Preparation, Characterization and Comparison of adsorbents from Kirfi kaolin clay with Commercial bleaching Clay

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Abstract*: Several adsorbents were prepared by acid-activating Kirfi Kaolin clay sample obtained from Kirfi village in Bauchi state, Nigeria using sulfuric acid. The raw clay and the prepared adsorbents were characterized for their physical properties (pH, moisture content, apparent bulk density, and adsorptive power) and their chemical compositions, and compared with the properties of a commercial bleaching clay (CBC). Bleaching study was used to determine the adsorptive power of the raw clay as an adsorbent, the adsorbents prepared from the raw clay and the CBC while chemical composition was done using AAS and XRF. The result of compositional analyses showed that the silica content of 50.07% to 74.32% and alumina content of 4.42% to 10.96 were the major components of the raw clay, CBC and the prepared absorbents. The adsorbents prepared with 1 M and 2 M H_2SO_4 had compositions and physical properties that are similar to that of the CBC, and also has an adsorption powers (81.35% and 94.05% respectively) that are comparable to that of CBC (96.25%).

***Keywords*: Acid activation, adsorbent, clay, edible oils, water purification, adsorption power**

I. INTRODUCTION

Adsorption is a process in which atoms, ions or molecules from liquid, dissolved solid or gas adsorbed (or adhere) to the surface of a solid. The molecule that is adsorbed to the solid surface is called the adsorbate while the solid surface is called the adsorbent. Adsorption is a surface phenomenon that takes place by physical forces, and sometimes weak chemical forces [1], [2]. It is a key separation tool in different industries such as chemical, water, petrochemical, food and pharmaceutical industries. Separation, the opposite of mixing (a process highly favored by the second law of thermodynamics), is a process that transforms a mixture of substances into two or more products having different composition [3]. Separation is a difficult process as a result, it accounts for the largest production costs of many industrial products. The performance of any adsorptive separation or purification process is determined by the physicochemical properties such as the particle size distribution, particle shape, density, pH, ion exchange capacity etc. of the adsorbent [4].

Majority of adsorbents fall into one of three classes: carbon-based compounds which are typically hydrophobic and non-polar, examples include activated carbon and graphite; oxygen-containing compounds which are typically hydrophilic and polar, examples include silica gel, alumina, clays and zeolites; and polymer-based compounds which are polar or non-polar depending on the functional groups in the polymer matrix [5], [6].

Clays are hydrous aluminosilicates defined as minerals that make up the colloidal fraction of water, sediments, soils and rocks. Clay may be composed of mixtures of fine grained clay minerals and clay sized crystals of other minerals such as quartz, feldspar, carbonates and metal oxides [7]. Clays contain exchangeable ions, such as Ca2+, Mg2+, H+, No3-, SO42-, etc., on their surface and act as natural scavenger of pollutants in the environment; a role achieved through ion exchange or adsorption or both [8]. Some clays in their natural state have very high adsorption power, majority however, have to undergo modification to improve their surface area, adsorption capacity, and range of applicability [9], [10]. It is because of the ability of clays to undergo modification, over and above their low cost and natural abundance, that clay adsorbents are acquiring prominence. In attempts to improve the adsorption properties and range of applicability of clays, a number of physical and chemical methods have been used. These including heat treatment, chemical activation, treating the cationic surfactants and polymer modification [9], [11] ─ [13].

Chemical activation of clay involves the treatment of clay with an acid (such as HCl, H2SO4, HNO3, CH3COOH, etc.) or alkali (such as NAOH, KOH, etc.) solution to affect the physicochemical properties: chemical composition, cation exchange capacity, specific surface area and so on and so forth.

Acid activation of clays has been a subject of many papers recently [14]. However in Nigeria not much of the abundant clay deposits have be exploited for adsorption applications. Kirfi Kaolin clay deposits in Kirfi village of Bauchi state, Nigeria is one of the clay deposits that have not been studied. This study aims to prepare several adsorbents from Kirfi clay and compare their properties with those of the raw clay and a commercial adsorbent.

