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ASSESSING INFLUENCE OF HYDROCHLORIC ACID LEACHING ON STRUCTURAL CHANGES AND BLEACHING PERFORMANCE OF NIGERIAN CLAY FROM UDI

Regina O. AJEMBA, Okechukwu D. ONUKWULI

Department of Chemical Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Anambra State, Nigeria, ginaajemba@rocketmail.com

Abstract: Clay from Udi in Nigeria was mined, ground, and acid-leached at different concentrations of hydrochloric acid to produce adsorbents of varying properties. The raw and acid-leached samples were characterized using x-ray fluorescence (XRF) and Fourier transforms infra-red spectroscopy (FTIR) to examine the structural modifications in the clay as a result of acid-leaching. The analysis showed that the acid-leaching process caused several modifications of the clay samples. The surface area, Si/[Al + Fe + Mg] ratio, adsorption capacity were found to have increased in the acid-leached samples. The acid-leached samples were tested in order to ascertain their performance in bleaching palm oil and it was observed that the bleaching efficiency increased from 29.8% to 66.7%. The acid-leached sample prepared with 7M hydrochloric acid yielded an adsorbent that was efficient in bleaching palm oil under the experimental conditions. The isotherm analysis showed that the bleaching process followed the Freundlich equation.

Keywords: acid-leaching, adsorption, bleaching, hydrochloric acid, isotherm

Introduction

Impurities present in palm oil can be reduced appreciably by adsorption process or bleaching by using clay mineral adsorbents. Clay minerals may be used both naturally and after some chemical or physical treatments such as acid activation, calcination, and ion exchange according to their area of application (Ayari et al., 2005, 2007). Clay minerals generally show limited adsorption capacity in their natural state, but their adsorption capacity is greatly enhanced by being treated with strong acids at slightly elevated temperature (Foletto et al., 2003; Nguetnkam et al., 2008). When clay minerals are acid activated, initially interlayer cations are replaced with hydrogen ions of the acid with subsequent dissolution of structural cations. The desired changes in

the adsorptive properties of clay minerals occurring as a result of acid activation depend considerably on the acid leaching conditions (Motlagh, et al., 2011). Several acid activation experiments under different operating conditions have been reported in the literature, in particular the choice of acid concentration, activation time and temperature, and clay-to-acid ratio (Al-Zahrani et al., 2000; Bakhtyar et al., 2011; Motlagh et al., 2008; Diaz and Santos, 2001; Makhoukhi et al., 2009; Salawudeen et al., 2007; Zhansheng et al., 2006; Foletto et al., 2011; Motlagh et al., 2011; Temuujin et al., 2006; Woumfo et al., 2007; Onal et al., 2002; Temuujin et al., 2004). Activation is the chemical or physical treatment applied to certain types of clays to develop a capacity to adsorb coloring matter and other impurities in oils (vegetable, animal, and petroleum). Acid activated clay materials are widely used in various fields, for example, catalysts, catalyst beds, adsorbents, and bleaching earth. The most important applications of the bleaching earth are purification, decolorization, and stabilization of vegetable oils, otherwise, bleaching. They are able to remove undesirable colors by decreasing the levels of chlorophyll, carotene, and other color species, to reduce traces of Cu^{2+} , Fe^{3+} , phospholipids, and soaps. Christidis et al. (1997) examined the bleaching capacity and acid activation of bentonite from Aegean, Greece, observing a five-fold increase of the specific surface area of the raw materials. The activated samples were rendered suitable for bleaching of rapeseed oil. It was determined that the optimum bleaching capacity is not associated with maximum surface area and the optimum conditions for activation are obtained by using a variety of combinations of acid strength and residence time. The preparation of acid-activated clay materials must be controlled in order to obtain maximum bleaching capacity (Kirali and Lacin, 2006; Rozic et al., 2010). Usman et al. (2012) investigated the applicability of clay from Ibeshe in bleaching palm oil. They observed that the clay after acid activation only increased the color reduction from 9.1 % to 27.3%, a poor performance as an adsorbent. Motlagh et al. (2011) reported that acid activation of clay from Khorasan, Iran, increased its adsorbing ability from 6.35% to 96.4% efficiency using 5N sulfuric acid.

