Bulletin of Pure and Applied Sciences.
Vol.33C-Chemistry (No.1-2);2014:P.27-42
www.bpas.in
DOI 10.5958/2320-320X.2014.00004.1

RECYCLING CLAYS USED IN BLEACHING VEGETABLE OILS

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Received on 30 March 2014: Accepted on 24 October 2014

ABSTRACT

The efficiency of recycled clays to bleach oils measured by decrease in absorbance of bleached oils was largest when recycled clays had been calcined at 450^{o}C and leached in boiling mixture of 20% acid strength for 16 hours. The Langmuir constant a varied from $0.4x10^{-2}$ to $16\ x10^{-2}$ and b increased from $4.7x10^{-2}$ to $95.38x10^{-2}$. The Freundlich constant n increased from $8x10^{-3}$ to $33x10^{-3}$ and k from $3.9x10^{-2}$ to $11.8\ x10^{-2}$ as concentration of acid increased. The enthalpy of adsorption increased from $-6.7x10^{-2}$ to $22.2x10^{-2}$ kJmol^{-1}.

Keywords: Recycling, Vegetable oils, Calcined, Bleaching, Clay, Absorbance.

INTRODUCTION

Spent bleaching earths are by-products of vegetable oil refining industries. The refining process of salad oils uses many tones of bleaching earths and spent bleaching earths are commonly disposed off at landfills. Landfills disposal of spent bleaching clays is an environment hazard; oils catch fire and percolate into the underground waters. As early as the middle of the 20th century, recovery of oils in spent bleaching earths had started (Feunge, 1951; Hamza, 1966). The scientists recovered and used the earths to bleach (Aoki, 1972; Kheoh, 1987; Kokama, 1980; Ong, 1983; Pushpinde., 1981; Sakakura, 1980). Spent clay in bleaching earths were reported to have been used to decolourise vegetable oils (Boukerroui, 2009).

The production of bleaching earth from bentonites comprises the reaction with acids at the boiling temperature, washing with water, drying and milling. During the acid attack, interlayer cations are replaced by protons and the octahedral cations, (Al^{3+}, Mg^{2+}, Fe^{3+}, Fe^{2+}) are dissolved (Fahn 1973; Beneke and Lagaly, 2002; Didi et al, 2009). This has to be repeated when recycling the clays for bleaching of vegetable oils.

The studies on the use and disposal of by-products and spent material from the vegetable oil processing in the U.S. was reported (Svensson, 1976; Watson, 1976). Attempts to regenerate spent bleaching clays (Boukerroui, 2009; Bahl, 1977) and recover oils from the earths (Penninger, 1979) was studied with water at elevated temperature and pressure (Ong, 1983). The regeneration of spent earth by wet oxidation was carried out by a number of authors (Kalam, 1988; Waldmann, 1991). Spent bleaching earth from the edible oil industry was converted to clay-carbon adsorbent for re-use in the adsorptive cleansing of vegetable oils (Boukerroui, 2009, Pollard, 1993)

Regeneration of spent bleaching clay by heat treatment (Shu-Chen, 2000) in a gas stream was performed thermo-gravimetrically and used to bleach oils. The effects of processing parameters such as atmosphere, temperature, time, airflow rate, and amount of clay on the regeneration efficiency have been investigated (Shu-Chen and Jung-Sung, 2000).

The spent bleaching clay from palm oil refinery (Nur and Waft, 2006; Pollard, 1993) may be recycled rather than disposing in landfill. The oil extracted from spent bleaching clay from palm oil refinery and spent bleaching clay from palm kernel oil refinery was found to be inferior as compared to crude oil as it contained higher quantities of contaminants (Nur and Waft, 2006). The specific surface area, total pore volume and average pore size of spent bleaching clay calcined at 500°C was highest and gave better bleaching efficiency than the clay calcined at 400 and 800°C (Nur, 2006; Shu-Chen, 2000; Pollard, 1993).

Kinetics of heat regeneration of spent bleaching clay (Li-Hwa, 2000) has been reported and the heat of regeneration of spent bleaching clay was conducted in a box furnace with air flowing through it.

Regeneration of spent bleaching earth (Abukalam, 1988) and its reuse in the refining of edible oil (Boukerroui, 2009) was shown to reach optimal value under controlled conditions. Removal of oil from spent earths opens the opportunity to use the spent clays in making building materials and special adsorbents.

In Uganda, spent bleaching earth is not used in any manufacturing, so its discard pauses problems for the environment as tons of oil laden spent clays are laid in landfills. The percentage of activated bleaching earth used for oil bleaching ranges from 1 to 2 % of the oil weight (Girgis, 2005). If discarded deactivated bleaching earth can be reused (after reactivation) for oil bleaching, it will reduce the amount of activated bleaching earth and it will also reduce production cost of oils at millions dollars per year. The objective of this study has been to find out the bleaching effects of recycling clays.

METHODOLOGY

Table 1: Impurity adsorbed, x, and relative impurity, Xe, in sunflower and cotton oils bleached with recycled Chelel earths.