II. MATERIALS AND METHOD

A. Sample Collection and Treatment

About 12kg of grey Kirfi kaolin clay sample used for this work was obtained from Bars Village of Kirfi Local Government Area of Bauchi State, Nigeria as dry lumped sample. The clay sample was first cleaned from weather crust by using acetic acid and distilled water, dried in an oven at 105^0C for 3 hours and sieved through a 200 mesh sieve. Bentonite, a commercial bleaching clay (CBC) used as reference and Crude palm oil were purchased from a chemical store and Yan Manja Market respectively in Jos North Local Area of Plateau State, Nigeria. The crude palm oil was degummed by stirring it with 0.1% phosphoric acid at 80^oC for 15 minutes, washing with distilled water and then centrifuging to remove phosphatides [15].

B. Preparation of Adsorbents

The adsorbents were prepared by activating several portions of the Powdered Kirfi koalin clay using analytical grade H_2SO_4 (BDH Chemicals Ltd, Poole England). 5g of the clay sample was re-fluxed with 50ml of 1.0M H_2SO_4 at 100^0C for 3 hours. The procedure was repeated with 2M, 3M, 4M and 5M acid concentrations. The prepared adsorbents were labeled K1, K2, K3, K4, and K5, where K stands for Kirfi and the Arabic numeral represent the acid concentration used for the preparation of the adsorbents. K0 was used to represent the raw clay as adsorbent.

At the end of each run, the acid was discarded and the sample was filtered and washed repeatedly with distilled water until the filtrate was free of SO_4^{2-} ions [16]. The filtered sample was then dried at 105^0C for 3 hours, crushed to a particle size that would pass through a 200 mesh size and stored in polythene bags.

C. Determination of Moisture Content

5g of raw clay (K0), CBC and each of the adsorbents (K1-K5) were accurately weighed into separate dried preweighed crucibles. The samples were heated to constant weight in an oven at 110^0C. After cooling in a desiccator the moisture content was determined using equation (1). Each sample was analyzed twice and then the average percentage was reported [17].

$$W\% = \frac{A-B}{A} * 100 \qquad (1)$$

Where W% = Percentage of moisture in the sample, A = Weight of initial sample (grams) and B = Weight of dry sample (grams)

D. Measurement of pH

5g each of raw kaolin clay (K0), CBC and the adsorbents (K1-K5)were soaked in 25ml of distilled water for twelve hours and their pH tested using pH meter (HANNA instrument, pH 211) after thorough mixing as described in similar studies [9],[18]

E. Determination of Apparent Bulk Density

Each of the raw clay (K0), CBC and the prepared adsorbents (K1-K5) was put into a graduated cylinder of known weight (100 cm^3) avoiding compression. The cylinder was vigorously tapped 50 times on a horizontal surface to constant clay volume. The volume was taken as constant after two successive tap readings showed no further decrease in volume and the apparent bulk density (ABD) calculated in g/cm^{-3} using equation (2) [9], [19]:

$$ABD = \frac{W_x - W_y}{V} \qquad (2)$$

Where

W_x = Weight of the cylinder plus clay, W_y = Weight of the empty cylinder V = Total weight of clay used after compression.

F. Determination of Adsorptive power

Bleaching study was used to determine the adsorption power of the adsorbents. To 10ml of the degummed oil at 70^oC, 0.1g of each was added, the temperature raised to 90^oC and allowed to stand for 30 minutes. The oil was cooled to 70^oC and then filtered under suction with a sinta funnel to remove the adsorbent.

The evaluation of the adsorptive power/bleaching power of the adsorbents was carried out by spectral analysis using UV – visible spectrophotometer (UV-1700). A solution of each of the bleached and unbleached palm oil was first prepared by diluting in acetone (LOBA Chemie PVT Ltd, India). The solution of the unbleached palm oil in acetone was used to obtain the wavelength of maximum absorbance (445nm) which was then used to access the absorbance of all the bleached palm oil samples, using acetone as reference. Equation (3) was used to calculate adsorptive performance/percentage bleaching performance [16], [20]:

$$BP\% = \frac{A_0 - A}{A_0} * 100 \qquad (3)$$

Where

A_0 and A are the absorbance of the unbleached and bleached palm oil respectively.

