www.arpnjournals.com

CHARACTERISATION AND OPTIMISATION OF DEFERRATION OF KANKARA CLAY

J. A. Lori[1], A. O. Lawal[1] and E. J. Ekanem[1]
[1]Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria
E-mail: lawal66@yahoo.com

ABSTRACT

The mineralogy of clay from the Kankara deposit in Katsina (Nigeria) has been studied by x-ray diffraction (XRD). Kaolinite is the dominant mineral phase with minor amounts of quartz, goethite and muscovite. The diffraction pattern of the glycolated clay sample did not indicate the presence of mixed layer clay (swelling clay such as smectites). Iron impurities (FeOOH), alumina (Al_2O_3) and silica (SiO_2) contents of untreated and beneficiated clays were monitored by Energy Dispersive X-ray Fluorescence (EDXRF). The total iron impurity (FeOOH) in the clay sample was 0.081%. Alumina (Al_2O_3) and silica (SiO_2) contents were 39.097% and 44.158%, respectively. The iron content of the oxalic acid-leached clay decreased with increase in oxalic acid concentration. The efficiency of the acid solution was more, when the iron/acid mole ratio was less than or equal to 0.045. Iron removal efficiency of the oxalic acid solutions was not dependent on the amount of iron present in the clay, but on the mole proportion of the acid used. The optimum conditions for about 99% deferration were temperature of 75°C, oxalic acid concentration of $1.8mol/dm^3$ and shearing time of 7hrs. The use of magnetic separator, showed no improvement on iron removal from the clay.

Keywords: kankara, kaolinite, clay, characterization, optimization, deferration.

INTRODUCTION

Clays have received considerable attention especially as potential adsorbents for environmental research. Deposits of this important raw material are widely distributed in Africa, especially, Nigeria (Elueze *et al.,* 1999*;* Borode *et al.*, 2000; Fasuba *et al.*, 2001; Omowunmi, 2001; Irabor, 2002; Gbadebo*, 2002;* Igbokwe and Ogbuagu, 2003; Odo and Nwajagu, 2003). Inspite of the extensive use and the demand for clay in industrial processes, beneficiation of the Kankara clay as potential adsorbent has not been reported. This is important, in order to add value to the clay as an industrial raw material for the production of adsorbent (Nakamura *et al.*, 2001). In this study, Kankara clay has been selected for evaluation largely because of its bulk availability (Macload, 1979). Presence of impurities, particularly iron-bearing materials impairs the characteristics of clay and affects its utility for various applications especially as adsorbent for environmental uses. The characterisation and possible beneficiation of the clay to remove or reduce iron impurities, is thus eminent and should be a prerequisite to the production of good quality adsorbent that minimizes isotherm hysteresis. X-ray diffraction patterns have been found very suitable for the mineralogy of clays (Saikia *et al.*, 2003; Capitaneo et al., 2004; Sei et al., 2004). Chemical leaching is one of the commonly practiced techniques for the removal of iron-bearing impurities both as surface coatings and discrete fine forms, because it is more effective, especially for extremely low iron (< 0.1% w/w) (Lee *et al.*, 2006). However, inorganic acids such as sulphuric or hydrochloric acids easily contaminate the clay products with SO_4^{-2} and Cl^- (Lee *et al.*, 2006). Amongst various organic acids, oxalic acid has been reported to be a more effective iron removal and clay brightness improver (Panias *et al.*, 1996; Ambikadevi and Lalithambika, 2000). This has been attributed to its high acid strength, good complexing capacity and reducing power. Compared to other leachants such as sodium hydrosulfite (dithionite), the use of oxalic acid is a more eco-friendly technique (Ambikadevi and Lalithambika, 2000). However, the reaction parameters such as time (12hrs), temperature (ambient), shearing rates (14,000 rpm) and reagent concentration ($0.4mol/dm^3$ oxalic acid), which were considered optimum by Saikia *et al.*, (2003) could not completely remove the iron impurities from samples of Kaolinite clay. The study, reported the trend of iron removal from different size fractions of clay with acid concentration as suggesting two types of iron in clay, of which some are easily soluble in acid (non structural or free iron) and others (structural iron) are difficult to leach with acid. Saikia *et al.*, (2003), however, suggested that at room temperature, use of appropriate oxalic acid concentration, shearing rate and time may further improve the removal of iron content of fine fractions of clay. In a 2^k factorial design, Guillermo *et al.*, (2005) used simplex methods to model the interactions between the conditions for leaching iron from clays. The results of this effort prompted the combined optimisation of the factors that influence the removal of iron from the kankara clay with acid leachant.

This present study therefore evaluates the different conditions that may influence efficient removal of iron from iron-stained Kankara clay. The extent of leaching was monitored by Energy Dispersive X-ray fluorescence as recommended by Funtua, (1999); Ambikadevi and Lalithambika (2000); and Sei *et al*., (2004).

MATERIALS AND METHODS

Oxalic acid solutions were prepared from oxalic acid dihydrate $((COOH)_2.2H_2O)$ with 98% purity. About 2kg of the Kankara clay was obtained from the

ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

underground local mines at mining sites in kankara. The sample was milled to different particle sizes ranging from 35-425µm and labelled as acid leached kankara clay (ALKC) using the acid concentration and untreated kankara clay (UKTC).

