STUDIES ON THE ADSORPTION INTENSITIES OF BENTONITE FROM AQUEOUS SOLUTION

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Abstract: **The acid activation of bentonite clay (at 1M concentration) was carried out using four different organic acids namely: propanoic acid (pka=4.88), lactic acid (pka=3.86), citric acid (pka=3.31) and oxalic acid (pka=1.25). Characterization was done using fourier transformed infrared analysis, x-ray diffraction analysis, adsorption capacity determination, and forster swelling factor. X-ray diffractogram shows the increase in the basal spacing in the order: UMB = 15.743Å; PAMB = 16.265Å; CAMB = 18.217Å; OAMB = 19.062Å. Oxalic acid displayed the highest adsorption capacity for xylene at 0.613, CAMB = 0.519, LAMB = 0.379, and lastly UMB = 0.051. The same trend was also seen in the swelling ability for xylene as OAMB = 1.2/2.0, CAMB = 1.0/1.8, LAMB = 1.0/ 1.6, PAMB = 0.2/0.4 and UMB = 0.0/0.0 being before agitation and after agitation values. The reduction in the pka value from PAMB to OAMB is observed to greatly influence the efficiency of adsorption. This is an indication that the pka of an acid is an important factor to be considered in the selection of adsorbent modifiers used in the treatment of petrochemical waste. This reduces the amount of pollutants that get into the environment from petrochemical effluents.**

Keywords: **Bentonite, Xylene, adsorption, adsorbent, pollutants, Acid.**

1. INTRODUCTION

Bentonite is a hydrophilic clay, and is capable of absorbing water and other polar solvents. When hydrated, bentonite swells; which is due to repulsion of platelets caused by osmotic pressure. The available sites, the exchangeable ions and the minerals affect the solvating ability of the clay; which possesses a high adsorption ability. When dispersed in water, bentonite forms extremely stable colloids. This suspension has properties such as high thixotropy and viscosity (Sipag, 2016). Bentonite is hygroscopic with a pH of about 8 - 10. It is observed to be dark and without taste or smell. Bentonite clay could be modified or activated to adsorb organic compounds (Odom 1984). Bentonite clay has many uses in the industries; due to their structure, composition and their physical properties.

Acid activation of Bentonite clay: This is a chemical process which involves the replacement by protons (H$^+$) of the interlayer cations and the reduction in the amount of metal ions in the octahedral sheet. Dissolving the octahedral sheet depends on the concentration and strength of the acid (Bujdak *et al*.,1998). The activation of bentonite clay with acids has been observed to affect certain property changes like: enlarge the surface area, alter surface functional groups, increase pore volume/size and increase the number of bronsted and lewis acid centres (Hussin *et al*.,2011). Srasra and Trabelsi-Aijedi (2000) analyzed the effect of the modification of bentonite using acids. This study indicated the increase in the number of bronsted and lewis acid sites from the unmodified clay to the acid modified clay. This was used to

adsorb the betacarotene, which is the pigment in palm oil. The adsorption was done by the hydrogen bond formation with the bronsted sites or coordinate bond formation with the lewis sites. Certain factors affect the acid activation process of clay such as the nature of the clay, the contact time, temperature, acid concentration and the type of acid used (Hussin *et al*.,2011).

Comparison between the bleaching capacities of bentonite modified by inorganic and organic acid was carried out using hydrochloric acid, sulphuric acid and acetic acid at varied concentrations. The bleaching power of the inorganic acid modified bentonite increased to maximum with increase in concentration. Acetic acid proved less effective in its bleaching capacity with increase in concentration (Oboh & Aworh, 1988). The use of organic acid modified bentonite in the removal of iron was carried out using three organic acids: oxalic, citric, and gluconic acids. They revealed that although all other organic acids had slight effects on the removal of iron; oxalic acid proved more efficient on a large scale. The work indicated a dependence on an acidic medium/low pH (Samsuri & Irawan, 2004).

