

Acid Activation and Bleaching Capacity of Some Clays for Decolourizing Used Oils

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Different types of clays found in Iraqi Kurdistan region have been characterized and used as bleaching earth for the decolourization of used lubricating oil. Acid treated and untreated used-lubricating oils were bleached by these clays. The clays were acid activated by mineral acids at various temperatures and time period of activations to optimize the best condition for production of good quality bleaching clay. 2M HCl, 1:15 clay/acid ratio, 800 rpm stirring at 70 °C for 2 h was found to be the optimum conditions. Bleaching experiments were conducted at temperature between 200 and 450 °C for 3 h. Best decolourization results were obtained from Kiffry region clay after acid activation, which was comparable with standard bleaching earth imported from China and Iran. The results were also compared with Standard Fuller's earth. The adsorption isotherms of the bleaching process were studied and Freundlich equation was more applicable than Langmuir equation for the bleaching process of used lubricating oils by the clay samples. The process is physical adsorption by weak bonds between the dark coloured compounds in oil and the clay adsorbent.

Key Words: Bleaching clay, Acid activation, Decolourization.

INTRODUCTION

The processing of used and waste oils has been practiced for many years, with organized recycling of engine lubricating oil from vehicle fleets being well established by the 1930s. The management of used oil is particularly important because of the large quantities generated globally, their potential for direct re-use, reprocessing, reclamation and regeneration and because they may cause detrimental effects on the environment if not properly handled, treated or disposed^{1,2}.

The processes of re-refining of used lubricating oils depend mostly on the nature of the oil base stock and on the nature and amount of contaminants in the lubricant resulting from operations. The contaminants are introduced either from the surrounding air and from the engine, which are called extraneous contaminants, or from the products of oil deterioration. These contaminants must be totally removed in order to reuse the lubricating oil³.

More than 20 processes are used in oil re-refining with variation in the number and the sequence of the processes. Primary treatment of the oil includes settling (separating water and sediments), filtration by coarse filters (to catch undesired objects such as rags) and the dehydration or preflash is carried out (removal of light compounds). Sulfuric acid treatment is to make the oil free from polar compounds like oxidized and

acidic products, residual additives and associated byproducts, particles in suspension⁴.

The removal of undesirable, highly coloured materials of an asphaltic or resinous nature from petroleum fractions performed done by adsorption process, bone char was first used originally for the decolourization of kerosene and finally for heavier oils, but was later displaced by Fuller's earth. The removal of asphaltic or resinous materials from lubricating oil stocks by acid activated bentonite, Fuller's earth and bauxite is still the most important commercial application of adsorption refining⁵.

The peculiar crystalline structure of some clay minerals generates a capacity of reversible exchange with organic or inorganic cations and metal-organic such as in this case of smectites. The exchange of specific cations can generate active centers in the clay minerals, making them good adsorbents, which can be used for adsorption and bleaching of large number of chemical contaminants from used lubricating oils, vegetable oils and of other types (animal, fish oils; waxes)^{6,7}. Bleaching clays in either powder or granular form are used for the refining of petroleum products using two main processes *i.e.*, contact and percolation. In the contact process, the recovered oil, paraffin wax or liquid paraffin is previously treated with sulphuric acid to remove acid tar and after its decantation the bleaching earth is added. In the percolation process, the solvent

to be treated is passed through a tower containing a bed of bleaching clay granules⁸.

Highest possible bleaching efficiency clays is favoured for the decolourization process of oils because: (i) the smaller amounts of the high activity clays needed to produce desired refined oil properties mean that lower inventories can be maintained by the oil refiner; (ii) oil losses are lower because refined oil losses depend somewhat on the amount of clay used and (iii) less spent clay is produced when using high activity clay and hence land-fill disposal costs are lower⁹.

Many attempts have been made to enhance the bleaching capacity of different types of clays in an efficient and economic way. Thermal treatment is used to activate bauxites, palygorskite-sepiolite⁸ and bentonite¹⁰⁻¹² clays. Acid activation of clay minerals has been a subject of many papers. The effect of acid activation was used to affect the physicochemical properties (chemical composition, cation exchange capacity, specific surface area, *etc.*) of bentonites^{13,14} and galuconite¹⁵⁻¹⁷.

A natural kaolinitic clay is metakaolinized at 550 °C and activated separately with H₂SO₄, HNO₃ and HClO₄ of varying concentrations. Silica/alumina molar ratio, surface area and the number of strong acid sites increase when the concentration of acid used for activation increases. Metakaolinite activated with 4M HNO₃ has the highest surface area and surface acidity¹⁸.