Kankara is located in Katsina state of Nigeria precisely around longitudes 7°26E and 7°28E and latitude 11°53N (Figure-1) (Macload, 1979). It is the local government headquarters of Kankara Local Government Area. The clay is a weathering product of a unit of the basement rocks in this area, most likely feldspars. The clay sequence overlies mica schists and underlain by marble (Macload, 1979).
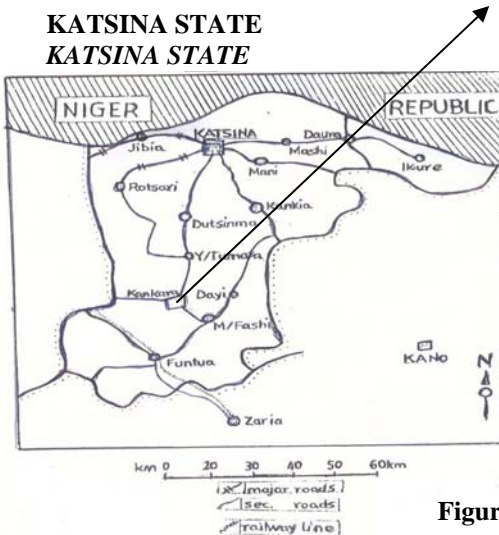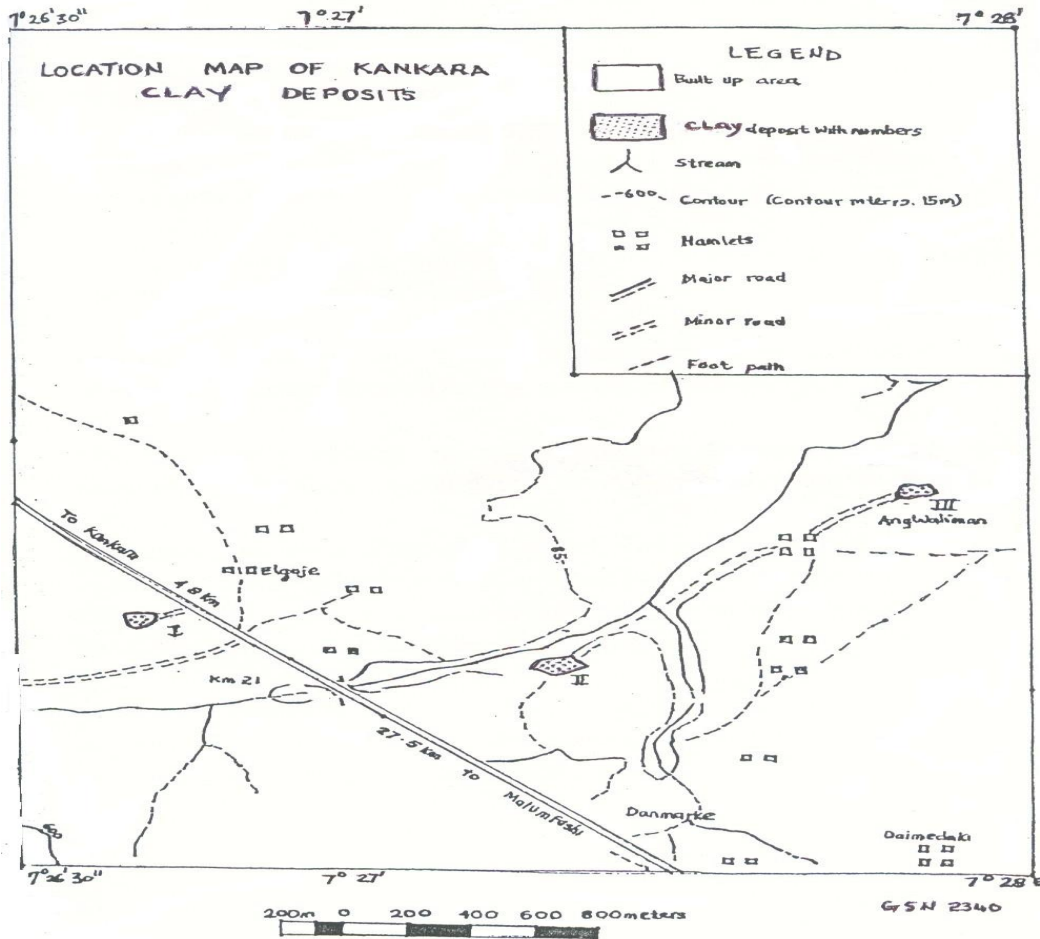

Figure-1. Location map of Kankara clay deposits.

The clay was milled with Autowest model Pascall Engineering grinding machine and sieved with the various Endecotts Laboratory test sieves on Omron No 17748 (manual timer) sieve shaker. The initial leaching conditions were based on the optimal conditions reported by Saikia et al., 2003 and Guillermo et al., 2005. The conditions which include 0.4mol/dm^3 oxalic acid, a room temperature of 30°C (Saikia et al., 2003) and 40μm particle size (Guillermo et al., 2005) were sequentially optimised in addition to the optimisation of the shaking time. In the initial experiments, 3g of the 40μm clay fraction was weighed and slurred in 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 and 2.2 mol/dm^3 oxalic acid solutions respectively in 250cm^3 round bottom flasks under identical conditions at room temperature (29°C). The clay mixtures were kept stirred using Griffin flask shaker at medium stirring condition for different experimental times of 1-6hrs to achieve clay whiteness closest to pure alumina. In each case the content of the flask was left for 15hrs to settle. The leached clay was separated and washed several times with 50cm^3 warm deionised water followed by sedimentation and decantation to ensure complete removal of residual acidity, which was monitored using litmus paper. The leached clays were dried in the oven at 110°C for 3hrs. Amongst samples leached with a particular acid concentration, clay which achieved whiteness closest to pure alumina was analysed by Energy Dispersive X-ray Fluorescence using PW40151 Minimate / Minipal X-ray Fluorescence machine. The untreated clay was characterized by X-Ray Diffraction using PW1800 X-ray diffractometer equipped with copper tube anode. To optimize the shaking time, the leaching procedure was repeated for the optimum acid concentration from the initial experiments, 40μm clay particle size at 29°C for various shaking times of 1-10hrs. In the next simplex, temperature was optimized by leaching 3g 40μm clay fraction with the optimum acid concentration, for the optimum shaking time at different temperatures of 15-95°C. Effect of clay particle size on the removal of iron was determined by leaching samples of different sieve sizes (35-425μm) with the optimum acid concentration, for the optimum shaking time at the optimum temperature. Prior to this final optimisation, the 35μm clay fraction was subjected to high intensity magnetic separation using Davies magnetic separator, model no. 13008/350/45v, equipped with Bercostat vibrator controller.