G. Determination of Loss on Ignition

Loss on ignition of the raw clay (K0), CBC and the prepared adsorbents (K1-K2) were determined according to the method described by Dawes et al. (2021) [9]. Equation (4) was used to calculate the Loss on ignition (LOI).

$$LOI = \left(\frac{a-b}{a}\right) \times 10 \qquad (4)$$

The determinations were carried out in triplicate for each sample and their average reported.

H. *Compositional analysis*

Chemical Composition was determined, and expressed as the oxide form in percentage, using AAS (Thermo Scientific iCE 3000 series AA Spectrometer) and XRF (Bruker AXS model S4 spectrometer equipped with a WD-XRF detector) as described in a related study [9].

III. RESULTS AND DISCUSSION

A. *Moisture Content of adsorbents*

The results, shown in fig. 1, reveal that there is a fairly large variation in the moisture content (1.76% - 6.94%). Comparing the moisture contents of the Kirfi adsorbents to that of the commercial clay (CBC), all the adsorbents have moisture content values lower than that of the CBC (8,8%). K1 adsorbent have the highest value (6.9%) followed by K2 (6.54%) while K5 has the least moisture content.

The results showed that at the initial stage the acid attack increased the capacity of the clay to hold water. Thereafter, the moisture content decreased as the acid concentration increases, a similar trend reported in the literature [9], [21]. This could be due to the increase in void spaces created as the exchangeable metal ions were displaced by the hydrogen ions with smaller volumes compare to the metal ions.

Bleaching clays normally contain from 10-18% free moisture. When a clay is dried, the water molecules escape and the layer collapses. This reduces the active surface area, thereby reducing the adsorptive capacity of the clay [22]. However, when used for bleaching oil, it is necessary to remove the moisture from the clay to obtain optimum adsorptive capacity. The coloring materials cannot be maximally adsorbed until all the water has been removed.

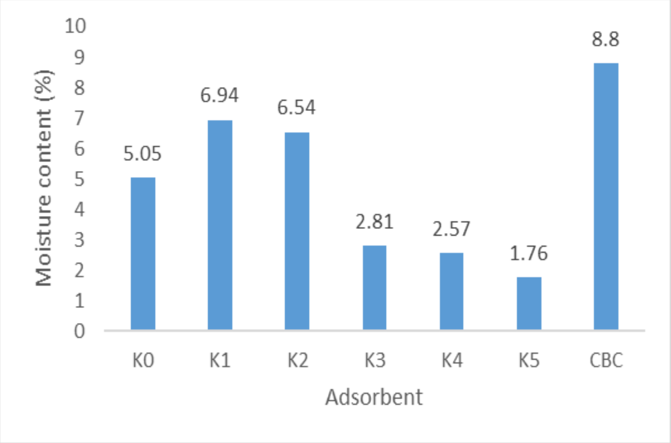

Figure 1. Moisture content of raw clay, adsorbents and CBC

B. *Apparent bulk density of adsorbents*

Apparent bulk density (ABD) is an empirical value defined as the weight per unit volume of clay when it is trapped to constant volume in a graduated cylinder [23]. ABD of a clay is inversely proportional to its adsorptive capacity and filtration rate [22]. Since ABD of a clay depends on the void space, ABD is inversely proportional to the amounts of oil retained by the clay [18], [23], when used for adsorptive bleaching.

Fig. 2 below shows the ABD of the adsorbents and the CBC. The CBC has ABD value (0.72%) that is less than that of the raw Kirfi clay, K0 (1%) and the K1 adsorbent but higher than those of K2– K5 adsorbents. The fig. Also shows that there is a decrease in apparent bulk density of adsorbents (from 1% for K0 to 0.45% for K5) with increasing acid concentration from 1M to 5M. According to this variation (0.45 – 1.00%), clay mineral properties are changed as the acid activation progresses

The variation of apparent bulk density, which conforms to reported trends [9], [21], implies a change in clay mineral properties with increasing acid concentration. This can be attributed to increase in clay surface area caused by the existence of vacancies in the lattice of the clay which led to reduction in mass.