The current world production of more than 60 million tons of oils is accompanied by the production of solid spent clay, containing 30-40 % oil, estimated at 600,000 tons worldwide. Recovery of oil and the reuse of spent bleaching clay are the areas where great opportunity exists for cost saving in the oil processing industry.

EXPERIMENTAL

All chemicals were from BDH, MERCK and Fluka of analytical grade; hydrochloric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, EDTA, EBT, silver nitrate, potassium thiocyanate, barium chloride.

The clay samples were taken from different locations of Iraqi Kurdistan region, named Kiffry, Chamchamal and Dokan (Table-1). Clay samples were wet sieved (120 μm) with distilled water, left for 24 h in (1 L cylinder) and the fine particles on the top of the sediment were taken of each clay. The clays were dried at (105 °C) for 48 h, crushed, sieved (230 mesh) and kept in tight closed glass bottles ready to use as unactivated natural local clays.

The first oil sample (dark oil 1) (D.O.1) was taken from (Asia Oil Refinery Company) after a stage of acid treatment. The second oil sample (dark oil 2) (D.O.2) was collected directly from waste oils of automobiles without any pretreatment (Table-2).

Clay chemical composition: Chemical composition of the clays were analyzed by two different methods: (1) X-ray fluorescence (XRF) of the clay powders; (2) Determination of the elements using (ICP) inductive coupled plasma after dissolution of the clays (NaOH fusion) and (HF, H₂SO₄ fusion).

The results of the two methods were close to each other and the chemical composition of clay samples are recorded in Table-3 according to the above two methods.

TABLE-1
EXACT LOCATIONS OF THE SAMPLINGS
WERE IDENTIFIED BY GPS

Clay No.	Area name	Location by GPS	Colour
C1	Xak Rangbar Iran	–	White
C3	Kiffry (12 emam)	N 34° 36.821 E 045° 00.667 A 182 m	Yellow
C4	Kiffry	N 34° 39.082 E 045° 00.745 A 189 m	Faint Brown
C5	Qashqoli-Dokan	N 35° 55' 19.48" E 44° 57' 49.50" A 4440 m	Gray
C6	Shiwaswr1	N 35° 33' 45.36 E 44° 51' 29.33 A 711 m	Red
C7	Shiwaswr2	N 35° 33' 45.36 E 44° 51' 29.33 A 711 m	Red
C8	Awa Taqiw gray	N 35° 33' 46.31 E 44° 51' 44.82 A 703 m	Gray
C9	Awa Taqiw yellow	N 35° 33' 46.31 E 44° 51' 44.82 A 703 m	Yellow
C10	Fuller's earth standard clay	–	Gray-Brown

TABLE-2
GENERAL PROPERTIES OF THE TWO
OILS WERE AS FOLLOWS

Test	Asia oil company (D.O.1)	Direct waste oil spills (D.O.2)
Specific gravity at 15.6 °C	0.877	0.886
API gravity	29.85	28.21
Viscosity at 40 °C/Cst	73.6	130.32
Viscosity at 100 °C/Cst	9.7	14.28
Flash point (c.o.c) °C	230	190
Pour Point (°C)	0.0	-13
Water content (w %)	0.1	0.6

Acid activation of the clays: Activation was carried out using HCl, H₂SO₄ and H₃PO₄ of analytical grade, with strength varying between 0.2N and 4.0N at 70 ± 1 °C and solid to liquid ratio of 1:15 with shaking rate of 150 rpm. Residence time varied between 0.5 h and 24 h. At the end of each run the acid was discarded and the clay was washed until pH of the supernatant becomes 4-5. The clay slurry was filtered and the collected material was dried at 105 °C for 24 h and subsequently ground gently so as to pass through a 200 mesh sieve.

Clay treatment of the oils: 100 mL of dark oil was mixed with a measured amount of the adsorbent (5-25 % w/v) in a heavy walled flask. A vacuum of (-600 mm Hg) was maintained throughout all the experiments to prevent oil oxidation. The experiments were performed at the constant temperature of (150, 200, 250, 300, 350, 400 and 450 ± 5 °C) on a hot plate magnetic stirrer with constant stirring 800 rpm. The residence time at the maximum temperature was 3 h for dark oil 1 and 4 h for dark oil 2. The treated oils were cooled to 120-150 °C, filtered under vacuum through medium pour filter paper.