RESULTS AND DISCUSSION

Characterization of the clay

The x-ray diffraction patterns of the oriented samples, scanned from 0-70°(2θ) showed several peaks due to the different minerals (Figure-2). This bulk analysis indicated sharp peaks at d = 7.16Å (12.5°(2θ)), and d = 3.57Å (25°(2θ)) due to kaolinite. Other peaks due to kaolinite were found at 1.67Å (55.110°(2θ)) and 1.54Å (60.050°(2θ)). The off-white appearance of the clay samples was due to traces of goethite (∝FeOOH) as the iron bearing impurity at 4.99Å (17.780°(2θ)), 3.34Å (26.725°(2θ)), 2.77Å (32.395°(2θ)), 2.56Å (35.110°(2θ)), 2.49Å (36.010°(2θ)), and 2.46Å (36.605°(2θ)). There were traces of quartz at 4.23Å (21.025°(2θ)), 2.29Å (39.365°(2θ)) and 1.37Å (68.285°(2θ)). Muscovite also appeared as trace at 9.99Å (8.855°(2θ)), and 3.29Å (27.110°(2θ)).
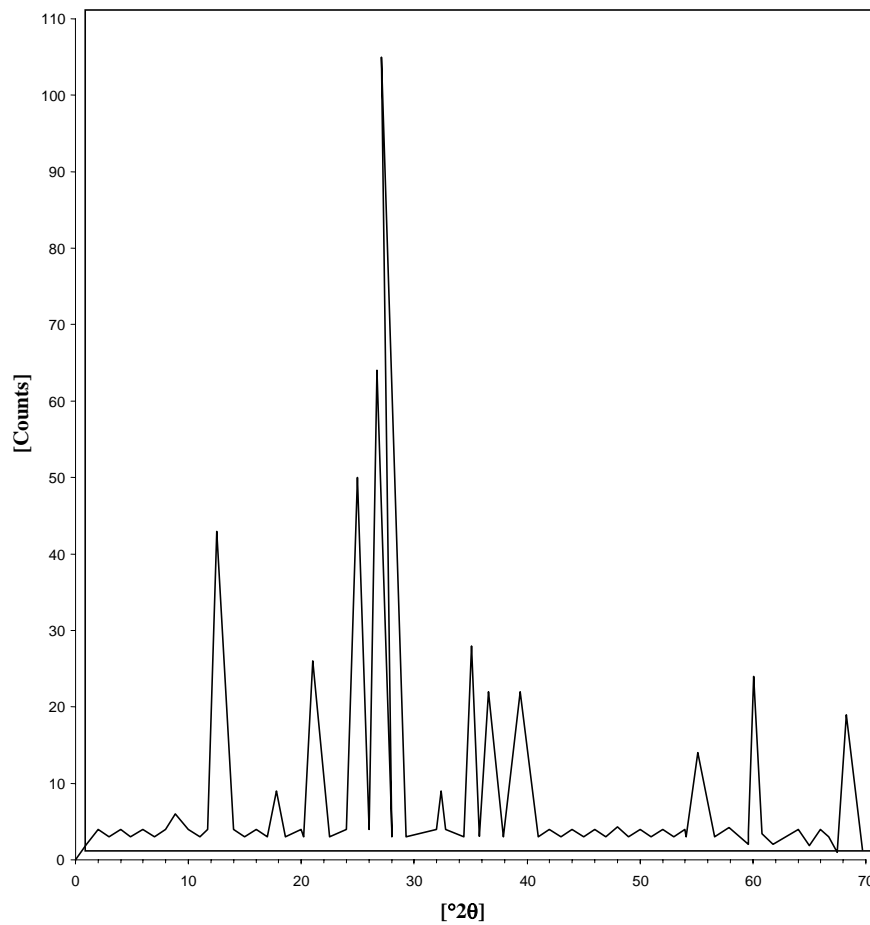
www.arpnjournals.com

Figure-2. X-ray diffractogram for kankara clay bulk analysis.

The 2 microns clay fraction diffractogram (Figure-3) showed two sharp peaks at d = 7.11Å (12.450°(2θ)) and 3.56Å (25.000°(2θ)) indicating that kaolinite was the dominant mineral phase. The diffraction pattern of the glycolated sample (Figure-4) did not indicate the presence of mixed layer clay (swelling clay such as smectites). However there was an improvement on clay peaks resolution, with enhancement in the kaolinite peaks (> 300 counts).
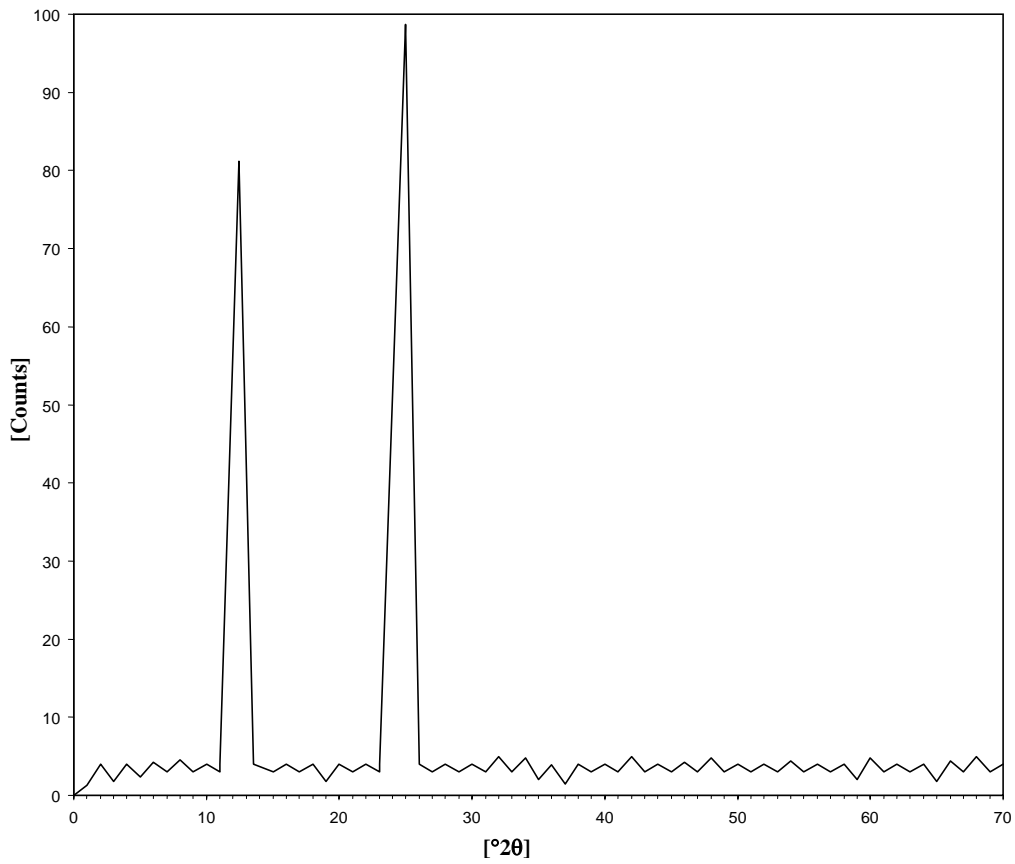
www.arpnjournals.com