	10% acid leached		20% acid leached		10% leach		20% leach	
Temp/°C	Xe	Xe(x/m)	Xe	Xe/(x/m)	Xe	Xe(x/m)	Xe	Xe/(x/m)
40	0.9446	17.0505	0.8517	5.743	0.99852	674.68	0.99231	129.039
50	0.9423	16.331	0.8504	5.6845	0.99793	482.09	0.99054	104.708
60	0.9407	15.89	0.849	5.6225	0.99704	336.838	0.98966	95.711
70	0.9381	15.155	0.8397	5.2383	0.99616	259.417	0.98847	85.745
80	0.935	14.3846	0.8316	4.9382	0.99566	224.551	0.98612	70.995
90	0.9342	14.1976	0.82345	4.665	0.99439	177.253	0.98079	51.056
nflower oil					Cotton oil			

Calcination of the spent clay

De-oiled spent clay (200g) was placed in a furnace operated at the temperatures ranging from 450-500°C for two hours (Puskar and Ridge, 1974; Al-Zaharani and Alhamed, 1996; Foletto et al, 2002).

Leaching of clays

Calcined recycling clay (100g) was mixed with acid (500mL) of appropriate concentrations (10, 20% v/v) in a flask. The mixture was heated at 105°C for 16 hours; then cooled and filtered. The residue was washed to neutrality with distilled water; then dried at 105°C in the thermo-stated oven.

The dried leached powders were labeled and stored for future use. The production of bleaching earth from bentonites comprises the reaction with acids at the boiling temperature, washing with water, drying and milling.

Degumming of vegetable oils

Crude oil (100g) was placed in a flask, 85% phosphoric acid (1g) was added, the mixture heated at 90^{o}C while stirring at 900 revolutions per minute for 10 minutes under nitrogen blanket. The oil was filtered under nitrogen. This method was reported by Car (1978) and modified by Saachia (1992).

Bleaching oils with recycled clay

The mixture of degummed neutralised oil (200g) was mixed with acid-leached spent bleaching clays (5g) was at various temperatures of 40, 50, 60, 70, 80 and 90^{o}C for two hours under nitrogen blanket (Al-Zaharani and Alhamed, 1996, Patterson, 1992). The mixture was then filtered, cooled and the bleached oil was tested for clarity by its absorbance at 550nm. The experiment was repeated to get comparable results.

Absorbance of bleached oils

The transmittance of bleached oil was determined using ultra violet – visible spectrophotometer, Shimadzu, 1201. The transmittance of the bleached oils at 550 nm was determined for each oil sample obtained at the different temperatures of activation (Krammer et al, 1963). The method was repeated to obtain comparing results.

RESULTS AND DISCUSSION

Recycling bleaching clay was done after its reactivation for the bleaching of sunflower and cotton oils. Bleaching is recognised as one of the most important steps in edible oil processing (Michael et al, 1992, Mag, 1990). Oils for human consumption are bleached with production of spent bleaching earth, an environment hazard. Bleaching is used daily in refining practices and aims not only at the removal of colouring bodies, pigments, pesticide residues etc., but also at the removal of residual amounts of phospholipids, mucilage, oxidized tri- or partial acyl-glycerols, metal traces in ionisable and non-ionisable (complexed) forms, and soap traces which survived the washing of the neutralised oil (Topallar, 1998; Kalam and Joshi, 1988; Young, 1987, Brimberg, 1982). On the other hand, many other processes for the regeneration of bleaching earth have been patented (Kalam and Joshi, 1988).

Spent clay from the this research was recycled through an extraction process using organic solvents for removal of residual oil, followed by reactivation through heat treatment, referred to as calcining at temperature of 450^{o}C in a furnace, followed by acid leaching for 16 hours. The regenerated clay was used to bleach cotton and sunflower oils separately. The absorbance of bleached oils decreased as temperature and concentration of acid used in leaching medium increased. The absorbance of bleached oils was used to calculate relative absorbance and equilibrium residual concentrations of impurities in bleached oils given in Table 1. The data shows that the clays regained bleaching capacity. The fact that absorbance of cotton and sunflower seed oils decreased on bleaching with

recycled spent earths indicates that the reactivated earths removed impurities from the oils. The results in part confirm what was obtained and published when discarded bleaching earths from the oil industries in Egypt were reused (Girgis, 2005).

It was found that the degree of regeneration of spent earth reduced according to the number of cycles (Kalam and Joshi, 1998). The regeneration of bleaching activity was more pronounced when the recycled clays had been activated for 16 hours with intermittent cooling to room temperature. This perhaps enabled more adsorptive sites to be created in clay matrices as impurities volatilized from the clay matrix.

