

Bleaching Efficiency of Activated Kaoma Bentonitic Clay Using Methylene Blue Dye as the Adsorbate

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Abstract– Most clay minerals are fine-grained and are widely used as adsorbents because of large surface area. Activation increases the surface area of clays and leads to more industrial applications. Chemical characterisation and activation of clay from Kaoma was carried out in order to promote its use in the edible oils industry. Activation was carried out by leaching with sulphuric acid for 2 hours in the temperature range 90–95°C. The effect of activation was assessed by measuring the absorbance of UV radiation of methylene blue dye solutions which were treated with powders activated at varying acid additions. Absorbance data for all solutions was obtained at a pH value of approximately 6.60. The dye solutions were bleached to different extents depending on the amount of acid employed. A bleaching efficiency of up to 99% was achieved. Bleaching efficiency results exhibited an optimum in the acid dosage range, 5–10%.

Keywords– Acid Activation, Bleaching Earth, Cation Exchange Capacity, Bentonite, Bleaching Efficiency and Aluminosilicate

I. INTRODUCTION

A) Objectives of the study

Activated clays are the major source of bleaching earth, a material applied in many industries. The industries include edible oil, foundry and paper industries. The edible oils industry is the major user of bleaching earth in Zambia. The national edible oil requirement was estimated at 120,000 tons per year in 2013 [1]. Presently the country has an installed refinery capacity of 161,000 metric tons of refined edible oils, which translates to over 700,000 tons of crude vegetable oils. Assuming a loading capacity of 2%, 14,000 tons of bleaching earth is required annually. Presently the requirement is met by importation. Yet the country has reserves of fine-grained clay in Kaoma which can be processed into bleaching earth. However, the deposit has not fully been chemically characterized. Preliminary studies [2], [3] indicated that the material could be activated but the work on bleaching efficiency was not optimized.

The aim of the present study was to determine the chemical composition of the Kaoma clay deposit and optimize bleaching efficiency after acid activation, particularly for acid additions below 20%. It is expected, ultimately, the material

will be mined commercially, processed and used for bleaching edible oils and related products.

The Kaoma clay deposit is bentonitic [4]. It is located about 4km East of Kaoma town. The clay is exposed on the banks of Luena River and it can be seen on both sides of the bridge on the Kaoma-Kasempa road. Reserves of the clay deposit are estimated at 15.0 million tons. The estimates are based on ten water bore holes that were drilled along the Luena River to supply water to Kaoma town. The bore holes intersect the clay deposit up to a depth of 30 meters.

B) Structure and Properties of Clays

Clay minerals are naturally occurring aluminosilicates with a sheet structure. Most clay contains kaolinite as the predominant mineral. Bentonitic clays contain montmorillonite which belongs to the smectite group of minerals. These have an articulated layer structure depicted below in Fig. 1:

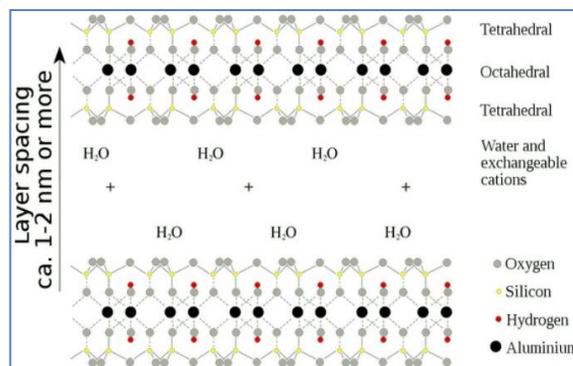
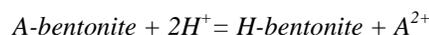


Fig. 1: Structure of montmorillonite

Smectites are fine-grained, swell in the presence of water and have high values of cation exchange capacity. They are highly absorbent. Swelling is due to the intake of water in the region between the layers. The interlayer region also contains exchangeable cations. During the reaction with acids the interlayer cations are replaced by H^+ cations as illustrated below for bentonitic clay.



Usually A is Ca or Na. Then, the bentonite is either Ca-bentonite or Na-bentonite.