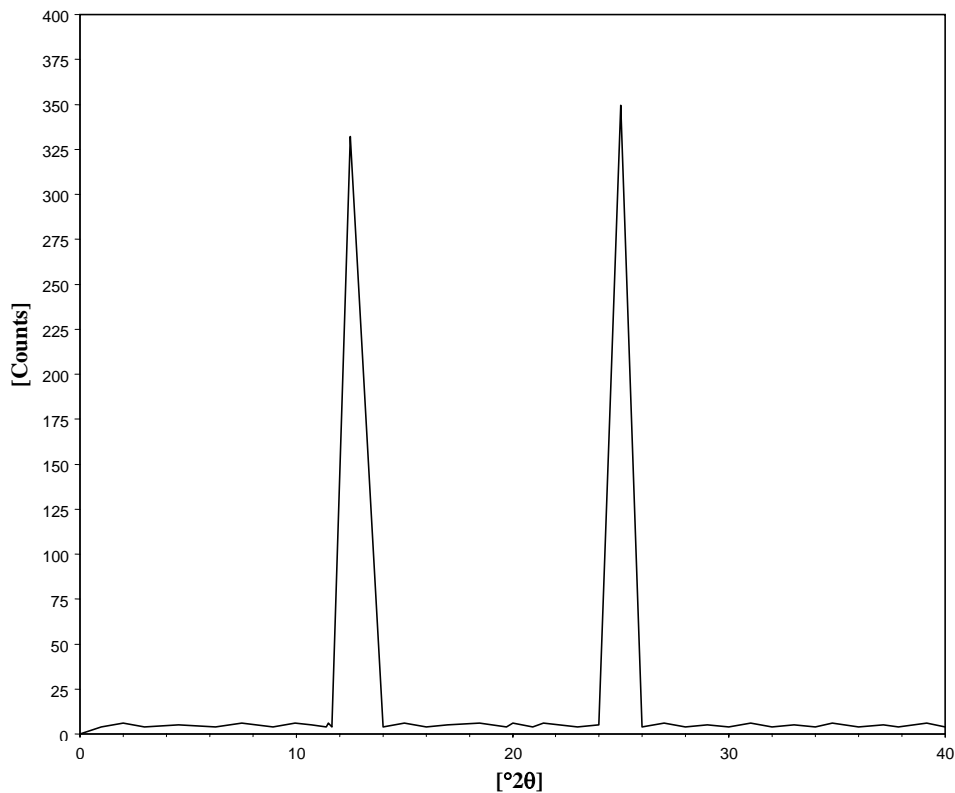**Figure-3.** X-ray diffractogram for 2microns clay fraction.

Figure-4. X-ray diffractogram for the glycolated Kankara.

www.arpnjournals.com

Heat treatment of the 2 microns clay fraction at 550°C for 1 hour collapsed the kaolinite peaks, thus confirming kaolinite as the dominant mineral phase (Figure-5). This test was necessary to distinguish the kaolinite from chlorites whose peaks appear at the same Bragg angles as kaolinites. The distinctions between the basal reflections of kaolinite and chlorite, premise on the collapse of the internal structure of the kaolinite at such temperature, to

mullite (amorphous), otherwise known as metakaoline, whereas the internal structure of the chlorites is not affected by heat at 550°C. The confirmation of kaolinite as the dominant mineral makes the Kankara clay suitable for other applications such as aluminosilicate nanocomposite that is not characterized by many unwanted atoms as may be obtained with smectites and chlorites.
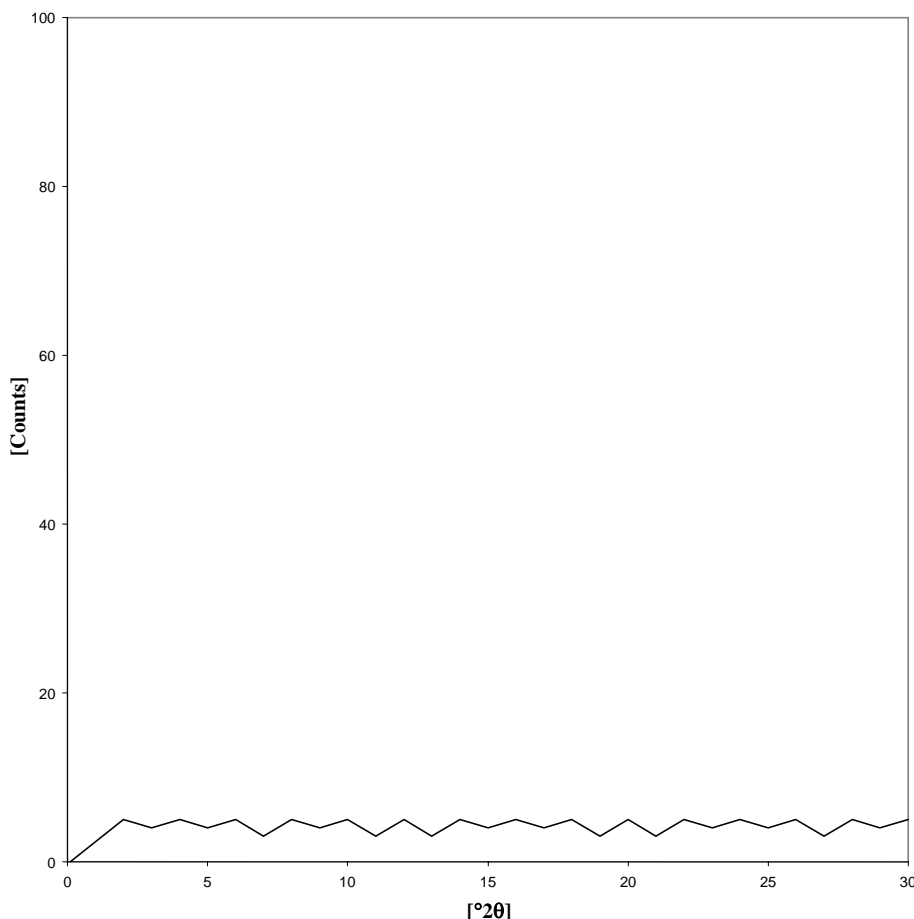

Figure-5. X-ray diffractogram for the heated (550°C) Kankara clay fraction.

Beneficiation of the clay

The percentage iron impurities removed, proportions of alumina and silica in the acid leached clay, have been used to measure the effect of oxalic acid solutions on the clay samples, towards beneficiation. The results of energy dispersive x-ray fluorescence analysis of the raw and acid treated clay samples from the initial experiments are presented in Table 1. The total iron impurity (FeOOH) in the clay sample was found to be 0.081%. Alumina (Al_2O_3) and silica (SiO_2) contents were 39.097% and 44.158% respectively. The iron content of the oxalic acid-leached clay decreased with increase in oxalic acid concentration. This shows the dependence of iron extraction from the clay, on the oxalate and H^+ ions concentrations, which have been found to promote iron dissolution due to enhanced surface-active centers (Ambikadevi and Lalithambika, 2000). This observation is

consistent with previous findings on the removal of iron impurities from clay (Ambikadevi and Lalithambika, 2000; Saikia *et al.*, 2003). The maximum iron impurities removed was 96.296% with oxalic acid concentration of 1.8mol/dm^3. This resulted in the improvement in whiteness of the 40µm fraction of the clay sample. The trend of iron removal with the different concentrations of acid gradually increased to 1.8mol/m^3 addition of oxalic acid and flattened to a plateau (Figure-6), to probably indicate the acid resistance of the little amount of iron that may still be trapped in the internal structure of the clay. From Figure-7 it is clear that iron removal efficiency of the oxalic acid solutions was not dependent on the amount of iron present in the clay, but on the mole proportion of the acid used. It is also clear, that the efficiency of the acid solution was more, when the iron/acid mole ratio was less than or equal to 0.045. A mole ratio greater than this value

www.arpnjournals.com

is shown to have little effect on iron removal, thus suggesting, that % iron removal reduces with increase in iron / acid mole ratio (Figure-7). The residual iron following the acid leaching also increases steeply beyond iron / acid ratio of 0.045. The intersection of the curves for % iron removal and residual iron in the leached clay indicates that the iron / acid ratio that may lead to deferration that is greater than 60% falls between 0.068-0.081. The alumina/silica ratio of the leached clay increased steeply with increase in concentration of the acid used (Figure-8).