Characterization of Bentonite Clay: This is the analysis of bentonite clay to know the various components and constituents. This further improves the understanding of the properties and uses. The use of certain analytical techniques could aid in the elucidation of elemental and chemical composition of clay soil. Other characteristics such as the surface area, pore size and the characterization of clay minerals are carried out using scanning electron microscope (SEM), x-ray diffraction (XRD) and thermogravimetric analysis (TGA) respectively (Steudel *et al*.,2009). The knowledge of surface chemistry and various oxides can be accounted for through the use of Fourier Transformed Infrared (FT-IR) Spectrophometer (Madejora,2003).

Adsorption Capacity: This is the interaction or adherence of a molecule (adsorbate) to the surface of another molecule (adsorbent). The adsorbent (bentonite) has the ability to interact and hold on to the molecule attached to its surface. This property is known as adsorption capacity.Isomorphous substitution generates a negative charge on the surface of the bentonite to adsorb other molecules.

Forster Swelling Test: Natural bentonite has the ability to take in water; this is due to the fact that clay is considered to be dissociable colloidal electrolyte that ionizes in water. In bentonite, the magnesium and ferrous ions replace aluminium in the octahedral mineral layer: this creates a net negative charge which is balanced by exchangeable cations bonded electrostatically and located in the interlayers. When hydrated, bentonite ionizes and swells; due to ionization which is depended on the exchangeable cations and the nature and amount of isomorphous exchanges. The amount of ionization caused by isomorphous exchanges is the driving force behind the extent of swelling.

The population of exchangeable cations in the clay interlayer is increased by the absorption of water, which leads to more ions in solution and electrostatic interactions causing expansion of the clay. Organic acid modified bentonite has organic molecules fixed in between its layers or on its external surface. This is achieved using quarternary ammonium compounds (QAC). This results in swelling of the OMB clay in organic solvents and little or no swelling in water (Apemiye et al.,2017).

Adsorption: This is the use of an adsorbent to attach molecules or ions either in gaseous or liquid form to its surface in a physical or chemical process, separating them from the solution. The adsorbent is usually a solid such as bentonite alumina and zeolite with a favourable large surface area. This property improves the adsorption of the adsorbate through the use of intermolecular forces (Demirbas et al., 2008). Two methods of adsorption are involved: batch adsorption and column adsorption. Batch adsorption is carried out in a vessel where a defined amount of adsorbent is placed with an equally known amount of adsorbate. All at once, this vessel is then agitated for a given period of time. They are then separated by filtration and then decanted. In column adsorption,the adsorbent is packed tightly in a vertically placed column and the adsorbate is let in slowly and allowed to flow through. The flow rate is calculated and the filtrate collected. Unlike batch adsorption, column is done without agitation (Loebenstein, 1962). The continuous expansion and evolvement of the petroleum and petrochemical industry has prompted unfavourable effects on the environment.

This could be due to mishandling of these products that leads to spillage, which takes place during transportation (Yakimov et al., 1998). Vanderlization of oil pipelines and also large production and accumulation of untreated waste water discharged into the environment, constitute some of the major pollutants both land and water plaquing our environment (Cavalcanti *et al*., 2012). The contents of these petrochemical discharges range from various organic compounds, the aliphatics, cyclic, aromatics, heterocyclics, BTEX (Benzene, Toluene, Ethyl benzene and xylene). Heavy metals and suspended solids at different aromatics (Jorrge *et al.,*2012). Some of these compounds are harmful to humans at various levels of exposure and intake.

2. EXPERIMENTAL

Materials

Sodium bentonite, one of the natural forms of bentonite, was collected from Mansid Nigeria limited., East-West road, Port Harcourt, Nigeria. This bentonite clay is in natural form from Ebenebe in Anambra State and was milled prior to sample collection.