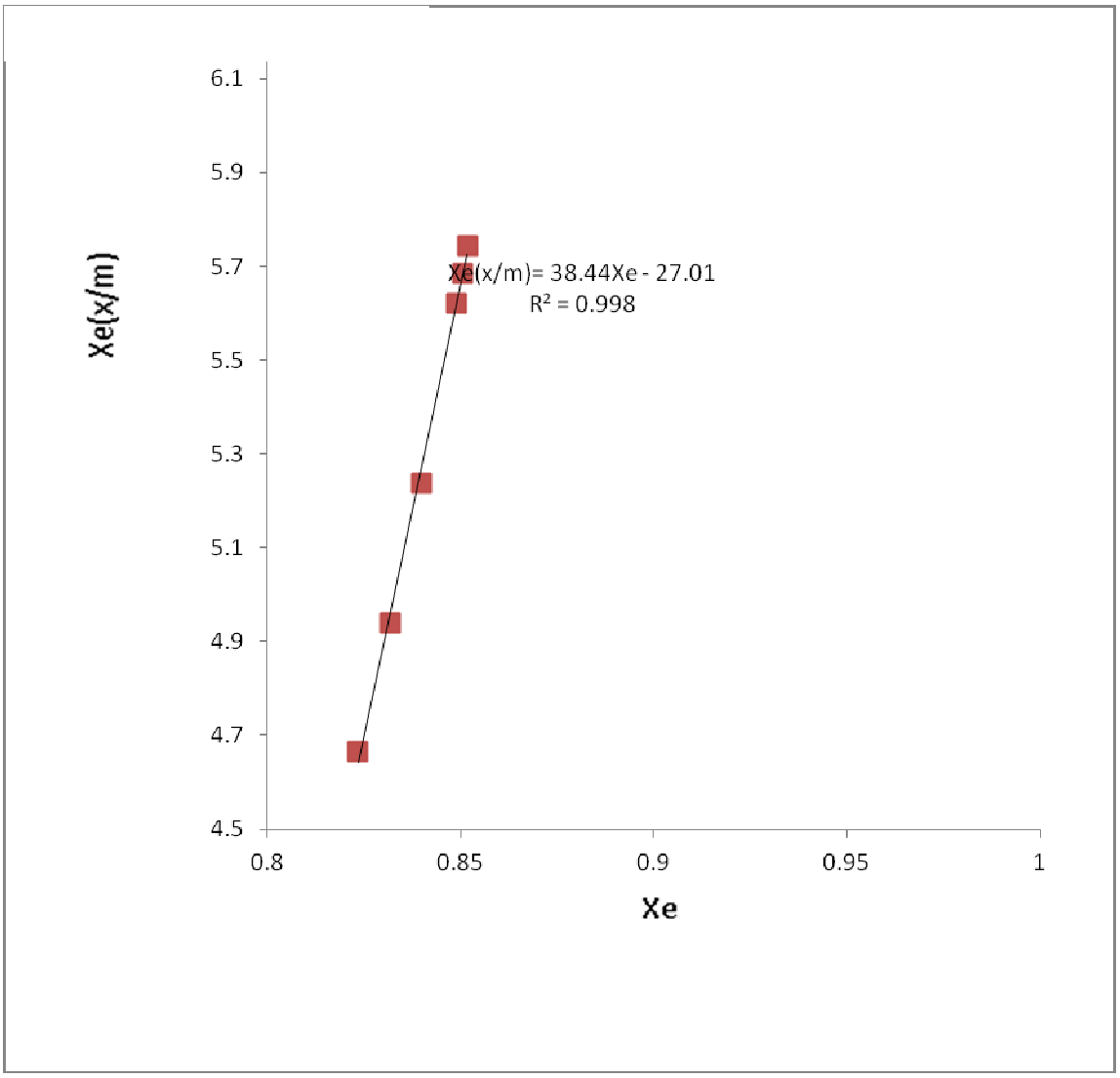

Figure 1: Langmuir isotherms for impurities in sunflower oils on recycled Chelel clays

The data in Table 1 shows decrease in relative residual impurity concentration, Xe and amount adsorbed, x. These data indicate that recycled clays were effective at binding

the impurities in oils but their capacity to bleach was not prolonged. The data in Table 1 was plotted to give the Langmuir adsorption isotherms in Figures 1 and 2. Data in Table 3 was obtained by computing the logarithm of relative residual impurity concentration, logXe and logarithm of product of ratio impurity adsorbed to mass of clay used which is referred to as Freundlich data.

As shown in Figures 1 and 2 consists of lines of high linearity, it indicated that recycled clays were effective at binding impurities in both cotton and sunflower seed oils.