Table-1. Effect of oxalic acid concentration on removal of iron-bearing impurities from Kankara clay.

| Samples	Oxalic acid Conc. (mol/dm^3)	Residual conc. after leaching			Al$_2$O$_3$/SiO$_2$ Ratio	FeOOH/ Oxalic Mole ratio	FeOOH removed (%)
		Al$_2$O$_3$(%)	SiO$_2$(%)	FeOOH(%)			
UKTC	0	39.097	44.158	0.081	0.885	-	-
0.2ALKC	0.2	38.980	43.958	0.052	0.887	0.405	35.803
0.4ALKC	0.4	38.900	43.330	0.049	0.898	0.203	39.506
0.6ALKC	0.6	38.784	42.922	0.042	0.904	0.135	48.148
0.8ALKC	0.8	38.680	42.509	0.039	0.910	0.101	51.852
1.0ALKC	1.0	38.576	42.097	0.036	0.916	0.081	55.556
1.2ALKC	1.2	38.471	41.685	0.029	0.922	0.068	64.198
1.4ALKC	1.4	38.367	41.273	0.022	0.923	0.058	72.840
1.6ALKC	1.6	38.263	40.861	0.010	0.936	0.051	87.654
1.8ALKC	1.8	38.159	40.449	0.003	0.943	0.045	96.296
2.0ALKC	2.0	38.054	40.037	0.003	0.951	0.041	96.296
2.2ALKC	2.2	38.054	40.037	0.003	0.951	0.037	96.296

www.arpnjournals.com
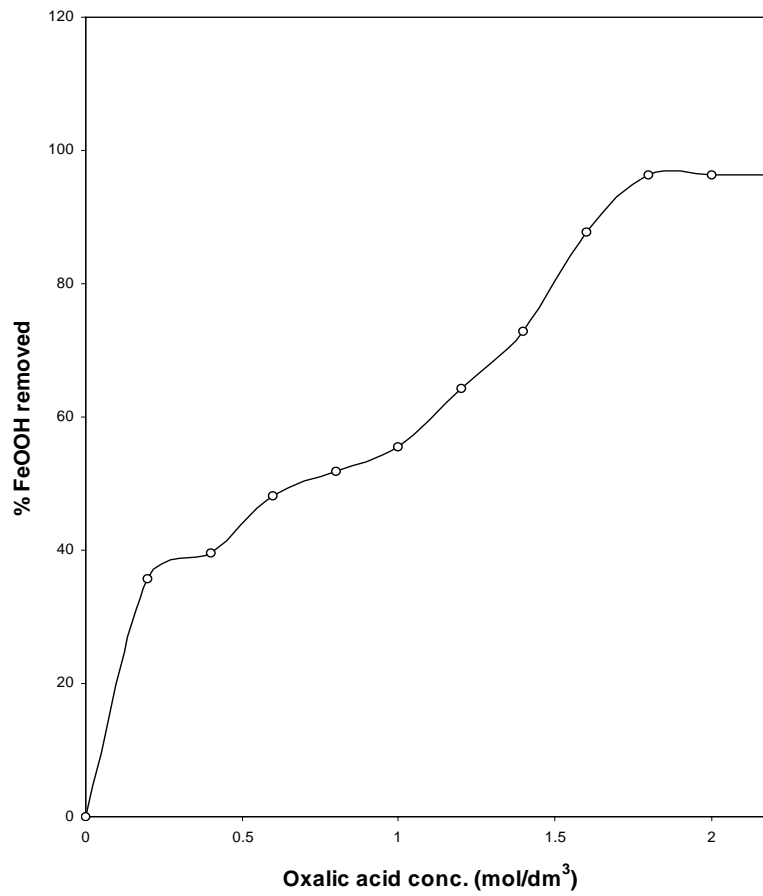
Figure-6. Effect of oxalic acid concentration on removal of iron-bearing impurities from Kankara clay.
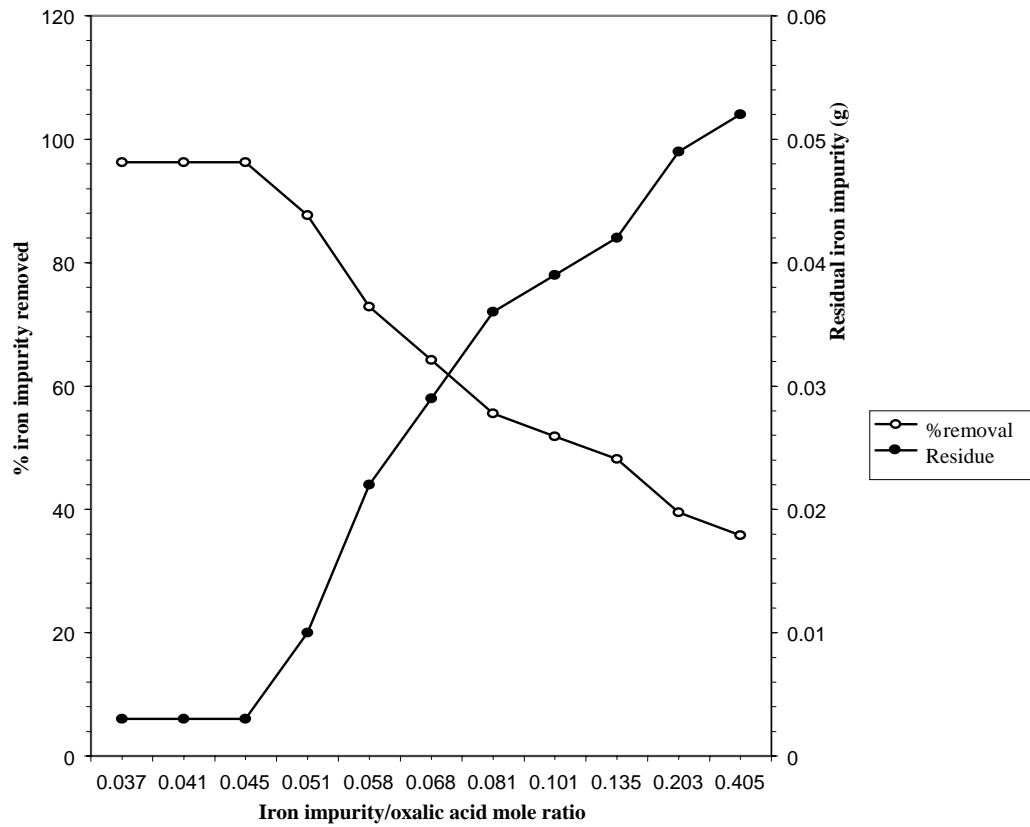
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