This work was carried out in order to investigate the structural effects on Udi natural clay after acid-leaching with hydrochloric acid and also verify the performance of the said acid-leached clay in bleaching palm oil.

Materials and Methods

Materials

Brown-colored clay material from Udi (N: 6° 31' 00"; E: 7° 43' 00"; A: 327 m) 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: 361 m). All chemicals used were analytical grade, bought from Conraws Company Ltd, Enugu.

Experimental Methods

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 hydrochloric acid solution was added. The resulting suspension was heated on a magnetically stirred hot plate at the temperature of 90 °C for 2 hours 30 minutes. At the end of the experiment duration the resulting slurry was poured into a Buchner funnel to separate the acid and the 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 hours. The dried samples were crushed and sieved again to 0.212 mm particle size. The activation process was repeated with varying acid concentrations of 2–7M of HCl, varying time of 30–150 minutes, and varying temperatures of 70–120 °C. The clay samples thus prepared were labeled UD0, UD2, UD4, UD5, UD6, and UD7, where the numbers indicate the acid concentrations used in the activation step.

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. The specific surface area was measured at 77 K by BET method with a Micromeritics Gemini 2360 instrument using N₂ gas.

Adsorption experiment

The adsorption/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 minutes 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 color 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:

$$\% \text{ bleaching efficiency} = [A_{\text{unbleached}} - A_{\text{bleached}} / A_{\text{unbleached}}] \times 100 \quad (1)$$

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

Results and Discussions

Characterization

The modifications observed in the chemical composition, surface area, bleaching efficiency, Si/[Al + Fe + Mg] ratio, and cation exchange capacity (CEC) of the natural and acid-leached clay samples are shown in Table 1. The table shows that the acid leaching process modified the chemical composition of the samples. As can be seen in the table, the Si^{4+} cations are not removed, but increased with increase in acid treatment, this could be as a result of depletion of the cations from the interlayer and octahedral sheets of the clay (Motlagh et al., 2011). More of the exchangeable cations were easily removed under mild treatment with the acid; such cations include Ca^{2+} and K^+ . Their dissolution remained almost constant after treating with 4M acid concentration. The dissolution of the octahedral cations (Al^{3+} , Fe^{3+} , and Mg^{2+}) was continuous as the acid concentration increased.

As the acid activation is increased, the surface area increased rapidly and reached a maximum and dropped. The rise in specific surface area is as a result of the unoccupied octahedron spaces remaining from Al^{3+} , Fe^{3+} , and Mg^{2+} ions that have left the layer. Then as the activation progresses, the empty spaces grow larger and the micro pores are transformed into mesopores and finally, because of the decomposition of the crystal structure at some locations, some of the mesopores disappear, leading to a drop in specific surface area (Onal et al., 2002; Motlagh et al., 2011). The maximum bleaching efficiency does not correspond to the maximum surface area value. As can

Table 1. Chemical analysis, specific surface area, maximum bleaching efficiency and cation exchange capacity (CEC) of the natural and acid activated Udi clay samples

Chemical composition (%)	Clay sample					
	UD0	UD2	UD4	UD5	UD6	UD7
Al_2O_3	24.42	19.75	17.42	15.06	14.27	13.04
SiO_2	42.28	52.69	59.76	64.48	67.33	70.47
Fe_2O_3	17.25	13.61	11.12	9.53	8.06	7.12
CaO	0.14	0.06	0.05	0.03	0.03	0.03
MgO	3.60	1.74	1.23	1.02	0.89	0.75
K_2O	2.33	1.03	0.87	0.72	0.71	0.71
TiO	4.35	2.31	1.95	1.47	1.25	1.07
LOI	5.73	3.28	2.65	2.33	2.06	1.92
S_{BET} (m^2/g)	70.2	187	207	232	245	237
Max. Bleaching efficiency (%)	29.8	37.5	46.4	51.8	58.9	66.7
Si/(Al + Fe + Mg)	0.93	1.50	2.01	2.52	2.90	3.37
Cation exchange capacity (CEC), meq/100g	78	67	60	51	45	38