TABLE-3
CHEMICAL COMPONENTS IN THE CLAY SAMPLES

Clay sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO ₂	LOI	Total (%)
C1	73.10	11.32	1.01	1.98	1.67	0.46	0.02	0.20	0.07	10.17	100.00
C2	43.56	9.07	4.39	15.52	3.96	3.16	1.98	0.74	0.08	17.37	99.82
C3	45.91	9.80	4.85	11.80	4.16	2.94	1.37	0.69	0.07	17.25	98.84
C4	44.08	9.46	4.65	14.10	4.01	2.53	1.32	0.80	0.10	19.26	100.31
C5	49.35	10.40	5.35	10.80	5.48	1.86	1.25	0.70	0.13	14.15	99.47
C6	44.82	10.22	5.14	12.63	4.20	3.41	2.29	0.80	0.10	16.22	99.82
C7	47.12	10.71	5.50	7.96	4.95	4.07	4.37	0.79	0.09	13.21	98.77
C8	53.57	12.24	4.74	5.83	3.26	5.12	3.41	0.89	0.07	9.86	98.99
C9	35.87	8.40	3.50	18.35	2.43	3.53	1.72	0.69	0.06	22.19	96.74

LOI = Loss on ignition

The oil was diluted (1:10) with *n*-hexane and scanned at the visible region using scanning spectrophotometer. The blank was (1:10) diluted fully bleached oil with standard Fuller's earth and the best wavelength is at 462nm as shown in Fig. 1. For selected runs the full absorption spectrum between 400 and 600 nm was obtained.

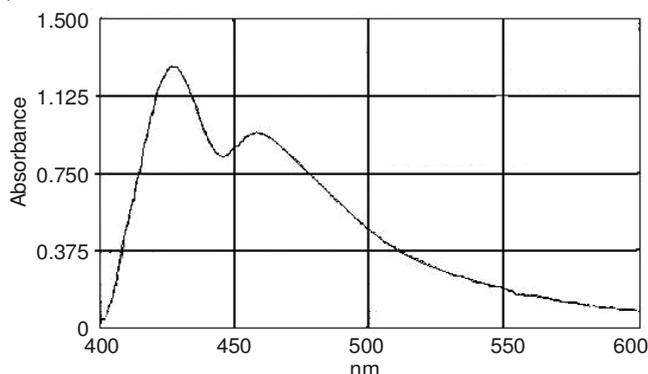


Fig. 1. Selection of best wavelength (λ) at visible region (Blank = 1:10 F.D.O, Sample = 10 g C7 2N H₂SO₄, 70 °C, 2 h)

10 g of non-activated C3 was mixed with 100 mL D.O.1 and adsorption processes were performed at different temperatures (150-450 °C) to select the optimum temperature for oil bleaching process which was 400 °C as shown in Fig. 2.

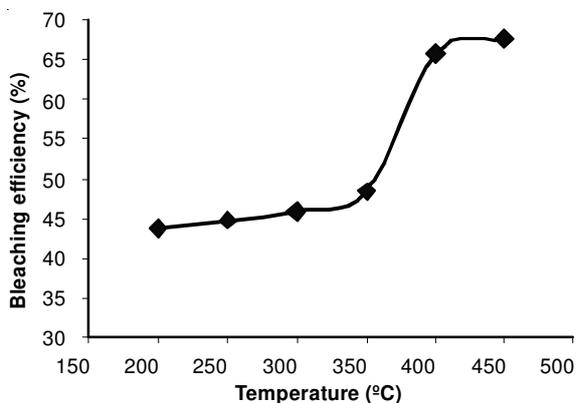


Fig. 2. Temperature optimization of adsorption process for D.O.1

The percentage of bleaching efficiency (% BE) (clarification capacity) is determined by Foletto *et al.*¹⁹:

$$\% \text{ BE} = \left(1 - \frac{A}{A_0} \right) \times 100 = 100(1 - \psi) \quad (1)$$

where A/A_0 is the relative absorbance, considering as reference an equilibrium clarified oil and ψ , a dimensionless pigment concentration (*i.e.*, $\psi = c/c_0$, pigment or darkness relative molar concentration in the oil), is assumed to be proportional to the relative absorbance¹⁹.

After that, optimization of bleaching time was studied at the optimum temperature (400 °C). It was found that optimum time for adsorption process at (400 °C) is 3 h for D.O.1 and 4 h for D.O.2, this is because of the higher viscosity of D.O.2 due to higher aromatic content (dark oil before acid treatment) (Fig. 3).