Method

Acid Modification of Sodium Bentonite Using Oxalic, Citric, Lactic and Propanoic Acid: The activation method was adorpted from Senturk et al.,(2009). This method proceeds as 10g of sodium bentonite is weighed and soaked in a beaker with 200ml of distilled water for 24 hours.Using a magnetic stirrer, the soaked bentonite was stiired for 30 minutes. Then 200 ml of the organic acid (oxalic, citric, lactic and propanoic) at one molar (1M) concentration was added to the mixture. This was done separately for each of the organic acids. The mixture was then stirred and heated with reflux at 75^0C using a magnetic stirrer/hot plate and a condenser for for 2 hours. The mixture was filtered using whatmann filter paper and rinsed with distilled water. The sample was then dried in an oven at a temperature of 105^0C for 3 hours and kept in sample bottles for further use.

Characterization of the modified samples

(a) **Fourier Transformed Infrared Analysis**: The solid sample was pulverized and then 10 - 50mg was weighed and mixed with 250mg of dry KBr in a mortar, using a pestle for 2 minutes. 100mg of the evenly mixed powder, was then placed in a KBr die and pressed to form a pellet using either a carver press or a pair of wrenches. The die with the pelleted sample was then placed in the infrared spectrophotometer and analysed using a deuteriated L- Alanine doped triglycine sulphate (DLaTGS) detector.

(b) **X-Ray Diffration Analysis:** In the x-ray diffraction analysis, the samples were first pulverized then using a 150 mesh size sieve. The powdered sample was loaded in the sample holder, which has a maximum capacity of 15 mg, and this holder was placed inside the external shaker (which permits the mobility of the sample holder). The movements help to provide a random orientation of the crystal lattice/diffraction pattern. This external shaker with the sample holder is then inserted back into the instrument. The samples are then analysed and the 1024 x 256 pixels 2D peltier-cooled charged coupled device detector elucidates the diffraction pattern.

(c) Adsorption Capacity Measurement In Static State: The method adopted is in agreement with the method used by Bandura *et al.*,(2017). A perforated mesh glass bucket was weighed and its weight was recorded. Half a gram of UMB or OMB (adsorbent) was also weighed and placed inside the bucket. A test cell was filled with various solvents (organic solvents and water) and the glass bucket with the adsorbent in it, was lowered into the test cell and suspended for 30 minutes. After this period, the glass bucket was removed from the cell and the liquid from the bucket flowed out through the perforations for 15 seconds. The final weight is measured and recorded. The petroleum solvents placed in the test cell (adsorbates) include diesel, pms/gasoline, kerosene, lubricating oil and crude oil. The petrochemical solvent used here is xylene and then water was used as a solvent to determine the hydrophilicity.

Forster Swelling Test: In the Burgentze` *et al.*,(2004) forste sweelling method, 0.5g of the test was weighed and placed in a calibrated glass tube with a minimum of 50ml volume capacity and a diameter of 1cm. The volume of the sample in the tube was measured and recorded after which 50ml of the organic solvent or water was added to the tube and left to stay umperturbed for 24 more hours. After this, the amount which the bentonite increased was increased. The difference was recorded indicating the ability of UMB and OMB to swell.

Batch Adsorption of Xylene: The method by Mebrek and Derriche (2010) was adopted in this study. To a plastic container of about 150ml, 0.5g of each sample (both unmodified and modified bentonite) was added. Using a measuring cylinder, 20ml of xylene solution was also added. This mixture of adsorbent and adsorbate was agitated for 1 hour at 400 r/m using a mechanical shaker. After agitation, the solution was allowed to settle and carefully decanted. The filtrate was centrifuged before analysis through a uv-visible spectrophotometer, to determine the amount of xylene left in the aqueous solution after adsorption using both the OMB and UMB. The filtrate absorbed at a wavelength of 254 nm, which is the lambda max for xylene. The analysis was carried out for all four organic acid modified bentonite and the unmodified

bentonite varying adsorbent weight (0.1 g, 0.2 g, 0.4 g, 0.5 g, 0.6 g), the concentration of the adsorbate (100 mg/l, 150 mg/l, 200 mg/l, 250 mg/l, 300 mg/l) and the contact time (30 min, 60 min, 90 min, 120 min and 150 min.). This was done to illustrate some of the various factors that have an effect on adsorption and used in the isothermal and kinetic model determination. A blank was also prepared as standards to enable the plotting of the calibration curve, to determine the amount of xylene adsorbed.