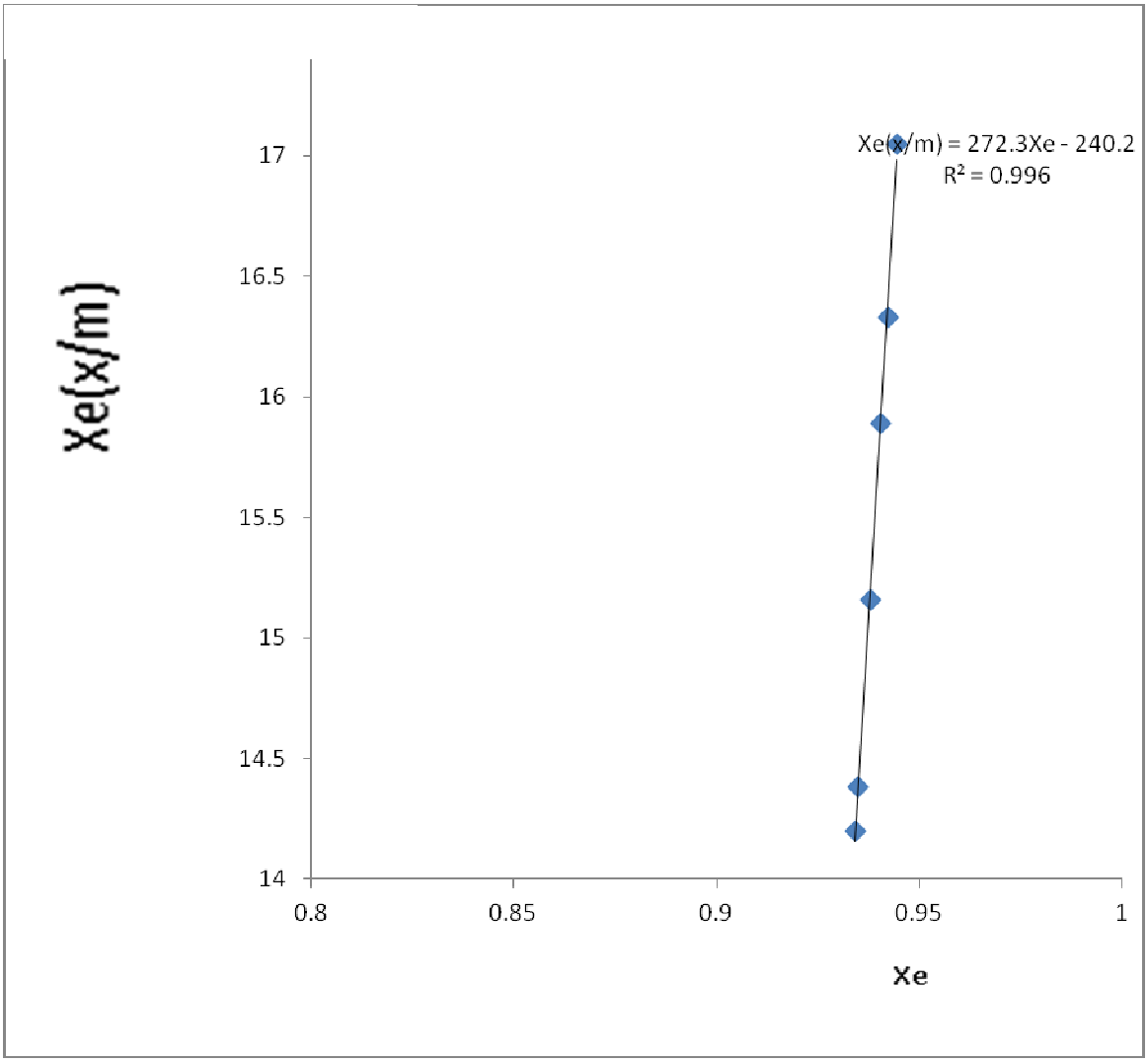

Figure 2: Langmuir isotherms for impurities in sunflower oils on recycled Kajansi clays leached in 20% acid.

Table 2: Langmuir constants for regenerated spent bleaching clay

Oil		10% acid-leached	20% acid-leached
Cotton$X10^{-4}$	a	1.6	0.87
Cotton	b	0.097	9.938
Sunflower	a	0.026	0.004
Sunflower	b	0.703	1.134

Straight line graphs were obtained in Figures 1 and 2 showing spent clays adsorbed impurities to monolayer capacity in nearly the same way as freshly activated clay. The linearity of Langmuir isotherms varied from R^2 value of 0.866$\pm$ 0.049 to 0.915 $\pm$ 0.049 (n=3) for recycled clays used to bleach cotton seed oils yet for sunflower seed oils bleached with regenerated clays it ranged from 0.996$\pm$0.002 to 0.990$\pm$0.002. The linearity of Langmuir isotherms is a function of impurity concentration, availability of surface adsorption sites and interactions between the adsorbed impurities and impurities still remain unadsorbed in the oil being bleached (Hundal 1988). As long as the clay material did not easily reach saturation with the adsorbed impurities, the Langmuir isotherms obtained were highly linear. The degree of linearity reduced as the saturation point for the clay was approached. It were clay matrices with less surface sites at which impurities could adsorb that easily deviated from linearity of Langmuir isotherms. Similarly, recycling clays whose surface sites had non uniform enthalpies of adsorption also failed to show Langmuir isotherm linearity as the sites were competing for the impurities in the oils being bleached (Fried and Shapiro, 1956; Travis and Etnier, 1981).