Figure-7. Effect of iron/oxalic acid mole ratio on iron residue & % removal from Kankara clay.
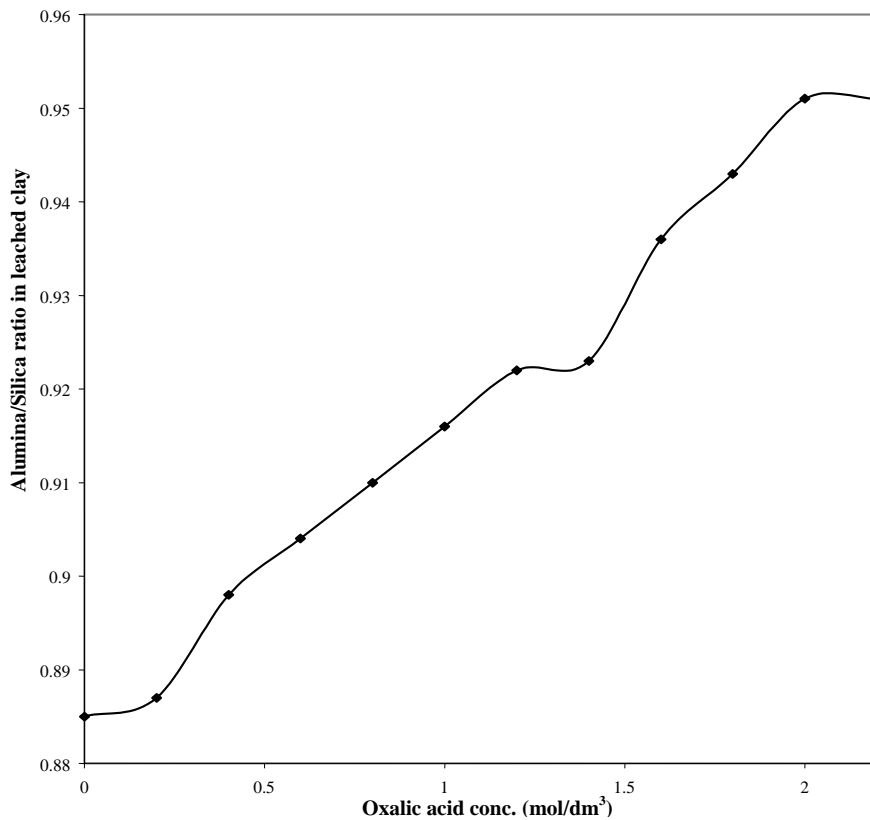
www.arpnjournals.com

Figure-8. Effect of oxalic acid concentration on Alumina/Silica ratio in
Leached Kankara clay.

Optimization of factors affecting iron removal

In order to have an optimisation and a variant of the oxalic acid extraction of iron in the goethite form, the optimum concentration (1.8mol/dm^3) from the initial experiment was used to optimize the shaking time. The % iron impurities removed was increased to 96.400% by extending the duration of shaking to the extent of 7hrs (Figure-9). An attempt at optimizing the reaction temperature further enhanced % iron removal (98.765%) by 2.365% at 75°C (Figure-10).
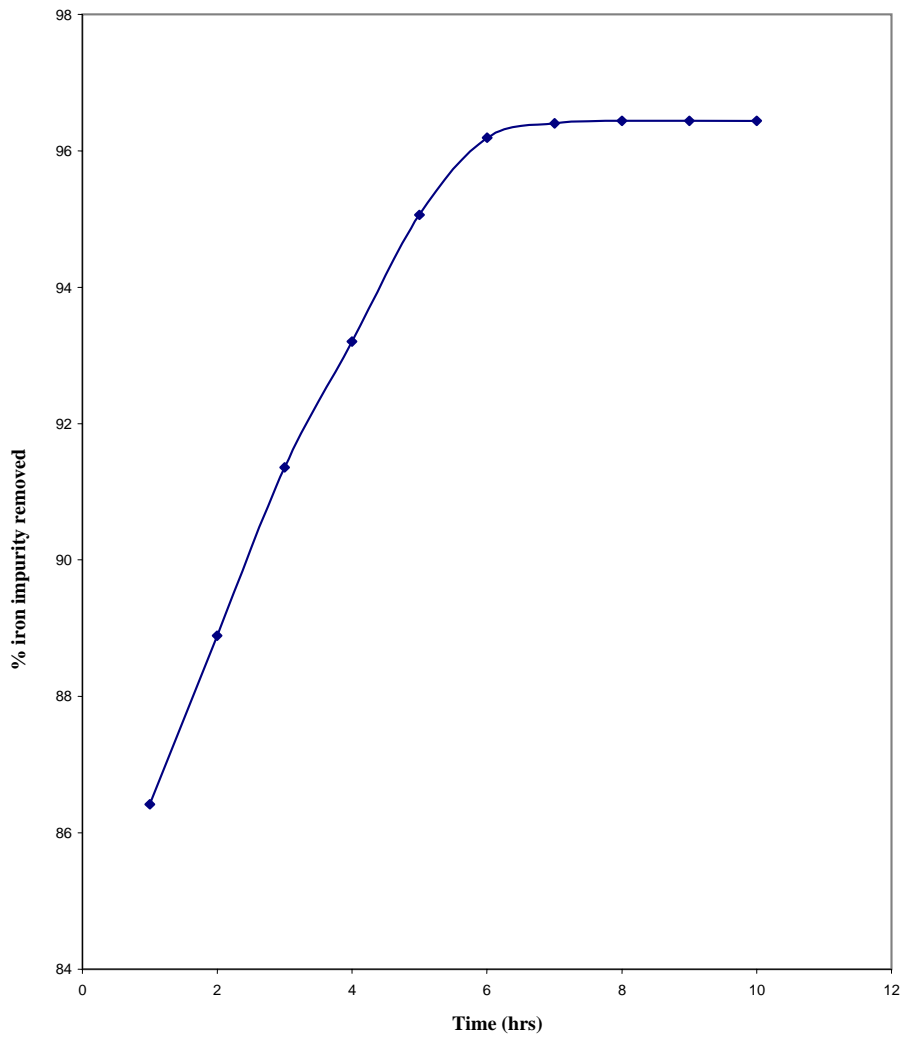
www.arpnjournals.com