3. RESULTS AND DISCUSSION

3.1. Fourier Transformed Infrared Analysis: The infrared spectra of UMB and OMB clay are shown in figures 4.1.1 - 4.1.3.
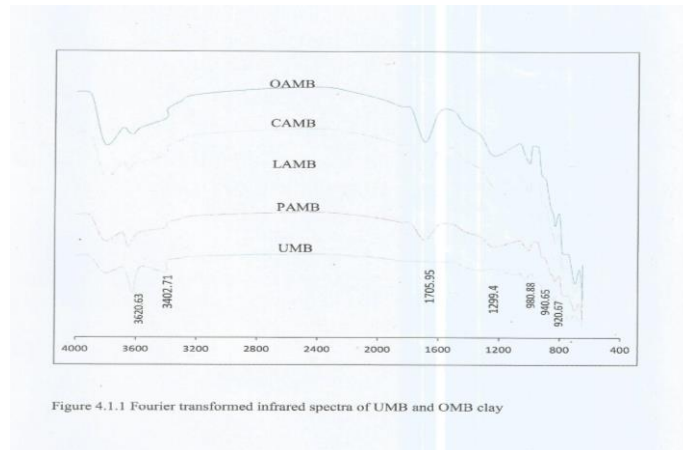

Figure 4.1.1 Fourier transformed infrared spectra of UMB and OMB clay
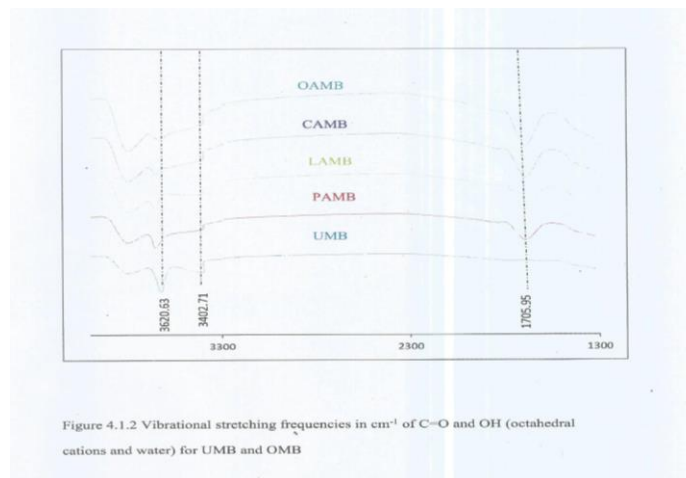

Figure 4.1.2 Vibrational stretching frequencies in cm⁻¹ of C=O and OH (octahedral cations and water) for UMB and OMB
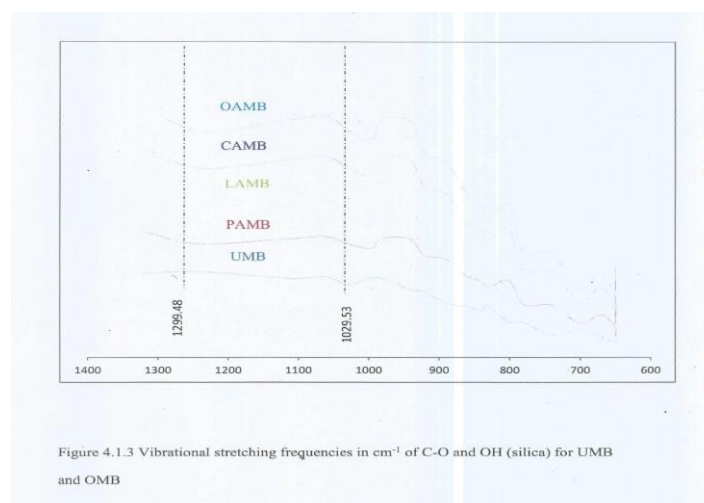

Figure 4.1.3 Vibrational stretching frequencies in cm⁻¹ of C-O and OH (silica) for UMB and OMB