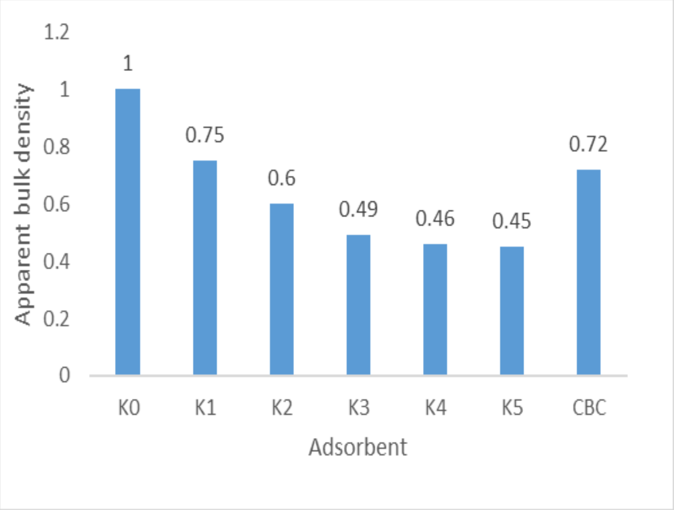

Figure 2. Apparent bulk density of raw clay, adsorbents and CBC

C. *pH of adsorbents*

Natural clays have a pH range between 4 – 7 and activated clays 2.5 – 4.0. For bleaching purpose, low pH has detrimental effects on oils. It causes an increase in the free fatty acid content of oils because H^+ causes some hydrolysis of the glycerides to free fatty acid and glycerine [24]. Oils rich in chlorophyll such as soya bean require bleaching earths of substantial acidity for optimum adsorption.

Fig. 3 shows the pH values of the raw clay, (K0), the prepared adsorbents (K1– K5) and the CBC. K0 has the highest pH (8.48) followed by K5 (7.48) and K4 (7.11). The CBC has a pH (6.91) that is lower than those of K0, K4 and K5 but higher than those of K1-K3.

The pH values, shown in fig. 3, shows a decreasing trend from 8.48 for the raw clay to 5.34 for adsorbent prepared with 3M acid concentration then increased again to 7.48 for adsorbent prepared with 5M acid concentration, a trend which differs from the trend reported in a similar study [9]

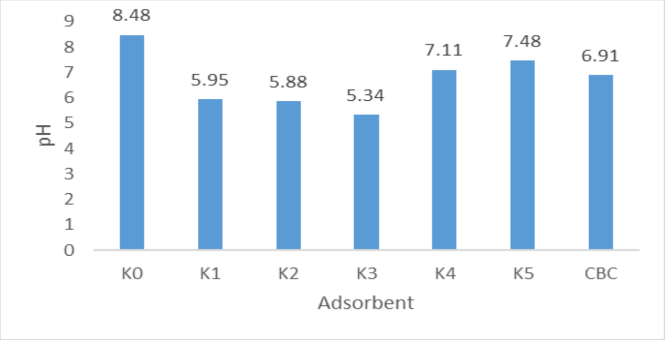

Figure 3. pH value of raw clay, adsorbents and CBC

D. *Adsorptive power of adsorbents*

Fig. 4 shows the adsorption Power (bleaching performance) of CBC the raw clay as adsorbent (k0) and the prepared adsorbents (k1-K5). The prepared adsorbents (K1-K5) adsorbed colour pigments from the palm oil more than the raw clay sample as an adsorbent (K0), raising the bleaching performance from 5.36% to 94.05%. K2 adsorbent has a better performance compared to K0; due to increase in surface area and pores volumes during acid leaching [25], [26], and the built up crystalline structure of the clay with the formation of silicon and aluminium oxide during the severe acid leaching [27].

The evolution of the bleaching performance of Kirfi clay with increase in activation acid concentration is similar to those obtained in past studies [9], [28]. These result show that as the acid concentration increased, the bleaching performance increased up to a maximum value of 94.05% for K_2, and compared to that of CBC (96.25%). Above this concentration, the bleaching performance decreased to 67.2%. This can be attributed to the destruction of the clay crystalline structure by the excess acid. Which is in agreement with similar investigations [15], [29]. The initial increase in bleaching performance with increasing acid concentration was probably due to the formation of active sites on kaolin surface, and the drop in bleaching performance could be due to passivation of the rest of the clay which protects the clay layers from further acid attack [30]. The initial increase in bleaching performance with increasing acid concentration may be attributed to the formation of active sites on the clay surface.