Figure-9. Effect of shaking time on removal of iron impurities.
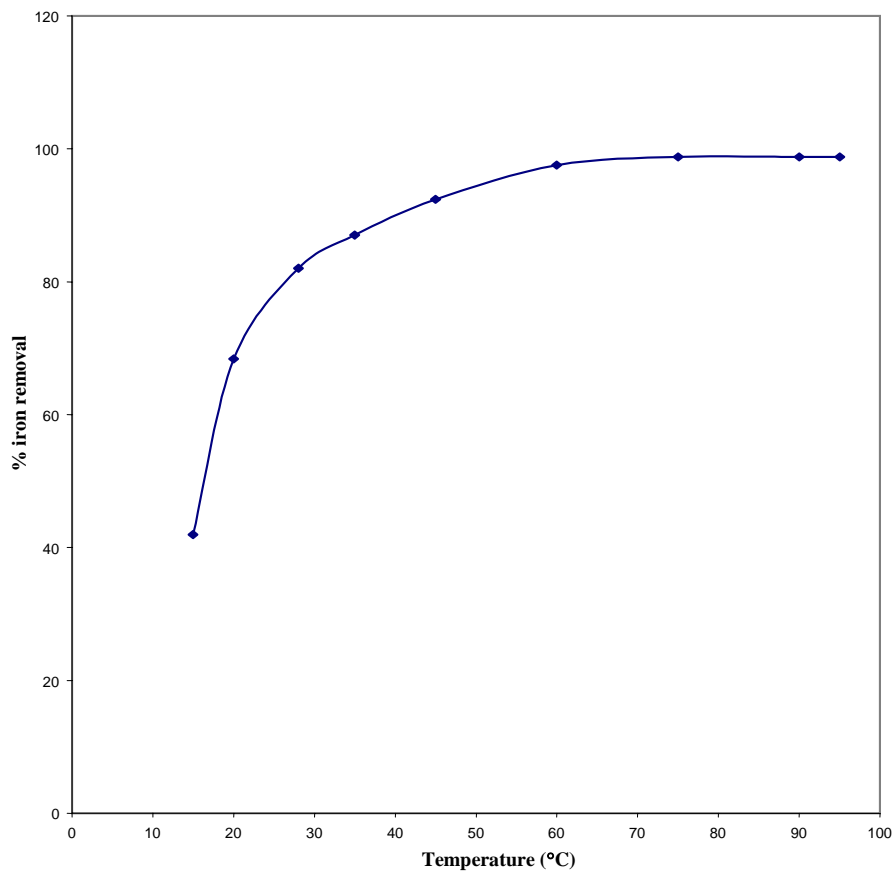
www.arpnjournals.com

Figure-10. Effect of temperature on iron removal from kankara clay.

Studies on the effect of clay particle size on deferration indicated, that 35µm particle sieve size is adequate for the already recorded optimum iron removal (Figure-11). This observation is supported by the fact, that it is easier to remove iron impurity from fine size fraction than medium and coarse size fractions. The order of iron removal from the three size fractions was suggested as fine > medium > coarse (Saikia *et al.*, 2003). The experimental conditions were found to be sufficient, to produce a desirable maximum iron removal of about 99%. Magnetic separation did not indicate the presence of magnetiseable iron in the Kankara clay sample.
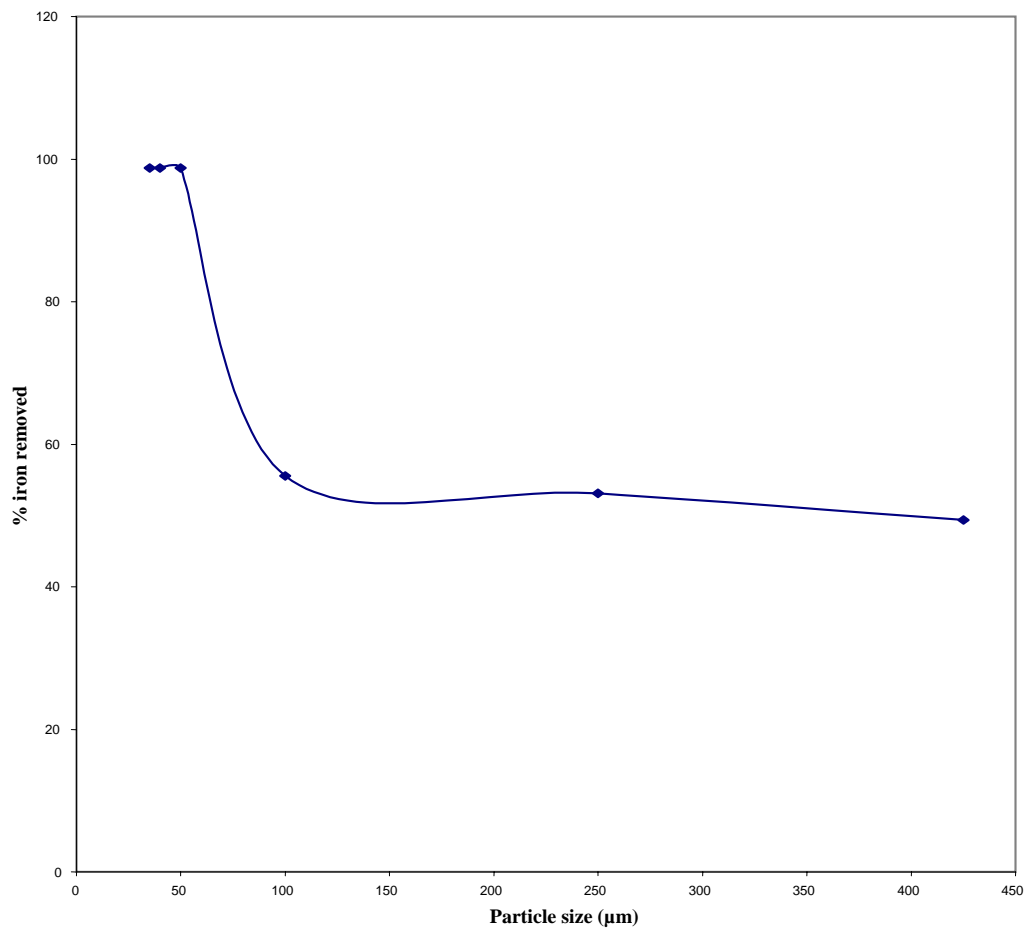
www.arpnjournals.com