be observed from Table 1, UD6 has a surface area of 245 m²/g and a maximum bleaching efficiency of 78.9%, while UD7 has a surface area of 237 m²/g with a maximum bleaching efficiency of 82.7%. Naturally, UD6 should be expected to have higher bleaching efficiency as a result of higher surface area value. It has been reported by researchers (Inglethorpe et al., 1993; Diaz et al., 2001; Engelhard, 1996) that the optimum decolorization ability of activated clay (for a given set of activating conditions) may or may not coincide with its maximum value of the surface area attained under those conditions.

FTIR analysis

The FTIR spectra of the untreated and treated clay samples are shown in Figs 1 and 2, respectively. Comparing Figs 1 and 2, it is clear that there were some structural modifications on the clay sample as a result of acid activation. The untreated clay sample shows absorption bands at 473, 559, 685, 793, 920, 1038, 1104, 1640, 3450, 3525, 3626 and 3692 cm⁻¹. After acid treatment, the bands at 3692.04 and 3626.29 cm⁻¹ attributed to the O–H stretching of kaolinite were modified to 3694 and 3623 cm⁻¹, respectively. The vibrational bands at 3525 and 1104 cm⁻¹ associated with Al–O–Al were completely absent after acid activation, while bands at 1037, 920, 792, 685, and 559 cm⁻¹ related to the Si–O–Si and O–Si–O stretching remained after acid leaching. This verifies the x-ray fluorescence analysis report that the Si⁺⁴ ion increases with acid treatment while the octahedral cations Al³⁺, Fe³⁺, and Mg²⁺ decreases with acid activation. This indicates that there is a minimal damage to the crystal structure of the clay material. This result is in agreement with the findings of other researchers (Mohamedbakr and Burkitbaev, 2009; Temunjin et al., 2004; Low et al., 1998; Chaisena and Rangswatananon, 2004; Hula et al., 2007; Taha et al., 2011).