C) Activation of Clays

Activation is the chemical and physical modification of clays. It is achieved by heating or treatment with acid. Acid activation is more widely practiced. The aim of activation is to open up the structure of the clay mineral in order to enhance the capacity for bleaching, the removal of contaminants and decolouring of crude oils or solutions. The enhanced bleaching capacity is a result of chemical and structural changes. For example Al^{3+} , Ca^{2+} and Mg^{2+} cations are removed from the lattice with an increase in surface area [5]. Structurally new pores are created and surface area increased [5], [6]. However the mechanism of bleaching is not fully understood. For example, chlorophylls and carotenes are considered to be removed by adsorption [7]. Yet bleaching can also be a result of the removal of metallic elements through cation exchange.

D) Calculation of Bleaching Efficiency

Bleaching efficiency of activated clay is assessed by recording the absorbance (of radiation) by the medium or solution before and after treatment with an activated clay sample. The bleaching efficiency, BE, is calculated as follows [8]:

$$\%BE = \left(\frac{A(\text{unbleached}) - A(\text{bleached})}{A(\text{unbleached})} \right) * 100$$

Where,

$A_{\text{unbleached}}$ = Absorbance of unbleached medium

A_{bleached} = Absorbance of bleached medium

Several workers have studied the bleaching efficiency of activated clays and bentonite [5]–[11] using used engine oils or crude vegetable oils as target media. A methylene blue dye solution has been employed in the present study. In this context a high value of bleaching efficiency is a measure of the extent to which the treated dye solution has been depleted of methylene blue molecules.

II. MATERIALS AND METHODS

A) Materials

Clay from Kaoma Western Province was the prime material for chemical characterization and activation. As-mined the clay is hard and lumpy as illustrated below (Fig. 2):



Fig. 2: Sample of Kaoma Clay

A methylene blue dye whose structure is shown below was used for bleaching experiments. Some properties of the dye are:

Molecular formula: $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$

Atomic weight: 319.851 g/mol

Density: 0.98 g cm^{-3}



Fig. 3 shows the two prominent absorption peaks of UV radiation. A wavelength of 664nm was chosen in the present study for optimum absorbance. Analytical grade sulphuric acid (98% concentration) was used for leaching.

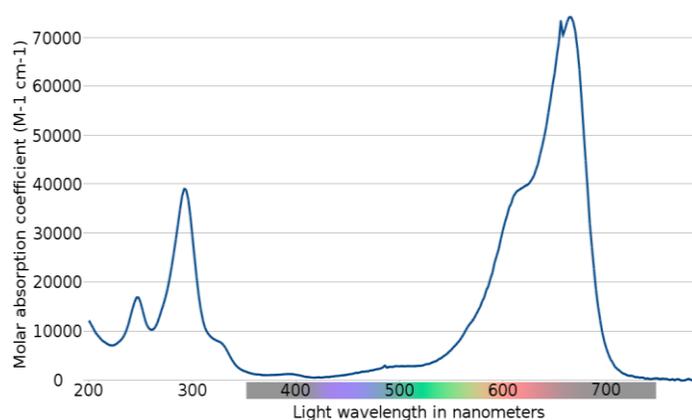


Fig. 3: Absorption peaks of methylene blue

B) Powder Preparation

The clay was initially passed through a jaw crusher followed by further size reduction in a gyratory crusher. The material from the gyratory crusher was sieved through a 2mm aperture sieve and transferred to 5 litre pot mill for final grinding. The pot mill was charged with one kg of material and 5 kg of milling media. The mill was allowed to run for 20 minutes.

Finally the clay was passed through a 250 μm aperture sieve analysis and leaching experiments.

C) Chemical Analysis

Mineralogical and chemical analysis was determined using an x-ray diffractometer, a portable xRF and an atomic absorption spectrophotometer.

Analyzing by X-ray spectroscopy was carried on as received sample.

D) Leaching and bleaching procedures

A sample of 100 g was used for leaching. Each sample was placed in one litre cylinder in which water was added up to

the 300ml mark capacity to form slurry of 33% solid to water ratio.

