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Adding Value to Animal Bone Marrow Byproduct via Adsorption onto Modified Local Bentonite.

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ABSTRACT

The present work aims to add value to animal bone marrow byproduct and explore the ability of its utilization in chemical industries as a starting material. Contaminants keep the possibility of it's using in the various chemical industries is so limited. Low- cost local bentonite clay has been chemically evaluated and activated to use as a marrow bleaching agent and pollutant removal. The bleaching power of the activated samples has been spectrophotometrically evaluated in the visible region and the physio-chemical properties enhancement of the marrow has been evaluated. The results show that the bleaching efficiency depends on bentonite dose and sulfuric acid concentration. The highest bleaching capacity was achieved with the bentonite sample of 35 % acid concentration, and 3% bentonite dose (based on the weight of fatty matter), at 95°C and 4 hrs stirring time. The activated clay could attain bone marrow bleaching and the properties of the marrow were better than before. The bleaching efficiency seems to be closer to a virgin commercial bleaching agent. In addition to the significant odor and color enhancement, the chemical evolution of the purified marrow proved that it has an industrial potential impact and its further use and benefit have been maximized.
Keywords: Acid activation – Bentonite - Bleaching clay – Bone marrow – By product

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INTRODUCTION

Bleaching is a critical step of bio-based byproducts treatment, particularly of oils and fats. The color and the odors have a significant effect on the utilization of the fats into the different industrial application **[1]**. Phospholipids, soap, trace metals, and carotenoids are the most undesirable pollutants that are contaminated into the bio-based byproducts. The fatty matter properties and its further utilization are strongly affected by the ratio of these pollutants. Bleaching clays are important common adsorbents for the process of impurity removal as well as the bleaching and decolorization **[2].** Hydrated aluminum silicates which are the main content of the clays are the basic material of bleaching clay. The smectite a 2:1 clay mineral contains an octahedral sheet between two tetrahedral sheets. The smectite crystals are negatively charged due to the substitution of the trivalent aluminum ions with bivalent ions like Mg^{2+} and Fe^{2+} and substitution of tetrahedral Si^{4+} by Al^{3+} **[3]**. Adsorption, bleaching, and catalytic activity are the properties of bentonite that make it an industrial material for wider applications. According to Foletto, Bentonite clays with high montmorillonite content are the main adsorbent earth used for bleaching of the oils or fats **[4]**. Acid activation increases the surface area and enhances the adsorption properties of the clay. Therefore, the activated bentonite tends to absorb water in the interlayer sites. According to Hymore, strongly protonated clay mineral can be obtained through a series of chemical reactions that involves the acid activation process **[5] .** The bentonite structure is partially destroyed under the effect of acid and the protons replace cations between the layers of the montmorillonite crystal **[6].** The bleaching process does not only remove coloring materials but also removes traces of metals, phospholipids, soaps and decomposed oxidation products such as peroxides **[7]** . The maximum bleaching point is not basically achieved with the activated bentonite having a high specific surface area. It is strongly dependent on the raw bentonite composition and the kind of oil to be bleached. The United States of America is considered the major producer in the world for bentonite. Its annual production is estimated to be $4.0 x 10^6$ tons **[8]**. Clay deposits are available in Aswan region, Upper Egypt, near the Nile River. The work aims to investigate the potential of the local bentonite samples as bleaching agent of animal marrow byproduct. Regarding our previous work, animal bone marrow was utilized in the leather industry as a leather lubricant agent without pre-treatment. Therefore, the marrow has considerable iodine and saponification values **[9] .** The acceptable iodine and saponification values are major advantages of the marrow. It is quick to response to chemical treatments such as sulfonation and phosphorylation. However, the predicament is that the further use of the fat is so limited due to its undesirable smell in addition to its pale brown color. Regarding the valuable fatty acids moieties in glycerides of the animal bone marrow (stearic, oleic, linoleic) and its chemical responsibility and the wide use of these fatty acids, the bone marrow seems as wealth for bio-based chemical industries. The research tries to raise the value and the benefit of fat marrow. The search is an attempt to enhance the properties of the side product waste material to be used as raw material for a range of the industrial applications as a bio-source and starting material.

