygorskite with hcl: Development of physico-chemical, textural and surface properties", *Applied Clay Science*, Vol. 10, No. 3, (1995), 247-258.
9. Vicente Rodriguez, M., De D Lopez gonzalez, J. and Banares Munoz, M., "Acid activation of a spanish sepiolite: Physicochemical characterization, free silica content and surface area of products obtained", *Clay Minerals*, Vol. 29, No. 3, (1994), 361-367.
10. Rodríguez, M. V., Barrios, M. S., González, J. L. and Munoz, M. B., "Acid activation of a ferrous saponite (griffithite): Physico-chemical characterization and surface area of the products obtained", *Clays and Clay Minerals*, Vol. 42, No. 6, (1994), 724-730.
11. Lian, L., Guo, L. and Guo, C., "Adsorption of congo red from aqueous solutions onto ca-bentonite", *Journal of Hazardous Materials*, Vol. 161, No. 1, (2009), 126-131.
12. Kara, M., Yuzer, H., Sabah, E. and Celik, M., "Adsorption of cobalt from aqueous solutions onto sepiolite", *Water Research*, Vol. 37, No. 1, (2003), 224-232.
13. Myriam, M., Suarez, M. and Pozas, J. M., "Structural and textural modifications of palygorskite and sepiolite under acid treatment", *Clays and Clay Minerals*, Vol. 46, No. 3, (1998), 225-231.
14. Jozefaciuk, G., "Effect of acid and alkali treatments on surface-charge properties of selected minerals", *Clays and Clay Minerals*, Vol. 50, No. 5, (2002), 647-656.
15. Liu, P., "Polymer modified clay minerals: A review", *Applied Clay Science*, Vol. 38, No. 1, (2007), 64-76.
16. Srasra, E., Bergaya, F., Van Damme, H. and Ariguib, N., "Surface properties of an activated bentonite—decolorisation of rape-seed oils", *Applied Clay Science*, Vol. 4, No. 5, (1989), 411-421.
17. Fahn R. and K., F., "Reaction products of inorganic dye molecules with acid treated montmorillonite.", *Clay Minerals*, Vol. 18, No., (1983), 447 - 458.
18. Mokaya, R. and Jones, W., "Pillared clays and pillared acid-activated clays: A comparative-study of physical, acidic, and catalytic properties", *Journal of Catalysis*, Vol. 153, No. 1, (1995), 76-85.
19. Panda, A. K., Mishra, B., Mishra, D. and Singh, R., "Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 363, No. 1, (2010), 98-104.
20. Osthaus, B., "Chemical determination of tetrahedral ions in nontronite and montmorillonite", *Clays and Clay Minerals*, Vol. 2, No., (1954), 404-417.
21. Ostltaus, B., "Kinetic studies on montmorillonites and nontronite by the acid-dissolution technique", (1956).
22. Breen, C., Madejova, J. and Komadel, P., "Characterisation of moderately acid-treated, size-fractionated montmorillonites using ir and mas nmr spectroscopy and thermal analysis", *Journal of Materials Chemistry*, Vol. 5, No. 3, (1995), 469-474.
23. STUCKI, J., "Dissolution of hectorite in inorganic acids", *Clays and Clay Minerals*, Vol. 44, No. 2, (1996), 228-236.
24. AJEMBA, R. O. and ONUKWULI, O. D., "Adsorptive removal of colour pigment from palm oil using acid activated nteje clay. Kinetics, equilibrium and thermodynamics", *Physicochemical Problems of Mineral Processing*, Vol. 49, (2013), 1.