A comparison of Langmuir isotherms in studying adsorption characteristics of soils and was found to be useful in a limited adsorbate concentration range where sorption maximum is likely to be reached (Vandenbruwane et al, 2007). It was found that once the sorption maximum is exceeded deviations from linearity occur in much the same way (Kothawala et al, 2008). The deviation of the Langmuir isotherms from linearity is attributed to existence of surface sites having multiplicity of adsorption free energies (Srinivasan and Fogler, 1990). So recycling clays obeyed Langmuir principles when bleaching the oils. This has been used as evidence showing that once recycled clay was calcined and acid-leached, it can ably bleached sunflower and cotton seed oils in much the same way as freshly mined would if calcined and acid activated.

The slopes and vertical intercepts of graphs on Figures 1 and 2, were used to calculate the Langmuir constants a and b were tabulated in Table 2.

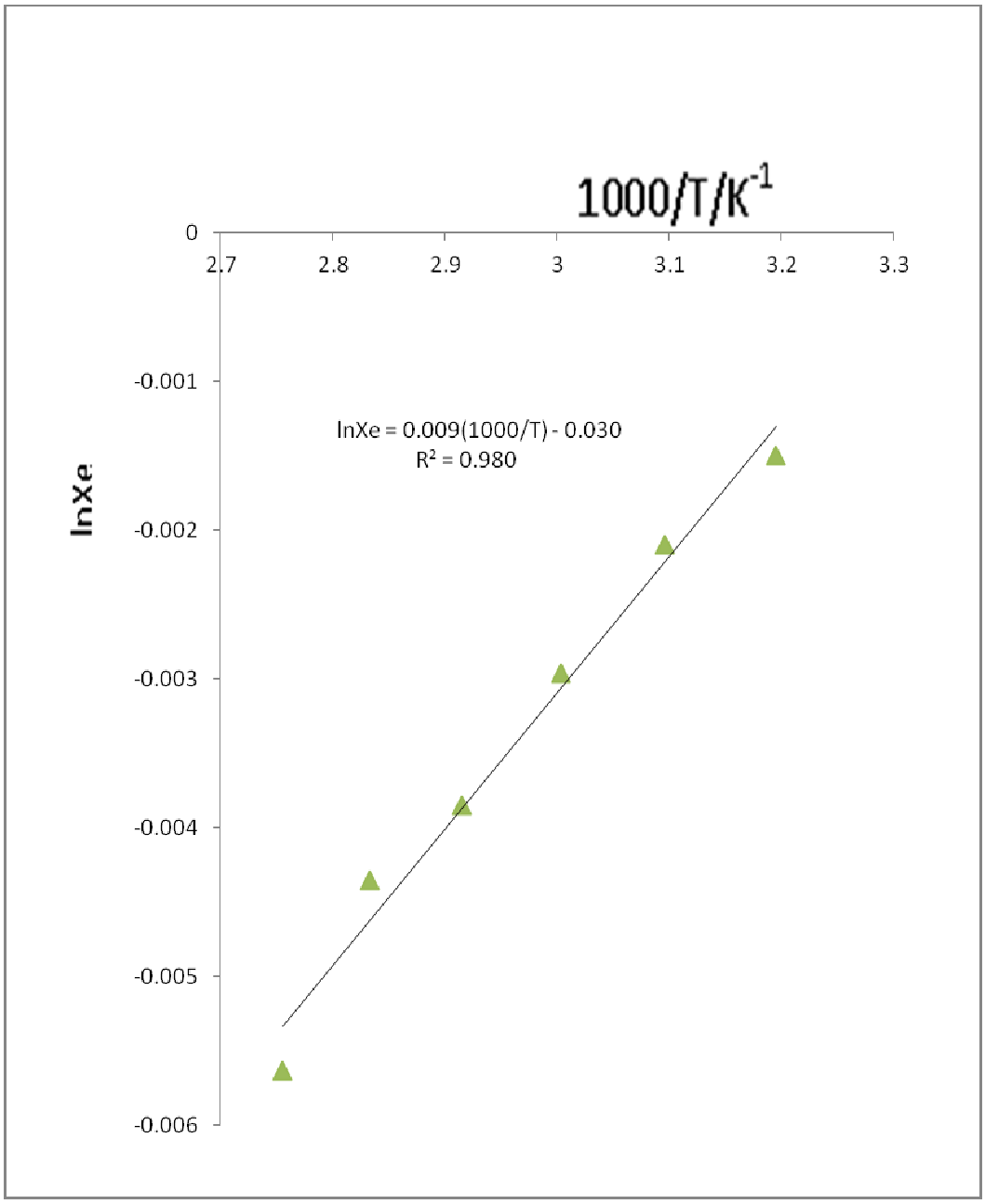

Figure 3a: Freundlich isotherm for impurities in cotton oils on recycled Chelel clay leached in 10% acid