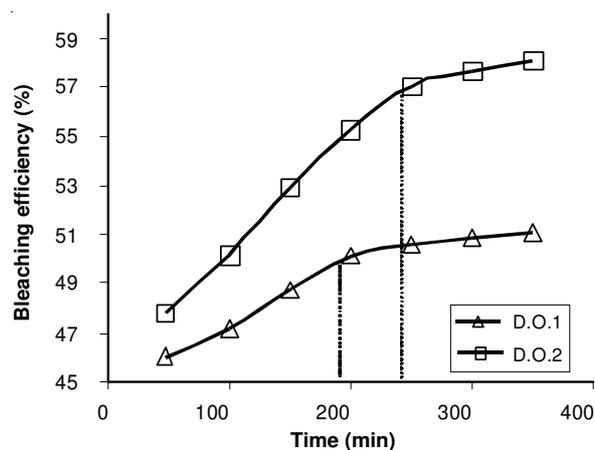


Fig. 3. Effect of adsorption time on the bleaching efficiency of non-activated C4 at 400 °C for decolourization of dark oil 1 (D.O.1) and dark oil 1 (D.O.2)

RESULTS AND DISCUSSION

Figs. 4 and 5 show the bleaching efficiency of un-treated and acid activated clays by 2M HCl for decolourization of D.O.2 oil assuming maximum 100 % efficiency for Fuller's earth standard clay result as reference. It is observed that C3 and C4 have best bleaching efficiency when activated with 2M HCl.

C9 seems to be a good clay for bleaching, but it is not much affected by the acid treatment. This may be due to the acidic property of the C9 originally.

For the acid activation with HCl at constant temperature (70 °C) and constant shaking rate of 200 rpm, the effect of time under constant acid strength and acid strength under constant time on the clay bleaching efficiency is optimized (2M HCl acid strength and 2 h activation time period) (Figs. 6 and 7).

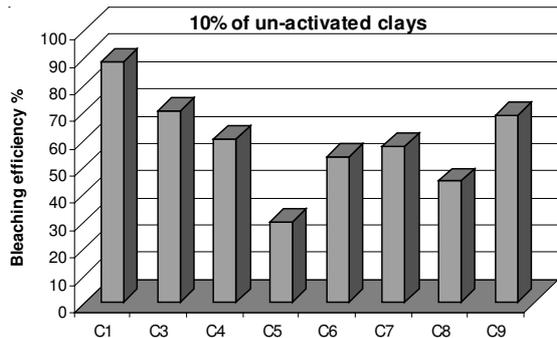


Fig. 4. % Bleaching efficiency of un-activated clays

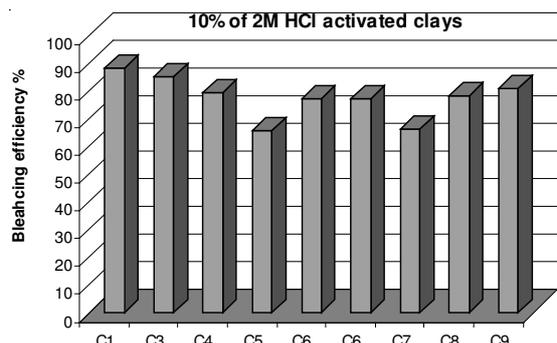


Fig. 5. % Bleaching efficiency of 2M HCl acid activated clays

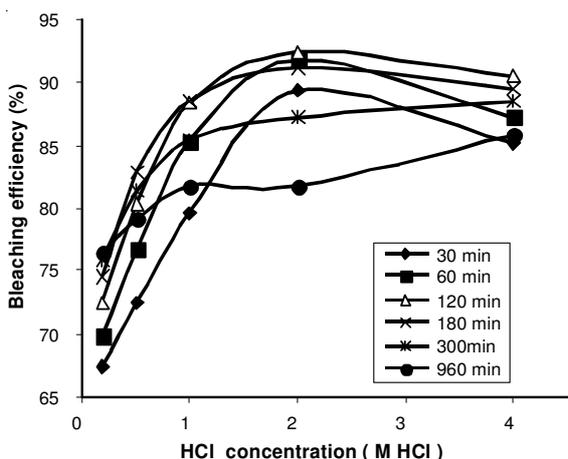


Fig. 6. Bleaching efficiency of C3 clay activated by various acid concentration for different time of activation

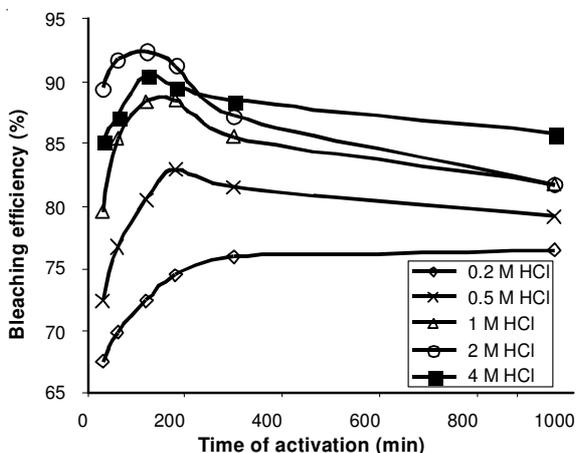


Fig. 7. Effect of activation period on bleaching efficiency at different acid concentration

Activation proceeds with partial dissolution of the clays, described by pseudo first order kinetics and is characterized by an initial replacement of the interlayer cations by H⁺ followed by dissolution of the octahedral sheets and subsequent release of the structural cations¹⁷.