Then each portion of slurry was treated with different amounts of acid (2.5 – 12.5g) or (2.5 – 12.5 %) and leached for 2 hours within the temperature range 90 – 95 °C. The sample was left to cool after leaching after which the pH was measured. The leached sample was filtered and washed with excess distilled water to attain a pH value of approximately 6.6. Finally the washed sample was dried over night at 110°C in oven.

Clays harden on drying. Hence the sample for use in bleaching experiments was pulverized in a pestle and mortar and sieved through a 250µm aperture sieve. Bleaching experiments were conducted using a 10% by volume solution of methylene dye. A clay sample of a known acid addition

and weighing 10g was mixed with 100ml of the dye solution and allowed to stand overnight. This was followed by filtration to obtain dye solutions bleached to different extents with activated clay. Absorbance of UV radiation for each solution was obtained using a spectrometer (Agilent Cary UV-Vis).

III. RESULTS AND DISCUSSION

A) Chemical Composition

The chemical composition of the raw clay sample, calculated in oxides, is shown in Table I. The composition is typical of aluminosilicate clay. The clay contains aluminium, silicon, magnesium and fluxes, K and Na.

Table I: Chemical analysis of the raw day using atomic absorption spectrophotometer

Oxide	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	MnO ₂	P ₂ O	SiO ₂
Wt.%	21.2	4.03	2.71	1.45	2.14	0.51	0.05	0.03	65.0

Table II: pH values

Mass acid (g)	pH after leaching	pH after washing
2.5	0.56	6.90
5.0	0.32	6.63
7.5	0.30	6.50
10.0	0.31	6.62
12.5	0.27	6.47

Table III: Absorbance and Bleaching Efficiency data

SAMPLE/ ACID DOSAGE (g)	ABSORBANCE	BLEACHING EFFICIENCY (%)
MB Solution	0.1871	0
Un-activated	0.1424	23.89
2.5	0.0929	50.35
5	0.0112	94.01
7.5	0.0072	96.04
10	0.0012	99.36
12.5	0.0620	66.86

XRF data revealed the presence of several elements (see Appedix1). It should be noted that proportions of some base metals are abnormally high for unknown reasons. However it could possibly be a result of non-uniformity in the composition of the sample. Data from Geological Survey of Zambia on a similar sample gives lower proportions of base metals as shown in Appendix 2. Values of some toxic elements are within safe limits. For example, Se (4 ppm) and Pb (57ppm).

B) pH data

pH values of clay-acid solutions after leaching are shown in Table II. Also shown in Table II are pH values of the filtrate solutions after washing with excess water for various acid fractions. The adjustment of pH to a constant value, approximately, was necessary to eliminate its effect on bleaching mechanisms [12].

C) Bleaching Efficiency Results

UV absorption data for MB dye solutions treated with treated clay samples activated at various acid additions is shown in Table III and graphically depicted in Fig. 6. The data includes the absorbance of untreated dye solution.

It is evident from the results that samples activated with acid exhibited higher values of bleaching efficiency. The enhanced bleaching efficiency is attributed to structural modifications of the activated clay, such as an increase in

surface area, as observed elsewhere [5], [6], [7]. It could also be attributed to chemical modifications resulting from cation exchange processes. Bleaching efficiency data exhibited an optimum. In the present study the maximum value of efficiency was obtained at 10% acid treatment. The decrease in bleaching efficiency at acid levels above the optimum could be attributed to the collapse of pores (or reduced surface area) as explained by Ajemba and Onukwuli [5].