The band at 3621cm^{-1} correspond to the octahedral cation, AlAlOH stretching. This also reveals little to no isomorphous substitution of Al^{3+} in the octahedral sheets. The bands corresponding to Al^{3+} and the other octahedral cations decreased in intensity with decreasing pka of the organic acids; this as is a result of the destruction of the octahedral sheets and the leaching out of Al^{3+} that occurs during acid activation. This encourages the increase in the amount of amorphous silica; this is in line with Farmer (1974) and Madejova *et al.*,(1994). The observation of a rise in the peak intensity at 1029cm^{-1} is synonymous with Si-OH stretching in the tetrahedral sheet.

The reaction of bentonite with organic acids led to a band at 1299cm^{-1} (figure 4.1.3) which corresponds to the asymmetrical and symmetrical stretching of C-O groups associated with carboxylic acids. The intense band at 1706cm^{-1} indicates stretching of the carbonyl functional group (C=O) bonds. The absence of these bands in UMB and the presence at various concentrations in the organo-modified clay illustrates the intercalation of organic compounds into the clay structure; this corresponds with Hussin *et al*.,(2011).

In accordance with Madejova *et al.*, (1994) the bands at 3403 cm^{-1} corresponds to the vibrational frequency (stretching) of water. This was observed to decrease in intensity from UMB to OMB clay and as the pka of organic acids used in the activation, decreased. This also explains the leaching out of water and the replacement by organic compounds, converting the clay from a hydrophilic to an organophilic clay.

X-Ray Diffraction Analysis: The analysis of bentonite clay samples was carried out for montmorillonite using an x-ray diffractometer. The diffractogram pattern (figure 4.1.4) for the various samples indicated structural modifications between UMB and OMB clays. The unmodified sample had the highest amount of montmorillonite at 28.2% as indicated in table 1, while OAMB had the least amount with 5.9%.

The alteration in the peak intensity at 6.60^0 which is matched to montmorillonite clay mineral reduces from UMB being the highest to OAMB being the lowest. This is proof of the decrease in the amount of montmorillonite clay mineral. The increase in the broadness of the peak illustrates a decrease in the crystallinity of the clay sample. The amount of quartz (SiO$_2$) tends to increase from UMB to OAMB. The partial breakdown of the octahedral sheet by the acids is reflected also by the increase in the amount of amorphous mineral.

The basal spacing calculated using Bragg's equation illustrates an increase in the basal spacing as the pka of the acid used to modify the bentonite reduced. UMB has a basal spacing of 15.743Å which is in line with a recent report by Mota *et al*.,(2011). PAMB=16.265Å, CAMB=18.217Å and OAMB=19.062Å.

Figure 4.1.4 X-ray diffractogram for UMB and OMB clay
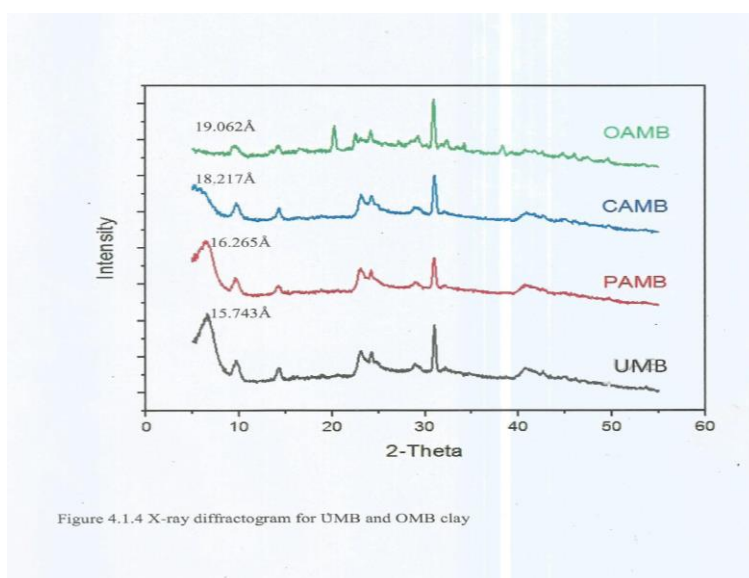
The presence of other impurities in table 1 such as quartz at 23.1%, chloritoid at 15.7%, kaolinite at 18.1%, vermiculite at 4.3% and gobbinsite at 6.9% were also noted. They had different trends, some increased and some decreased. The presence of eucryptite is also observed at 8.3% in OAMB, this indicates a major change in the composition of the clay. This mineral is not present in any other sample, even UMB.