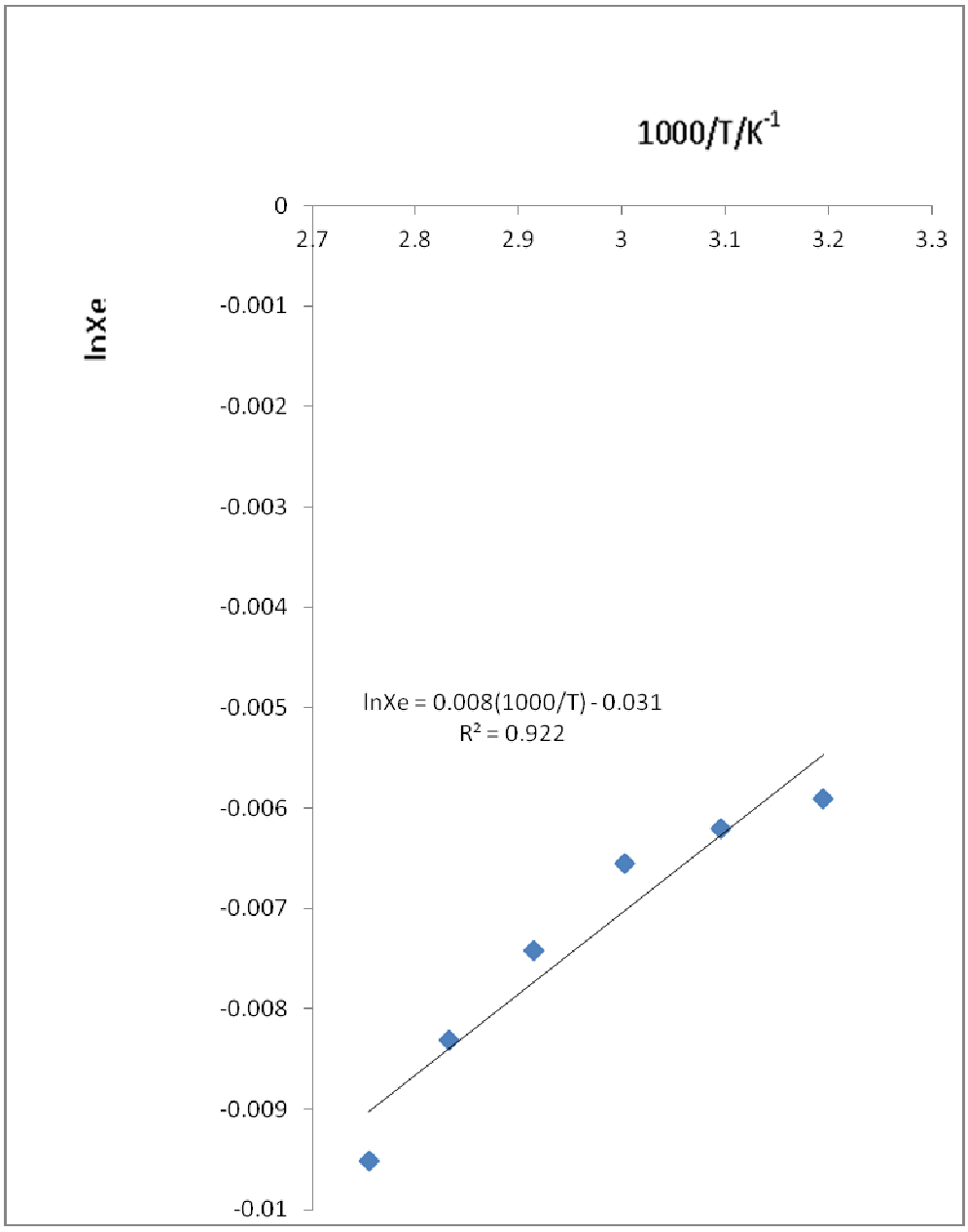

Figure 3b: Freundlich isotherm for impurities in sunflower oils on recycled Chelel clay leached in 10% acid.