MATERIALS AND METHODS

Local bentonite clay samples were collected from Aswan region, near the Nile River, Egypt. The samples were taken from average depths 4 -5 meters. The animal bone marrow brought from Pachin Company, Cairo, Egypt. The marrow is a byproduct of the animal charcoal factory. The commercial virgin acid-activated bentonite (tonsil) was used as a bleaching reference. Chemicals used for fatty matter analysis were supplied by international companies (Merk, Germany, and BDH, England).

Clay sample pre-treatment

Clay sample was ground using a pestle and mortar, soaked in distilled water, mixed thoroughly and then allowed to stand for two days. The obvious clear layer was siphoned out and the process was repeated for several times to get rid the heavy metals and impurities. The samples were dried at 105°C for 4hrs in a drying oven. The samples were grounded using porcelain mill to pass through a screen of 80µm mesh size. The samples were ready for chemical analysis, physical-chemical characterization and acid activation.

Analyses of the raw bentonite

After physical purification of the sample, the chemical tests were carried out. The bentonite composition and elemental analysis of the sample have been determined through XRF analytical technique **[10]**. The instrument used to achieve the goal was Philips PW 2400 spectrometer. The loss on ignition was determined through heating the samples up to 1000 ◦ C or two hours and the reduction in the mass has been calculated.

Clay sample activation

Acid-activated bentonite samples were prepared with different sulfuric acid concentration (15%, 25%, and 35 %) at acid to bentonite ratio 1: 2. The temperature of the reaction was controlled at 90°C for 4 hrs stirring time. The activated bentonite was washed repeatedly with distilled water. The mass was filtered, dried at 110°C for 8 h and re-ground to 75 µm.

Bleaching of the animal bone marrow

100 g animal bone marrow was fitted into 250 ml flat-bottom rotary evaporator flask. The flask was evacuated to 8.0-8.5 k Pa and preheated to 65-70° C under 240 r. $min.^{-1}$stirring. After that, acid activated clay was added and the flask was evacuated again. The reaction was heated to a constant temperature (96-98°C) with 30 min continuous stirring. The mixture was filtered under suction with double-layer filter paper. Then, the fat samples were ready for further tests **[11] .** The progress of the color development of the bleached fat was evaluated by the spectrophotometer (WFJ525-WUV visible). The bleaching capacity (BC %) was calculated as a percentage using the relation: BC % = $\{(A_0 - A) / A_0\} \times 100$ **[12]** , Where A_0 and A represent the absorbance of neutral and bleached marrow respectively at the maximum absorbance wavelength of the unbleached bone marrow.

Chemical analysis of bone marrow

The chemical properties of the bleached marrow have been identified. Saponification value, acid value, free fatty acids, iodine value, and peroxide value in addition to moisture and volatile substance were measured according to according to the methods established in A.O.C.S (1997) **[13]** .

RESULTS AND DISCUSSION

Chemical composition of raw and activated bentonite

The chemical composition of untreated and acid activated bentonite is shown in the table (1). The data show that the chemical structure of the activated bentonite has been modified. It is observed that there is a steady increase in SiO_2 which is the main component of the clay associated with of the sulfuric acid concentration increase (figure1). At the same time, a notable decrease in Mg, Fe, and Al ratios has been taking place. These results are in a good accordance with that reported by Kirali and lacin **[14]**. Accordingly, the decrease in the amount of cation within the octahedral sheet accompanied by an increase in Si / Al+Fe+Mg ratio confirm that the exchangeable ions (Ca^{+2}, K^+ and Na^+) were removed during the acid treatment leading to the formation of lattice vacancies. However, little of these elements remain in the activated samples. This may be due to the presence of insoluble impurities from non-clay minerals (quartz and calcite) in the acid solution which might be partially dissolved at a higher acid concentration **[15]**. The attack on the lattice structure is accelerated enhancing the ion migration increasing the lattice vacancies. In addition, the structural deformation keeps protons of hydroxyl groups become more delocalized. Then the protons of sulfuric acids can replace all empty spaces left by migrated ions in octahedral centers, as a result the absorptive power is improved **[16].** From the data in the table we can expect that the bleaching ability of activated sample increases with the increase of the acid concentration.