Table 1: Percentage weight (%W) of Crystallographic Phases

S/NO.	Crystallographic Phases	UMB	PAMB	CAMB	OAMB
1	Montmorillonite	28.2	25.8	21.2	5.9
2	Quartz	23.1	21.4	23.3	29.9
3	Kaolinite	18.1	17.6	15.6	8.1
4	Chloritoid	15.7	15.2	12.9	8.6
5	Gobbinsite	6.9	7.5	8.0	14.2
6	Vermiculite	4.3	4.4	6.2	7.7
7	Eucryptite	-	-	-	8.3
8	Amorphous	3.7	8.1	12.8	17.3

Adsorption Capacity: The results of the adsorption capacity are presented in figures 4.2.1-4.2.9 and table 2. In these results, UMB showed a high adsorption capacity for organic (petroleum and petrochemical) solvents than water. The change in the pka of the organic acid at lower concentration had considerably significant effects on the adsorption capacity. Oxalic acid having the lowest pka had the highest adsorption capacity in all the organic solvents.

Table 2: Adsorptive Capacity Values (mg/g).

S/NO	SOLVENT	UMB	PAMB	LAMB	CAMB	OAMB
1	Xylene	0.051	0.156	0.379	0.519	0.613
2	Lube Oil	0.036	0.154	0.359	0.573	0.602
3	Diesel	0.048	0.133	0.371	0.466	0.527
4	DPK	0.068	0.131	0.316	0.487	0.519
5	PMS	0.087	0.128	0.296	0.414	0.489
6	Crude Oil	0.089	0.092	0.235	0.343	0.415
7	Water	1.512	0.426	0.143	0.097	0.076

Citric acid followed, having significant changes in the adsorption capacity when compared to UMB, but was not up to oxalic acid as its pka is not as low. Lactic acid was in the middle as the third and propanoic acid was the last in the adsorption capacity of organic solvents for OMB'S. Their preference for solvents in the measurement of adsorption capacity is illustrated below:

Xylene>Lube Oil>Diesel>DPK>Gasoline/PMS>Crude Oil>Water

In the adsorption capacity of organic solvents especially xylene, all the OMB's indicated changes when compared to the UMB. They all increased in this order:

UMB < PAMB < LAMB < CAMB < OAMB

When water was the solvent as indicated in figure 4.2.7, they decreased in this order:
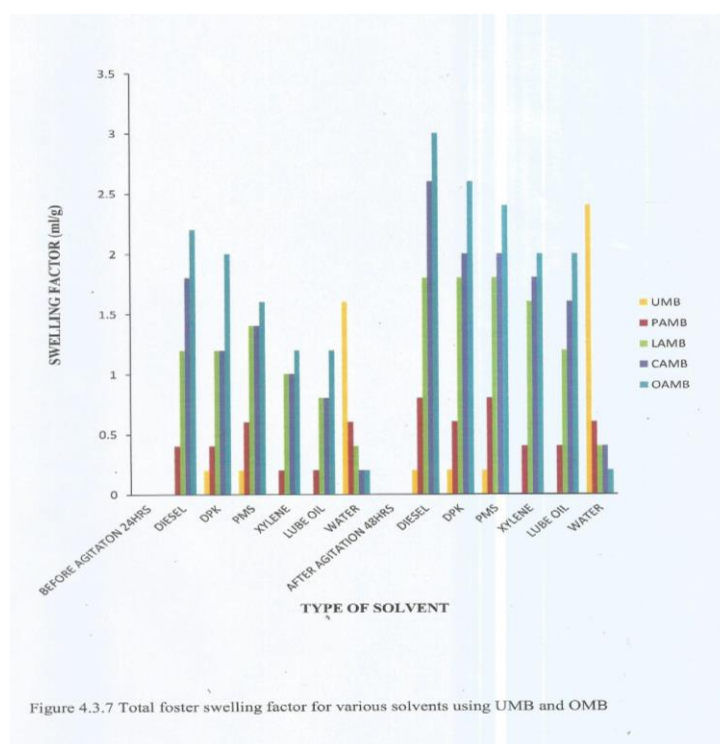
UMB > PAMB > LAMB > CAMB > OAMB