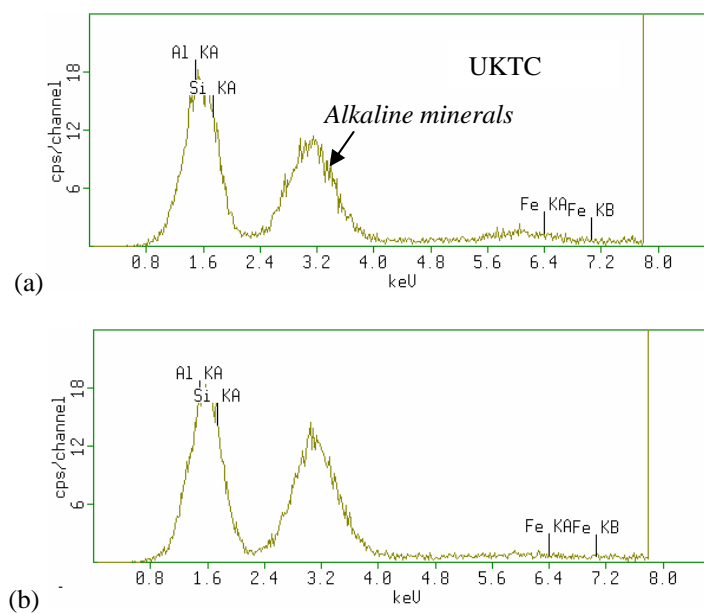**Figure-11.** Effect of clay particle size on iron removal.

Figure-12a-b. Energy Dispersive X-Ray Fluorescence (EDXRF) spectra for
(a) Untreated (UKTC) (b) acid leached Kankara clay.

The x-ray fluorescence spectra for the untreated and best-leached samples are in Fig. 12a-b. According to Saikia *et al.*, (2003), it is possible to bring down the Fe_2O_3 (hematite) content of fine clay fractions to about 1%, at room temperature. In addition to this finding, the present study has also shown that it is possible to bring down the

www.arpnjournals.com

goethite (FeOOH) level of fine clay fraction to about 1% with oxalic acid, at 75°C with moderate stirring for a shorter reaction time of 7hr.

CONCLUSIONS

The oxalic acid solutions have shown remarkable ability to leach out iron impurities associated with kankara clay. The optimum conditions for about 99% deferration were temperature of 75°C, oxalic acid concentration of $1.8mol/dm^3$ and shearing time of 7hrs. The clay deposit is thus suggested for evaluation for application as an adsorbent for environmental research.

REFERENCES

Ambikadevi, V.R., Lalithambika, M. 2000. Effect of organic acids on ferric iron removal from iron-stained kaolinite. Applied Clay science. Vol. 16, pp.133-145.

Borode, J.O., Onyemaobi, O.O., Omotoyinbo, J.A. 2000. Suitability of some Nigerian clay as refractory raw materials. Nigerian Journal of Engineering Management Vol. 1, pp.14-18.

Capitaneo, J.L., da, Silva., Caffarena, V.R. 2004. Aluminosilicate Nanocomposite Material. Applied Mineralogy Pecchio Ed. Pp.45-48.

Elueze, A.A., Ntekini,, E.E., Ekwere, J.J. 1999. Compositional and industrial assessment of clay bodies in Itu area, South Eastern Nigeria. Journal of Mining and Geology Vol. 35, No.2 pp.117-124.

Fan, Zhuangjun., Lang, Liu., Jiangang, Li., Jinren, Song., Junling, Chen Jingli Shi., Gengtai, Zhai. 2003. Preparation of fine-grain carbon-ceramic materials by a ball illing dispersion method. Carbon Vol. 41, pp.1316-1319.

Fasuba, O.A., Egunlae, O., Jimoh, B. 2001 Metallurgical analysis of Orin-Ekiti alumina clay deposite for use as a refractory. Journal of Engineering Technology and Industrial Applications. 1(4): 67-71.

Funtua, I.I. 1999. Application of the Transmission-Emission Method in EDXRF for the determination of trace elements in geological and biological materials. J. Trace Microprobe Tech. 17(3): 293-297.

Gbadebo, A.M. 2002. Evaluation of Engineering and Industrial Potentials of Tidal Flat clays in parts of Niger Delter, Nigeria. Nigerian Journal of Engineering Research and Development 1(3): 20-27.

Guillermo, D. Terrazas Calderon., Jorge Ibarra Rodriguez., Ortiz-Mendez U., Leticia M. Torres-Martinez. 2005. Iron leaching of a Mexican clay of Industrial Interest by oxalic acid. Azojomo journal of materials online. *http://www.azom.com/oars.asp* Vol. 1, pp.1-8.

Igbokwe, P.K., Ogbuagu, J.O. 2003. Effects of process parameters on the extraction of alumina from indigenous kaolinitic clay deposit. Nigerian Journal of Engineering Research and Development. 2(2): 23-26.

Irabor, P.S.A. 2002. Physical and Chemical Investigation on some Nigerian Kaolinite Clays for use in the Ceramics and Allied Industries. Nigerian Journal of Engineering Research and Development. 1(1): 54-59.

Lee Oh Suong, Tam Tran, Yi Yong Park, Seong Jun Kim and Myong Jun Kim. 2006. Study on the kinetics of iron oxide leaching by oxalic acid. Internatonal Journal of Mineral processing. 80(2-4): 144-152.

Macload, W. 1979. Kaolin Deposit near Kankara, Katsina State. Geological Survey Report No.1442.

Nakamura, T., Kawasaki, N., Hirata, M., Oida, Y., Tanada, S. 2001. Adsorption of Hydrogen Sulphide by Zinc-containing activated carbon. Toxicological and Environmental Chemistry Vol. 82, pp.93-98.

Odo, J.U., Nwajagu, C.O. 2003. Possible Application of Eha-Alumona clay deposit in the production of refractories and ceramic ware. Proceedings of the Nigerian Materials Congress and Meeting of the Nigerian Materials Research Society at Conference Hall, Engineering Materials Development Institute, Akure Nov. 12-14, pp.109-111.

Omowunmi, O.J. 2001. Characterisation of some Nigerian clays as refractory materials for furnace lining. Nigerian Journal of Engineering Management. 2(3): 1-4.

Panias, D., Taxiarchou, M., Paspaliaris, I., Kontopoulos, A. 1996. Mechanism of dissolution of iron oxides in aqueous oxalic acid solutions. Hydrometallurgy Vol. 42, pp.257-265.

www.arpnjournals.com

Saikia, N.J., Bharali, D.J., Sengupta, P., Bordoloi, D., Goswamee, R.L., Saikia, P.C., Borthakur, P.C. 2003. Characterisation, beneficiation and utilization of a kaolinite clay from Assam, India. Applied Clay Science Vol. 24, pp.93-103.

Sei, J., Toure, Abba A., Olivier-Fourcade, J., Quiquampoix, H., Staunton, S., Jumas, J.C., Womes. 2004. Characterisation of kaolinitic clays from the Ivory Coast (West Africa). Applied Clay Science Vol. 27, pp.235-239.