Table 1: Clay chemical composition

Components	Content %			
	Non-activated bentonite	activated bentonite		
		Sulfuric acid concentration		
		15%	25%	35%
SiO_2	63.9	79.3	80	81.5
Al_2O_3	15.8	12.9	11.7	11.2

Fe_2O_3	3.6	1.5	1.4	1.4
MgO	7.9	2.9	2.6	2.5
CaO	3.3	3.1	2.1	2.3
Na_2O	0.2	0.02	0.01	0.01
K_2O	0.5	0.4	0.3	0.3
L.O.I	7.8	6	5.8	5.8
SO_3	Nil	Nil	Nil	Nil

Table 2: Bentonite dose and acid concentration effect in the bleaching efficiency

Bentonite dosage %	Bleaching efficiency %				
	Un treated bentonite	10% acid concentration	20% acid concentration	30% acid concentration	Reference sample (Tonsil earth)
0.5	53.24	59.94	60.54	61.18	67.32
1.0	55.61	61.27	63.76	64.97	69.11
1.5	58.87	62.53	64.24	70.12	71.76
2	61.15	63.97	66.19	71.00	75.11
2.5	68.14	66.96	69.31	74.54	80.12
3	74.12	82.24	82.31	83.80	86.5
3.5	74.94	82.30	82.33	83.85	86.5
4	74.94	82.40	82.51	83.89	86.6

Table 3: animal bone marrow evaluation

Property	**Non-bleached marrow**	**Bleached marrow** (3% bentonite dose- 30%acid activation)
Color	Redish to yellow	White -yellow
Melting point	35 - 40º C	36-40◦ C
Moisture	2.90 %	3.1%
Ash	2.80	2.21
Iodine value mg I_2/g fat	40.00	35.50
Acid value mg KOH/g fat	60.00	69.58
Free fatty acids %	30 %	34.79.79
Saponification value mg KOH/g fat	165	192.00
Unsaponified matters %	4.880	1.22

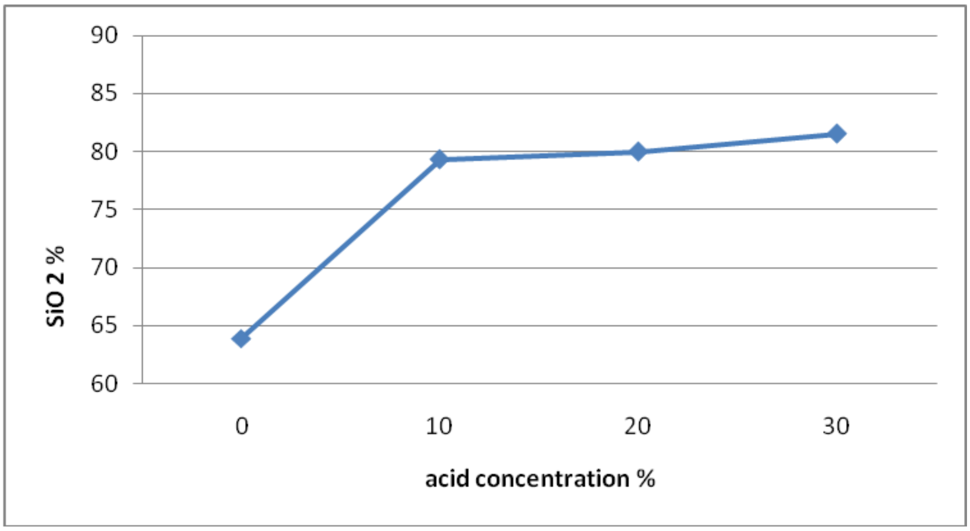

Figure 1: The relation between acid concentration and major component SiO_2 ratio