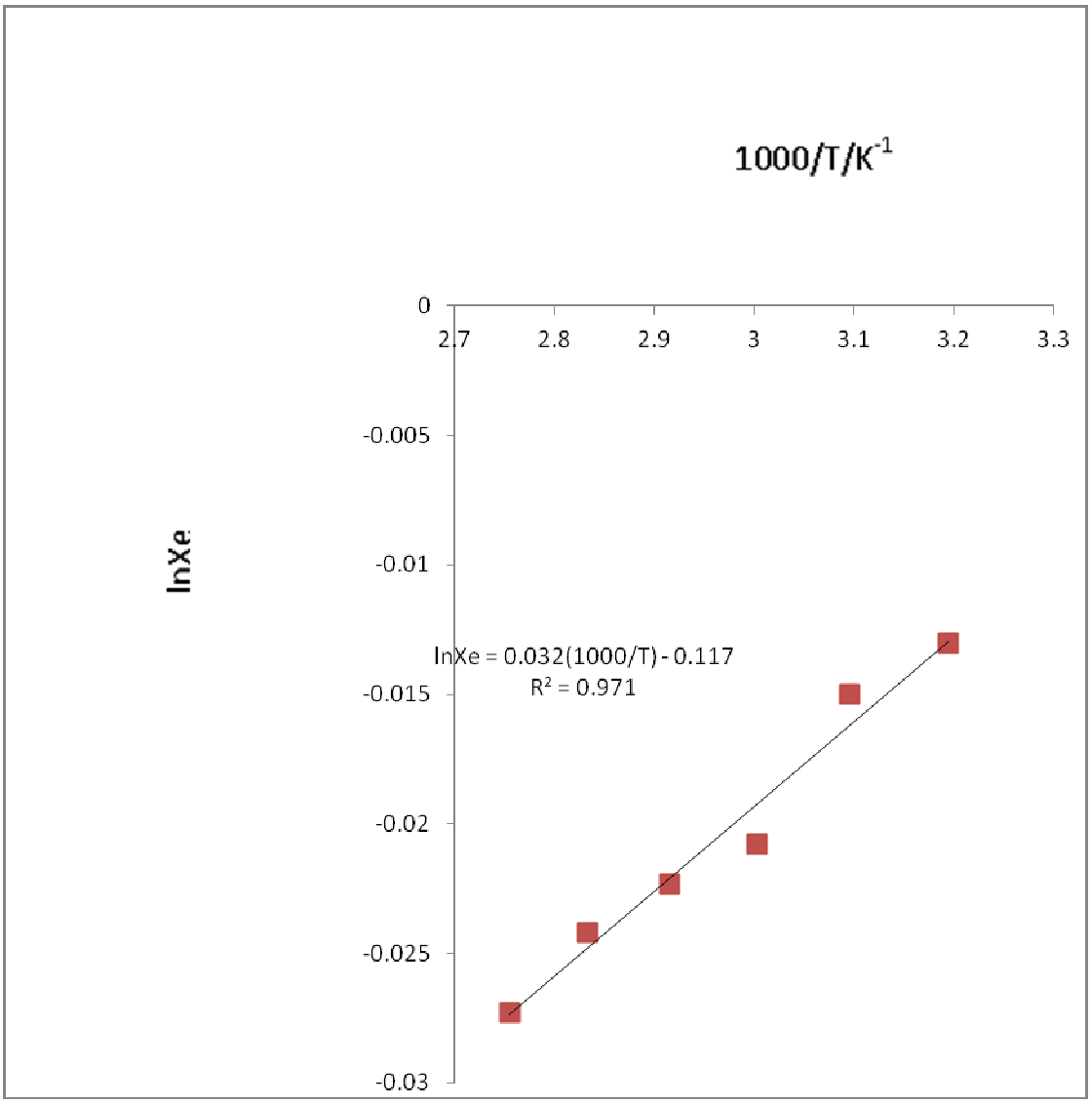

Figure 3c: Freundlich isotherm for impurities in sunflower oils on recycled Chelel clay leachedin 20% acid

Table 3: Freundlich data on recycled Chelel clays

1000/T/K^{-1}	**In Xe for 10% leach**	**In Xe for 20% leach**	**In Xe for 10% leach**	**In Xe for 20% leach**
3.195	-0.006	-0.013	-0.002	-0.008
3.096	-0.006	-0.015	-0.002	-0.010
3.003	-0.007	-0.021	-0.003	-0.010
2.915	-0.007	-0.022	-0.004	-0.012
2.833	-0.008	-0.024	-0.004	-0.014
2.755	-0.010	-0.027	-0.006	-0.019
	sunflower	Oil	Cotton	Oil

The Freundlich data in Table 3 was plotted to give Figures 3a, 3b and 3c which are highly linear.

The linearity that has been observed (represented by Figure 3a) while bleaching cotton seed oil with recycling clays has R^2 values ranging from $0.863^{\pm}0.117$ to 0.980 ± 0.117 yet the linearity of Freundlich isotherms for bleaching sunflower seed oil (represented by Figures 3b and 3c) varied from 0.922 ± 0.049 to $0.971\ \pm0.049$. The linearity of the isotherms dictated that monolayer adsorption of impurities occurred even when recycled clays were tested. So the clays studied can be used to exhaustion and be recycled if calcined and leached with acid. This reveals that the acidity of recycling clays was not strong, so their capacity to bind coloured impurities was poor as they would easily become saturated with impurities and deviate from linearity of the Freundlich isotherms (Nodvin et al, 1986). The linearity of Freundlich adsorption isotherms developed using recycling earths showed R^2 value ranging from 0.863 ± 0.117 to 0.980 ± 0.117 showing that recycling clay materials obeyed Freundlich isotherms reasonably. These clays had no limitations resulting from overcrowding, steric interference, thermodynamic instability at high impurity concentrations (Hundal, 1988). The strongly adsorbing recycled clays have been better described by the Freundlich isotherms within lower concentration ranges (Kothawala et al, 2008). As Freundlich adsorption isotherms assume monolayer adsorption capacity complications arise when clays and clays minerals exhibit multi-layer adsorption tendencies and this causes deviation from linearity of the isotherms plotted. Recycled clays showed poorer adsorption capacities for impurities in cotton oil than for impurities in sunflower oils as their isotherms deviated from linearity more strongly than sunflower oils. The clays easily got saturated with impurities from oils leading to steric interactions between the adsorbed and unadsorbed impurities as cotton oil was more intensely coloured than

sunflower oils (Nodvin et al, 1986). The Freundlich constants n and k in Table 4 were calculated using Figures 3a, 3b and 3c.