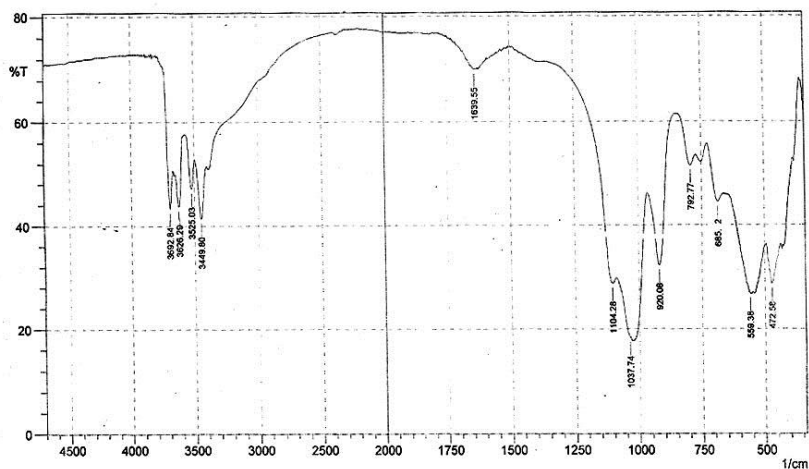


Fig. 1. FT-IR spectra of natural Udi clay

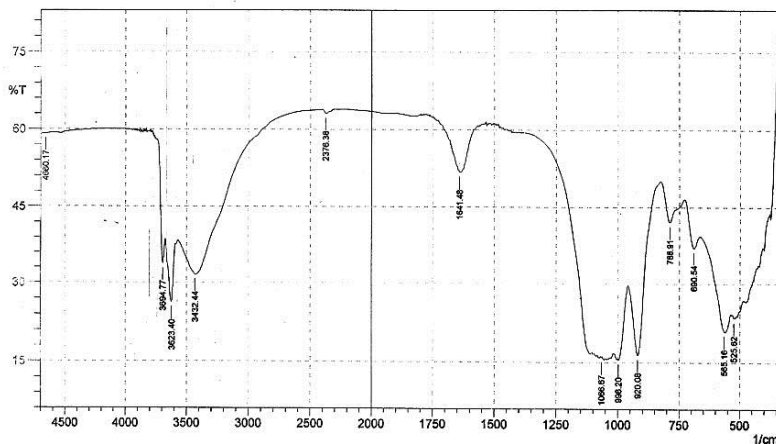


Fig. 2. FT-IR spectra of acid-activated Udi clay

Bleaching efficiency

The results of the bleaching studies performed using the natural and acid-leached samples are shown in Figure 3. The figure shows that the bleaching efficiency increases with an increase in the acid concentration used in the activation step. It is to be seen from the figure that the sample activated with 7M hydrochloric acid shows the highest bleaching efficiency. The figure also shows that time is an important factor, as can be seen, the bleaching efficiency increases with increase in time.

Figure 4 indicates that the bleaching efficiency of the clay samples increases with loss of octahedral cations of Al^{3+} , Fe^{3+} , and Mg^{2+} during the activation process.

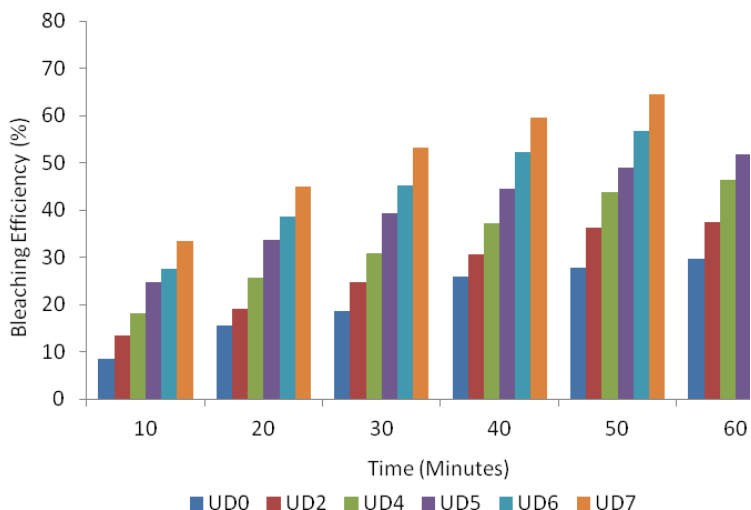


Fig. 3. Bleaching efficiency of the natural and acid-activated clay samples

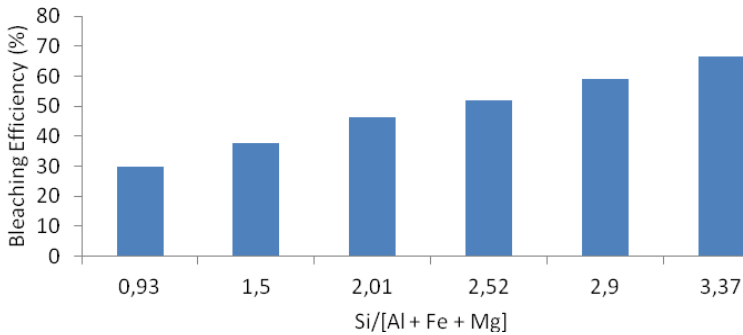


Fig. 4. Variation of bleaching efficiency with Si/[Al + Fe + Mg]

Adsorption isotherms

Langmuir considered adsorption to distribute molecules over the surface of the adsorbent in the form of a monomolecular layer and for the dynamic equilibrium between adsorbed and free molecules. He proposed the following relation:

$$\frac{P}{X/m} = \frac{1}{a} + \frac{a}{b}P \quad (2)$$

where P is equilibrium pressure for a given amount of substance adsorbed, X is the amount of substance adsorbed, m is the amount of adsorbent, a and b are constants.