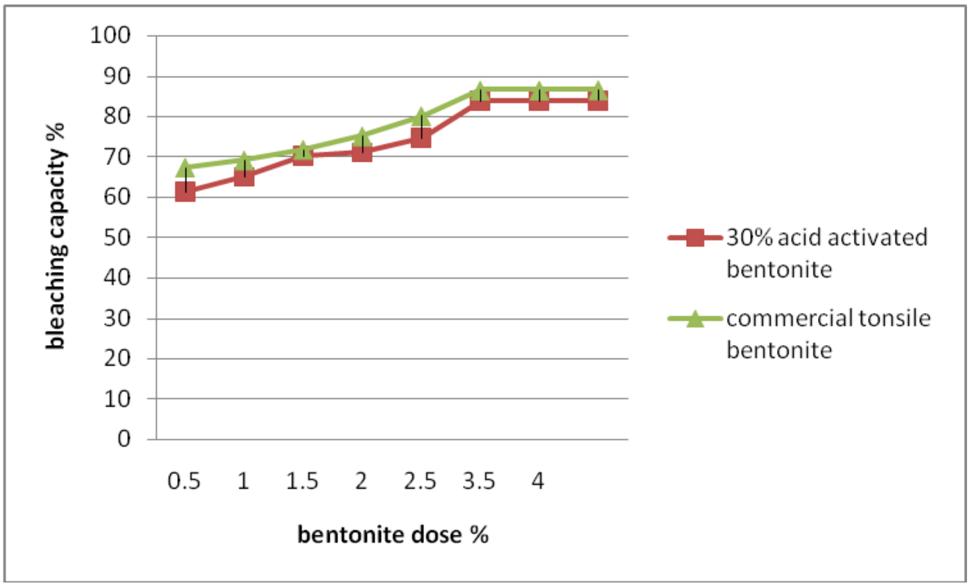

Figure 2: The relation between bentonte dose and bleaching capacity at 30% acid concentration

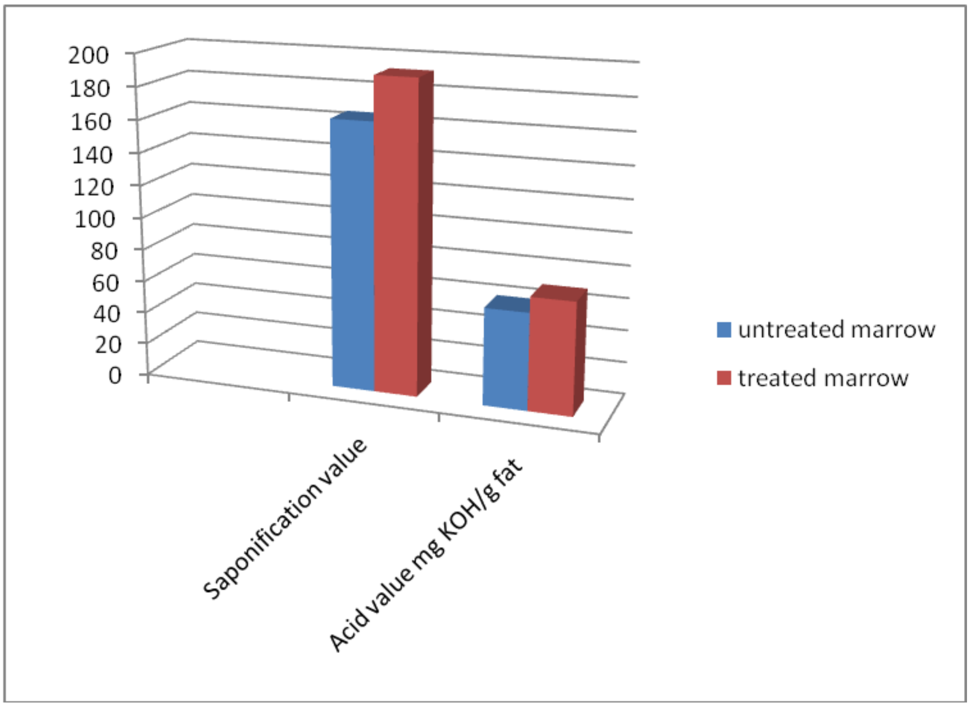

Figure 3: improvements of the saponification value and acid value of treated and untreated marrow