Table 4: Freundlich constants for regenerated spent bleaching clays

Oil		10% acid-leached	20% acid-leached
Cotton	n	0.009	0.023
Cotton	k	0.031	0.081
Sunflower	n	0.008	0.033
Sunflower	k	0.031	0.118

In experiments involving recovery of spent clay using solvent extraction, various solvents were used to extract the impurities. The solvents used included methanol, ethanol, isohexane, butanone, propanone and petroleum ether. The solvents used showed the following order in the efficiency of oil extraction: butanone > propanone > petroleum ether = isohexane > ethanol > methanol. Results have shown that extraction process, using just a solvent, is insufficient to recover the bleaching power of the spent clay, needing then a further high temperature treatment. The bleaching power of the regenerated clay is dependent of temperature and duration of thermal activation. The regenerated clay samples presented a similar bleaching efficiency for sunflower-seed oils to freshly prepared acid-leached clays probably due to less intensely coloured impurities in the oil.

It was found that recycling spent bleaching earth can be carried out effectively after high temperature treatment for hours. Mere de-oiling of spent bleaching earths does not revitalize prolonged bleaching activity because impurities chemically react and block the active centres for the adsorption of impurities. Calcining burns away the impurities creating vacancies for the adsorption process (Wafti and Nur, 2006; Boukerroui and Ouali 2009; Shu-Chen, 2000).

Spent bleaching clay produced by direct heat treatment produced higher regeneration efficiency than the de-oiled spent bleaching clay, produced by solvent extraction and heat treatment. The data available showed that the heat treated spent earths at 500°C possessed the highest specific surface area and total pore volume due to sintering (Wafti and Nur 2006) and gives better bleaching efficiency than that calcined at 400°C.

The values of enthalpy of adsorption (shown in Table 5) for colour impurities on the regenerated spent clays studied increased with increase in mass percent of acid used to leach the clay because acid activation creates sites for the adsorption of impurities. And the number of sites created per unit mass of the clay increases with increase in concentration of acid used. The values of enthalpy of adsorption are lower than 20kJmol^{-1} because the forces of adsorption are weak van der Waal's forces (Rich, 1993; Li-Hwa, 2000). To volatilise the impurities, the recycling clays are heated and this should be followed with acid-leaching to remove any octahedral metal ions that could have replaced the hydrogen ions during the previous bleaching process.

As Freundlich and Langmuir isotherms for impurities removed using recycling clays, showed highly linear plots, it can be deduced that the recycling clays once calcined and acid-leached, effectively bind the impurities in vegetable oils on themselves. Thus showing that bleaching activity can be rejuvenated. This implies that once the structure of the clay has been ruined by acid-leaching, it does not undergo further structural deformation on being used to bleach oils. The removal of impurities present in the recycling clays requires temperatures as high as 450^{o}C .

Table 5: The enthalpy of adsorption of colour impurities on regenerated spent bleaching clays

Acid concentration/%	**Enthalpy of adsorption**	**/ΔHa/kJ/mol^{-1}**
	Cotton oil	Sunflower oil
10	-0.076	-0.067
20	-0.194	-0.272

The fact that recycled clays showed Langmuir and Freundlich isotherms revealed that recycling spent bleaching earths in this study is in agreement with data produced by Adel (2005) in which he found reactivated bleaching earth was suitable for the bleaching of sunflower, soybean and corn oils and gave similar results when compared to those obtained from virgin activated bleaching earth, which produced great colour reduction. So reuse of spent bleaching earths can be carried out in Ugandan oils industries to reduce on importation of clays.

The results acquired on recycling clays used to bleach cotton-seed and sunflower-seed oils showed decrease in absorbance of bleached oil indicating that recycling worked well.

CONCLUSION

By measuring absorbance of oils bleached with recycled clays, it can be suggested that it is possible to recycle bleaching clays especially if the clay is calcined at temperature above 450^{o}C and the leached with acid of concentration above 10%. More effective bleaching occurred with clays leached in 20% acid than 10%.

De-oiled spent clay calcined at 450^{o}C, leached in boiling acid mixture of concentration between 10-20% for 16 hours bleached cotton and sunflower oils. The decrease in absorbance bleached oils followed both Langmuir and Freundlich principles resulting in highly linear isotherms. The Langmuir and Freundlich constants as well as enthalpy of adsorption obtained in recycling experiments were low indicating physical adsorption occurred.

Recommendation

The results produced in this research need to be tested in industrial settings.

ACKNOWLEDGEMENT

We thank Mr. Edward Ssekubunga for heating the clay samples studied in the furnace, Mr. Moses Nkolongo for availing us chance to use the spectrophotometers in the analytical laboratories.

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