The mathematical expression relating adsorption to residual solute concentration was developed by Freundlich:

$$\frac{X}{m} = K C^n \quad (3)$$

where C is the amount of residual substance, and K and n are constants.

Since the absorbance measurements are taken in all experiments for the bleaching process, the relative amount of pigment adsorbed (X) and the residual relative amount at equilibrium (X_e) are obtained from Eqs 2 and 3:

$$X = \frac{A_0 - A_t}{A_0} \quad (4a)$$

$$X_e = \frac{A_t}{A_0} = 1 - X \quad (4b)$$

where A_0 is the absorbance of unbleached (crude) palm oil and A_t is the absorbance of bleached oil at time t . Thus, by means of Eqs 4a and 4b, by writing X_e instead of

equilibrium pressure P and the residual substance C , Equations 2 and 3 are rearranged as follows (Topallar, 1998):

$$\frac{X_e}{X/m} = \frac{1}{a} + \frac{a}{b} X_e \tag{5}$$

$X/m = K X_e^n$ or the linear form

$$\log \frac{X}{m} = \log K + n \log X_e \tag{6}$$

A plot of $X_e/(X/m)$ versus X_e and $\log X/m$ versus $\log X_e$ should give straight lines and the least squares analysis can be used to calculate the parameters (a, b) and (K, n) from intercept and slope of straight lines of the isotherms.

Plots of the Freundlich isotherm for the differently prepared adsorbents are depicted in Fig. 5. As can be seen in the figure, straight lines were obtained in the plots with high regression coefficient.

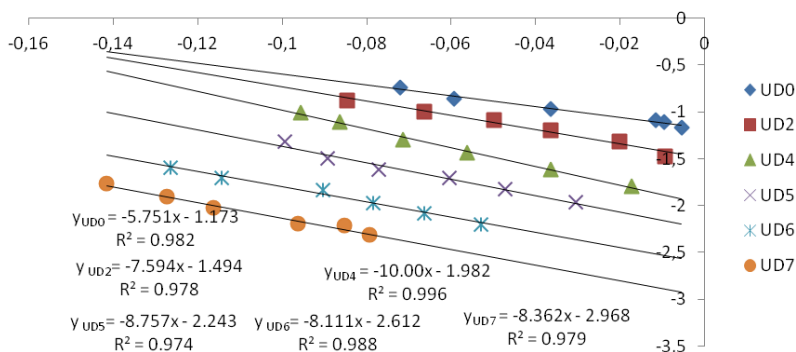


Fig. 5. Freundlich isotherm plot for color pigment removal from palm oil using Udi clay activated with different concentrations of hydrochloric acid

Table 2. Isotherm constants for the un-activated and HCl activated samples

Isotherm	Constants	Clay type					
		UD0	UD2	UD4	UD5	UD6	UD7
Langmuir	a	-0.028	-0.041	-0.065	-0.076	-0.084	-0.089
	b	-2.57	-2.15	-2.08	-1.97	-1.82	-1.70
	R^2	0.876	0.869	0.890	0.881	0.889	0.888
Freundlich	N	-5.751	-7.794	-10.00	-8.757	-8.111	-8.362
	K	0.067	0.032	0.010	0.006	0.002	0.001
	R^2	0.982	0.978	0.996	0.974	0.988	0.979

Since the fit of the plots of Freundlich isotherm is more linear, it can be concluded that the Freundlich isotherm is more applicable to the bleaching performance of acid activated clay from Udi. The values of the constants calculated from the slopes and intercepts of the plots are presented in Table 2.

Conclusion

The effect of hydrochloric acid activation on the structural and bleaching performance of Udi clay has been successfully investigated. The structure of the clay was modified by the acid activation process and the bleaching efficiency was increased from 29.8 to 66.7%. Based on the results activated clay from Udi performs better than the un-activated one and the acid concentration play an important role in the activation step.

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