Acid activation affects mainly chemical composition of the octahedral layer, while the tetrahedral layer is less prone to it because of strong bonds among silicon and oxygen ions. The amount of major ions removed of the octahedral layer is presented in Fig. 8 for C3 and C4¹⁵.

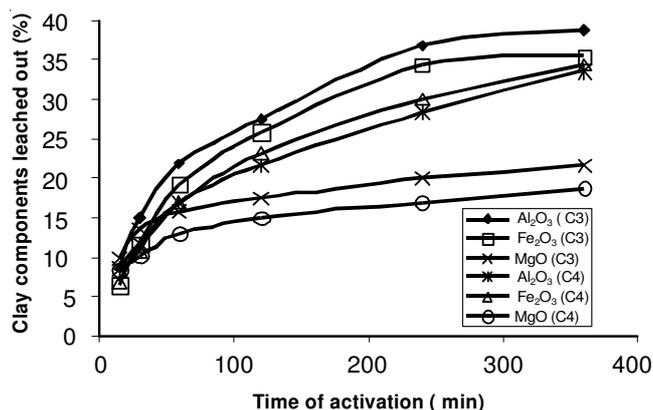


Fig. 8. % of Al₂O₃, Fe₂O₃ and MgO leached out during acid activation using 2M HCl (70 °C, 200 rpm, 1:15 clay/acid ratio)

Adsorption isotherms: Langmuir considered adsorption to distribute molecules over the surface of the adsorbent in the form of a unimolecular layer and for the dynamic equilibrium between adsorbed and free molecules, using the following relation:

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

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:

$$\frac{X}{m} = KC^n \tag{3}$$

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 eqns. 4 and 5:

$$X = \frac{A_o - A_t}{A_o} \tag{4}$$

$$X_e = \frac{A_t}{A_o} = 1 - X \tag{5}$$

(X) represent the bleaching efficiency, where A_o is the absorbance of unbleached lube oil and A_t is the absorbance of bleached oil at time (t).

Thus, by means of eqns. 3 and 4, by writing X_e instead of equilibrium pressure P and the residual substance C, eqns. 2 and 3 are rearranged as follows⁷:

$$\frac{X_e}{X/m} = \frac{1}{a} + \left(\frac{b}{a}\right) X_e \quad (6)$$

$$\frac{X}{m} = KX_e^n \quad (7)$$

By taking the logarithm of eqn. 7, we get:

$$\log X/m = \log K + n \log X_e \quad (8)$$

(K) is a general measure of the activity or decolourizing power of the adsorbent, whereas (n) is an indication of its characteristic manner of adsorption.

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 isotherms⁵.

As shown in Figs. 9-24, the points of the Langmuir isotherm plots were present more randomly on the lines ($R^2 = 0.11$ to 0.86), whereas a better fit with a straight line was obtained in the Freundlich isotherm plots ($R^2 = 0.86$ to 0.98).

Since the linearity of Freundlich isotherms are much better than Langmuir isotherms, it can be seen that Freundlich equation is more applicable than Langmuir equations for the bleaching process of used lubricating oils by the clay samples and the process is physical adsorption by weak bonds between the dark coloured compounds in oil and the clay adsorbent. This leads to the think of regeneration of the spent clay samples.

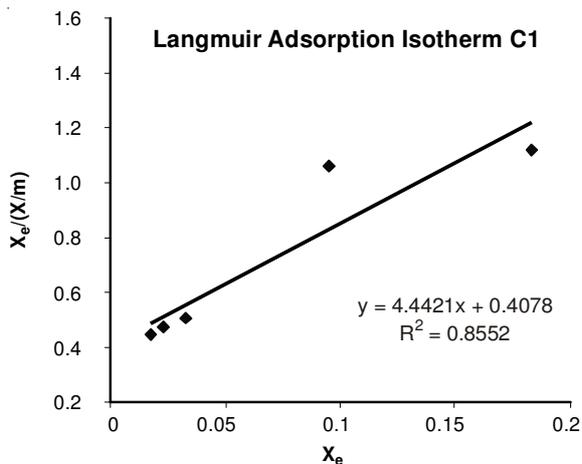


Fig. 9. Langmuir isotherm for C1 (standard)