25. Carter, D., Heilman, M. and Gonzales, C., "Ethylene glycol monoethyl ether for determining surface area of silicate minerals", *Soil Science*, Vol. 100, No. 5, (1965), 356-360.
26. Mortland, M. and Kemper, W., "Specific surface", *Methods of Soil Analysis. Part 1. Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling*, methods of soilana, (1965), 532-544.
27. Chiou, C. T., Rutherford, D. W. and Manes, M., "Sorption of nitrogen and ethylene glycol monoethyl ether (egme) vapors on some soils, clays, and mineral oxides and determination of sample surface areas by use of sorption data", *Environmental Science & Technology*, Vol. 27, No. 8, (1993), 1587-1594.
28. Inglethorpe, S., Morgan, D., Highley, D. and Bloodworth, A., "Industrial minerals laboratory manual: Bentonite", *British Geological Survey Technical Report WG/93/20*, (1993).
29. Dias, M., Suarez, M., Prates, S. and MartinPozas, J., "Characterization and acid activation of portuguese special clays", *Clay Minerals*, Vol. 38, (2003), 537-549.
30. Pesquera, C., González, F., Benito, I., Blanco, C., Mendioroz, S., and Pajares, J., "Passivation of a montmorillonite by the silica created in acid activation", *Journal of Materials Chemistry*, Vol. 2, No. 9, (1992), 907-911.
31. Christidis, G., Scott, P. and Dunham, A., "Acid activation and bleaching capacity of bentonites from the islands of milos and chios, aegean, greece", *Applied Clay Science*, Vol. 12, No. 4, (1997), 329-347.
32. Komadel, P., Schmidt, D., Madejová, J. and Cíćel, B., "Alteration of smectites by treatments with hydrochloric acid and sodium carbonate solutions", *Applied Clay Science*, Vol. 5, No. 2, (1990), 113-122.

Nitric Acid-activated Nteje Clay: Structural and Bleaching Properties

RESEARCH NOTE

R. O. Ajemba, O. D. Onukwuli

Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Anambra, Nigeria

PAPER INFO

چکیده

Paper history:

Received 02 July 2012

Received in revised form 08 November 2012

Accepted 13 December 2013

Keywords:

Activation

Bleaching

Surface Area

Characterization

Cation Exchange Capacity

Clay

ساختار و خاصیت رنگبری نیتریک اسید-رس Nteje فعال شده به منظور بررسی توانایی آن به عنوان جایگزین برای هزینه های بالای وارداتی سفید کننده های خاکی مطالعه شده است. خاک رس پس از استخراج، آفتاب خشک شده، آسیاب شده و سپس تحت واکنش با غلظت های مختلف از اسید نیتریک از ۲ تا ۱۵ mol.L⁻¹ قرار گرفته است. نمونه های واکنش داده و واکنش نداده برای تاثیرات فرایند فعال کردن بر ساختار آنالیز و بررسی شده اند. نمونه های فعال شده به منظور رنگ بری روغن خرما تحت شرایط کنترل شده متغیر های فرایند به کار گرفته شده اند. نتایج آنالیز نشان دادند که مساحت سطح، ظرفیت تبادل کاتیون (CEC) و خواص حفظ شده روغن نمونه فعال شده با واکنش فعال سازی تحت تاثیر قرار گرفته اند. طی فعال سازی با اسید، مساحت سطح به ۴ برابر (288.8 m².g⁻¹) مقدار اولیه (68.5 m².g⁻¹) افزایش داده شده است در حالیکه CEC از ۱۵۴ به ۶۵ meg.100⁻¹.g⁻¹ کاهش پیدا کرده است. مطالعات بر رنگبری نشان داده اند که نمونه های رس فعال شده با ۱۳mol.L⁻¹ اسید نیتریک دانه های رنگی روغن خرما را بیش از رس فعال نشده با بازدهی رنگبری از ۳۷/۸۲٪ به ۸۹/۷۶٪ جذب کرده اند. این تحقیق نشان داده است که اسید نیتریک به طور رضایت بخشی برای فعال سازی رس Nteje به منظور بهبود توانایی رنگبری آن به کار میتواند گرفته شود که نمونه بررسی شده می تواند به عنوان یک جایگزین برای سفیدکننده های وارداتی خاکی مورد استفاده قرار گیرد.

doi: 10.5829/idosi.ije.2013.26.05b.05