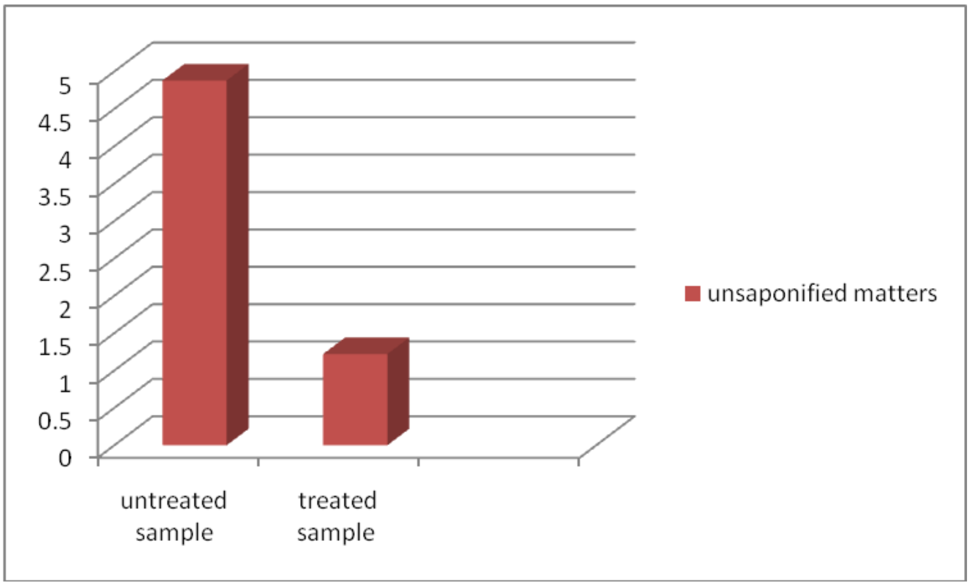

Figure 4: improvements of the unsaponified matters of treated and untreated marrow

Bleaching capacity of raw and activated bentonite for waste animal bone fat

The bleaching capacity versus the bentonite dosages of the different sulfuric acid concentration of activated bentonite samples is illustrated in table (2). The analysis of the data shows that the bleaching capacity was directly affected by the acid concentration and bentonite dose at all acid concentration. The maximum bleaching capacity has been attended at 3 % bentonite dose, no significant effect above this dose. The most effective acid concentration in the bleaching capacity was 35 %. The separation behavior of the octahedral cations accompanying a process of activation is well explaining this result. Moreover, the increase in cation migration allows surface area increase and adsorption capacity enhancement **[17]**. In conclusion, the maximum bleaching efficiency has been attained at 35 % sulfuric acid concentration and 3 % bentonite dose. Figure 2 show the relation between bentonite dose and bleaching efficiency for activated bentonite and the commercial tonsile at the effective acid concentration (35 %). It was obvious that the color removal by the local activated bentonite was seemed to be closer to those obtained with commercial tonsil. The results confirm that the activated bentonite can be used as a low-cost bleaching agent and an alternative to the commercial tonsile with a functional bleaching capacity.

Evaluation of bleached fat

The chemical properties of the untreated and bleached marrow are shown in the table (3). In addition to the clear improvement in the outlook color and odor, a significant increase in saponification value of the marrow, as well as the decrease of unsaponified matters ratio have been observed. This indicates the impurities removal and color material uptake **[18]**. The slight decrease in unsaturation is attributed to the addition reaction saturations on unsaturated centers in the glycerides moieties within fat molecules. The significant increase in the acid value and free fatty acid ratio attributed to partial hydrolysis of some glycerides at an elevated temperature during the bleaching process **[19]**. Figures 3& 4 illustrate the remarkable improvement in saponification value, acid value and unsaponified matters after bleaching process. In general, the results provide clear confirmation constancy to effective impurities and color uptake. So the activated bentonite has an effective bleaching capacity on the bone marrow. So the properties of the byproduct have been clearly enhanced, allowing using them as a starting material in the chemical industry. In addition, an activated bentonite with significant bleaching capacity that closer to the commercial tensile has been developed using local abundant clay.

CONCLUSION

Local activated bentonite clay has been modified through activation process to be utilized as a bleaching agent and pollutant removal for animal bone marrow byproduct. There was a big improvement the physical and chemical properties of the marrow after it was treated with the activated clay. Therefore, the benefits of marrow have been maximized; making its use as a raw material in large-scale in the chemical industries is possible.

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