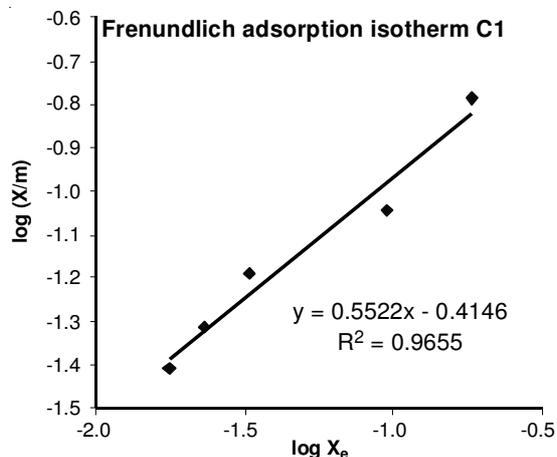


Fig. 10. Freundlich isotherm for C1 (standard)

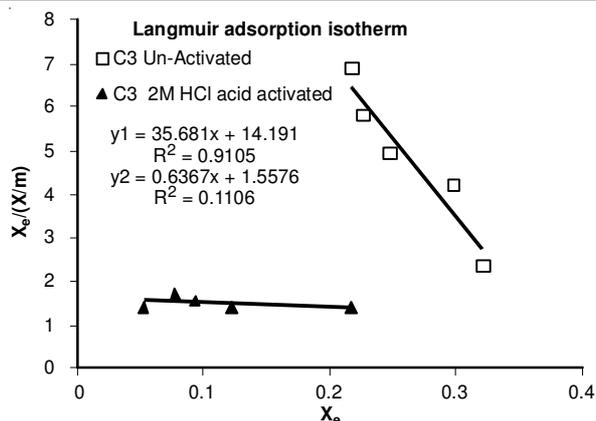


Fig. 11. Langmuir isotherm for C3 before and after 2M HCl activation

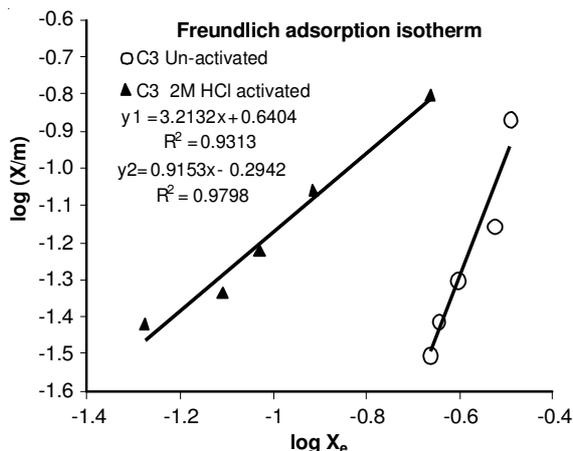


Fig. 12. Freundlich isotherm for C3 before and after 2M HCl activation

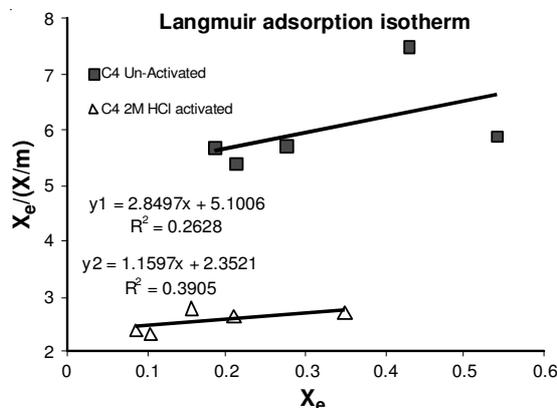


Fig. 13. Langmuir isotherm for C4 before and after 2M HCl activation

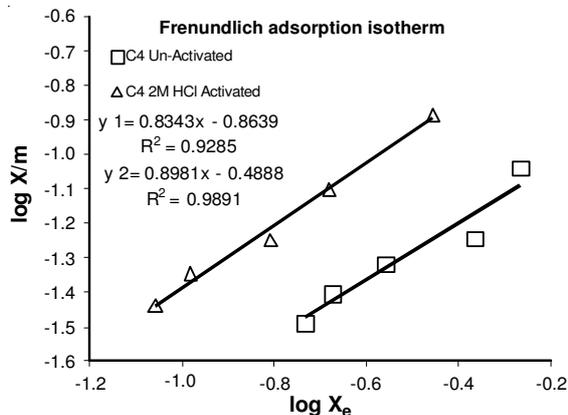


Fig. 14. Freundlich isotherm for C4 before and after 2M HCl activation

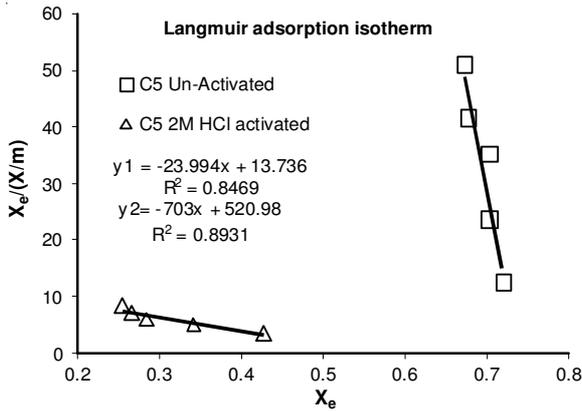


Fig. 15. Langmuir isotherm for C5 before and after 2M HCl activation

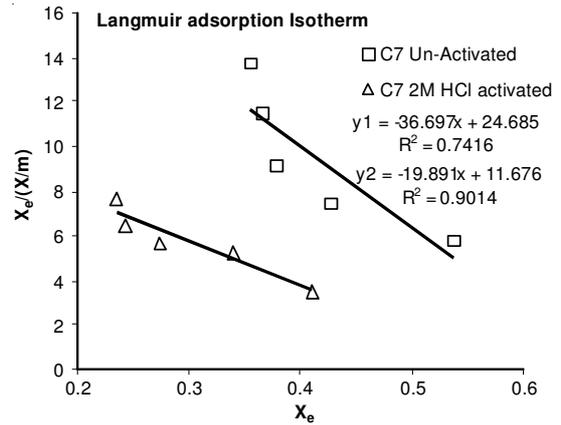