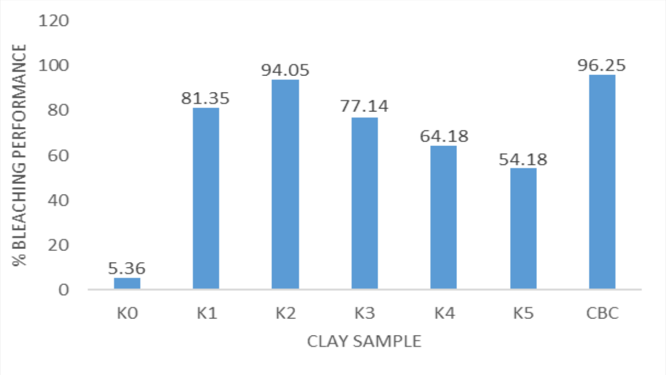

Figure 4. Bleaching Performance of adsorbents and CBC

E. *Chemical Composition of adsorbents*

The results of compositional analysis (Table I) shows that the raw clay (K0), CBC and the prepared adsorbents (K1-K2) are composed majorly of metal oxides particularly SiO_2, Al_2O_3, Fe_2O_3 and CaO, MgO. According to the results given in Table 1, the adsorbents prepared with 1M acid (K1) and 2M acid (K2) has Al_2O_3, SiO_2 and loss on ignition values that are similar to those of the Commercial bleaching clay (CBC). Among the chief elements, SiO_2 varies from 59.05% to 74.32%, Al_2O_3 from 4.42% to 11.75% and Fe_2O_3 as Fe^{3+} from 0.21% to 1.35%. The content of Fe_2O_3 is low, which characterizes the studied clay sample as white clay. Alkaline fluxes contents (K_2O and Na_2O) are low. MgO and CaO contents indicate that the clay sample are non-carbonatic. The loss on ignition which is due to the loss of water, Sulphur (VI) oxide and carbon (IV) oxide has values ranging from 5.37% - 13.56%. The Silica (SiO_2) component showed a consistent increase in values as the acid concentration increases while the composition of other components in the clay sample showed a decrease after activation.

The marked increase in silica (SiO_2) content and decrease in the other components of the clay, which is in agreement with similar studies [9], [17], [31], is an indication of a partial destruction of the octahedral sheets by dissolution of exchangeable cations [32] changing the clay structure thereby creating new pores and resultant increase in surface area [31].

Table I. Chemical Composition of adsorbents and CBC.

Component (%)	K_0	K_1	K_2	K_3	K_4	K_5	CBC
SiO_2	50.07	59.05	62.25	70.6	74.32	74.14	65.89
Al_2O_3	10.96	9.75	7.56	6.36	5.87	4.42	7.39
Fe_2O_3	0.81	0.74	0.65	0.49	0.35	0.21	0.61
CaO	1.25	0.67	0.68	0.70	0.93	0.73	1.21
MgO	2.20	0.50	0.43	2.80	0.60	0.70	0.46
Na_2O	4.10	0.99	0.90	0.88	0.52	0.45	0.13
K_2O	5.81	1.56	0.63	0.57	0.50	0.45	0.51
LOI	10.54	13.56	12.56	7.24	6.40	5.37	13.98

IV. CONCLUSION AND RECOMMENDATION

This study has shown that Kirfi clay responded well to acid attack evidenced by the marked difference in properties (Physical and chemical) between the adsorbents and the raw clay making it a viable raw material for the preparation of adsorbents through activation with sulfuric acid.

Evaluation of acid activated Kirfi clay revealed that the crystalline structure of the clay was modified as a result of the acid treatment. Activation with 2M H_2SO_4 produced the best result with respect to bleaching performance followed by 1M H_2SO_4.

We recommend that reduction of peroxide value and phosphorous present in palm oil by the adsorbents should be investigated, Studies on other industrial uses of the adsorbents, such as wastewater treatment, should be undertaken, and since the morphologies of kaolinite influence their adsorption properties, the effect of particle size and surface charge on kaolin's bleaching capacity should be studied.

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