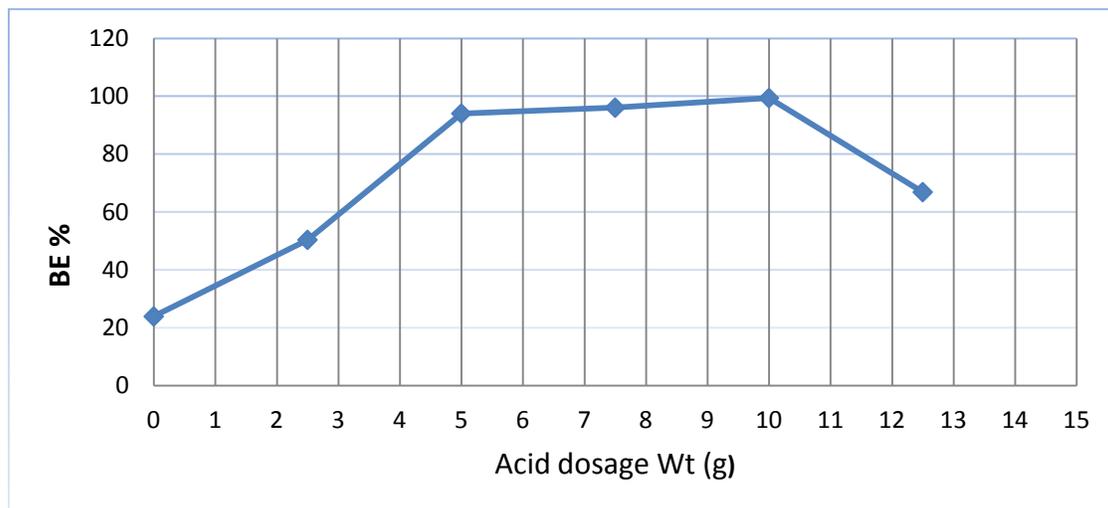


Fig. 4: plot of BE% against Acid dosage

An interesting feature about the optimum value of bleaching efficiency is that it has been obtained at different acid additions by different workers even when acid fractions are relatively high. For example, Muyembe [2] and Siwila [3] attained optimum values at relatively higher acid fractions using a methylene blue dye. Ajemba and Onukwuli [5] obtained an optimum at 4M concentrations, bleaching palm oil. Mohammed et al. [7] obtained an optimum value at 20% acid addition using edible oil and transformer oil as absorbing media. The apparent optimum value of bleaching efficiency obtained could be a result of other factors other than the proportion of acid added. For example, adsorbent particle size and distribution could have an effect. And adsorbent dose, contact time, pH and the concentration of the absorbing media have been demonstrated to have an effect [12].

The above observations suggest that data on bleaching efficiency should be interpreted with caution. However, from an economic point of view the results of the present study are significant as they have been obtained at comparatively lower values of acid additions. The results of the present study are also important as they demonstrate the potential use of the Kaoma clay deposit in the processing of edible oils. However the bleaching efficiency results need to be investigated further and optimized using crude vegetable oils as absorbing medium.

IV. CONCLUSIONS

Bentonitic clay from Kaoma District of Zambia has been chemically analyzed and acid activated. A bleaching efficiency of up to 99% has been achieved. Efficiency data exhibited an optimum consistent with results of similar studies elsewhere. Further work is required to demonstrate the bleaching efficiency of the activated clay in bleaching crude vegetable oils in an industrial setting. And the work could be extended to other bentonitic clays such as the deposits in the Luano Valley in the country.

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APPENDIX 1: Chemical Composition of Kaoma Clay Obtained With A Portable Olympus Xrf Analyser

ELEMENT	COMPOSITION (ppm) +/-		ELEMENT	COMPOSITION (ppm) +/-	
Mo	338	40.18	Ca	8.48%	0.2222%
Fe	13.94%	0.4040%	Cl	2.47%	0.2584%
Th	145	13.83	K	1979	216.47
U	26	6.17	Mo	66	4,06
Cu	13.58%	0.3446%	P	653	77.17
Co	4864	145.76	Rb	19	2.94
Sr	29	3.01	S	9494	426.96
Zn	932	62.63	Se	4	0.57
Zr	54	4.72	A!	1.14%	0.3266%
Pb	57	9.72	Mg	10.09%	2.14305
LE	44.91%	1.159C%	Si	1.51%	0.12915
AU	175	10.33	Y	12	3.37

APPENDIX 2: Chemical Composition Of Kaoma Clay Sample

ELEMENT	COMPOSITION %
Fe	153.
Co	0.03
Cu	0.54
V	0.114
Al	2.91
Pt	18 (ppm)
K	1.82
Ca	1.42

COURTESY OF THE GEOLOGICAL SURVEY OF ZAMBIA, 2015