Fig. 19. Langmuir isotherm for C7 before and after 2M HCl activation

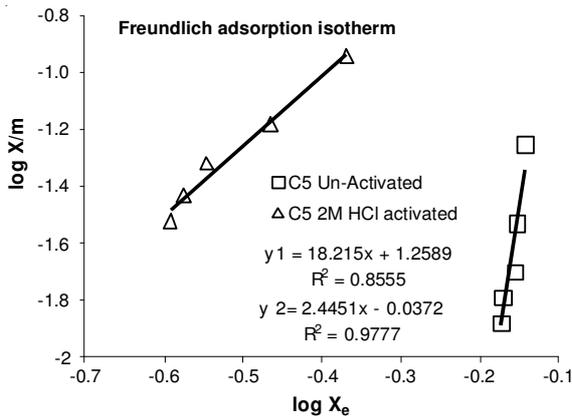


Fig. 16. Freundlich isotherm for C5 before and after 2M HCl activation

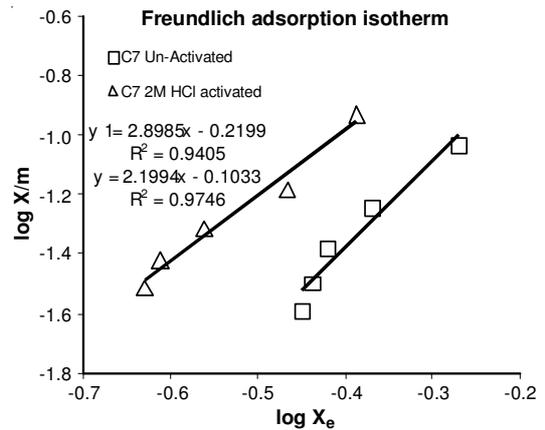


Fig. 20. Freundlich isotherm for C7 before and after 2M HCl activation

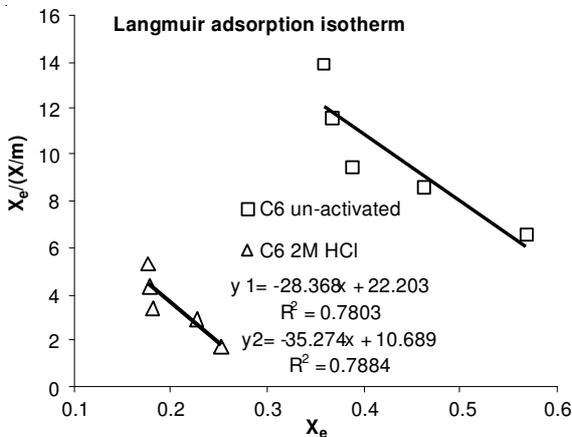


Fig. 17. Langmuir isotherm for C6 before and after 2M HCl activation

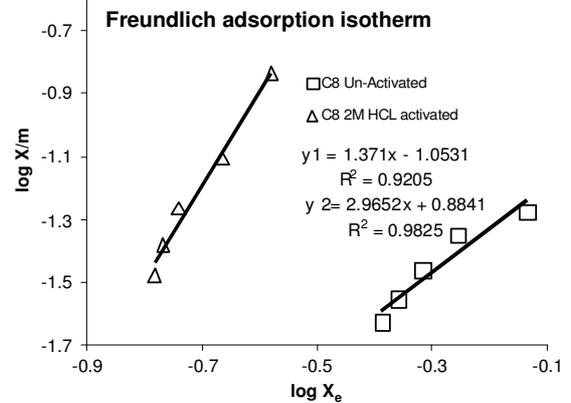


Fig. 21. Freundlich isotherm for C8 before and after 2M HCl activation

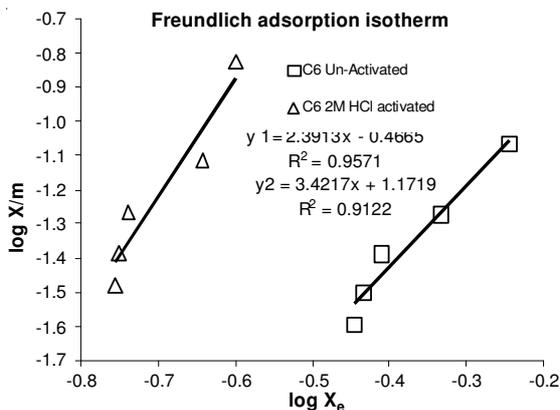


Fig. 18. Freundlich isotherm for C6 before and after 2M HCl activation

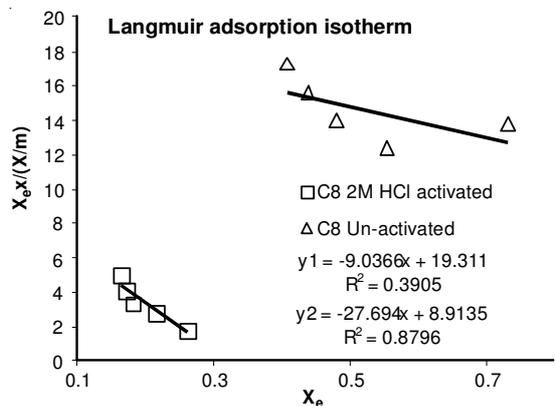


Fig. 22. Langmuir isotherm for C8 before and after 2M HCl activation

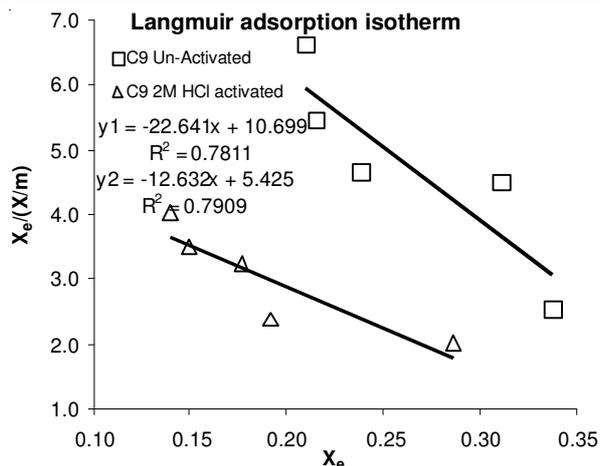


Fig. 23. Langmuir isotherm for C9 before and after 2M HCl activation

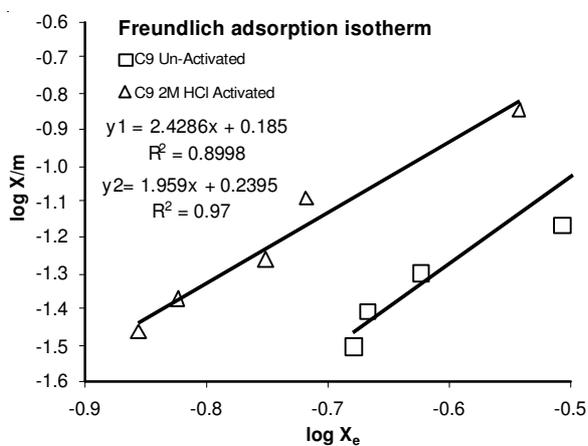


Fig. 24. Freundlich isotherm for C9 before and after 2M HCl activation

Finer particle sizes of clays, having greater specific surface areas, produce better bleaching results, but filtration rate and oil retention can be adversely affected. Therefore it is necessary to have tight control of particle size distribution of the bleaching clay to allow an adequate filtration rate, thereby reducing, as much as possible, the level of ultra-fine particles⁸.

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