This illustrates the effect of the acid and its pka on the modification of bentonite, the changes in its adsorptive properties and the conversion from a hydrophilic clay to an organophilic clay.

Foster Swelling: The forster swelling test results presented in table 3 indicated a higher amount of swelling in OMB than UMB in all the organic solvents.

Table 3: Forster Swelling Factor(ml/g)

S/NO.	SOLVENT	TIME	UMB	PAMB	LAMB	CAMB	OAMB
1	DIESEL	Before agitation After agitation	0.0 0.2	0.4 0.8	1.2 1.8	1.8 2.6	2.2 3.0
2	DPK	Before agitation After agitation	0.2 0.2	0.4 0.6	1.2 1.8	1.2 2.0	2.0 2.6
3	PMS	Before agitation After agitation	0.2 0.2	0.6 0.8	1.4 1.8	1.4 2.0	1.6 2.4
4	XYLENE	Before agitation After agitation	0.0 0.0	0.2 0.4	1.0 1.6	1.0 1.8	1.2 2.0
5	LUBE OIL	Before agitation After agitation	0.0 0.0	0.2 0.4	0.8 1.6	0.8 1.6	1.2 2.0
6	WATER	Before agitation After agitation	1.6 2.4	0.6 0.6	0.4 0.4	0.2 0.4	0.2 0.2

Figure 4.3.7 Total foster swelling factor for various solvents using UMB and OMB

Oxalic acid modified bentonite had the highest swelling capacity in organic solvents (especially diesel). Citric acid followed with values almost as high, then lactic acid. Propanoic acid modified bentonite and UMB, showed little to no swelling ability.

The order for the bentonite swelling capacity in petroleum solvents is as follows:

OAMB > CAMB > LAMB > PAMB > UMB

The order above elucidates the reduction in the modification of bentonite owing to the increase in the pka values. The descending order for the solvents in the forster swelling factor of modified bentonite is :

Diesel > DPK > PMS > Xylene > Lube Oil > Water

UMB showed the highest swelling capacity for water and very low swelling capacity for all organic solvents. Propanoic acid displayed the second highest swelling capacity for water as illustrated in figure 4.3.6. The other organo-modified bentonite samples (LAMB, CAMB and OAMB) had lower values in the swelling ability when water was the solvent. The forster swelling factor for water of both OMB and UMB clay increased in this order:

OAMB < CAMB < LAMB < PAMB < UMB

Table 4: Concentration of Xylene (mg/l) after its adsorption from an aqueous solution using UMB and OMB varying adsorbent concentration.

Adsorbate Concentration(mg)	UMB	PAMB	LAMB	CAMB	OAMB
100	98.43	88.61	64.35	54.70	38.47
150	147.91	133.02	106.94	77.13	52.46
200	196.33	181.76	143.66	100.67	88.61
250	245.28	229.50	189.13	137.94	103.07
300	294.03	274.88	216.71	179.22	124.19

These results shown in figures 4.3.7 and table 4 indicate the effects of the pka values of organic acids on the modification and the swelling properties of bentonite clay. Oxalic acid exhibited the most notable conversion when modified from a hydrophilic to an organophilic clay and propanoic acid showed the least.

Effect of Adsorbate Concentration on the Adsorption of Xylene: Adsorption of Xylene varying the adsorbate concentration presented in fig. 4.41 and tables 5 and 6 was effective using OMB and highly ineffective using UMB.
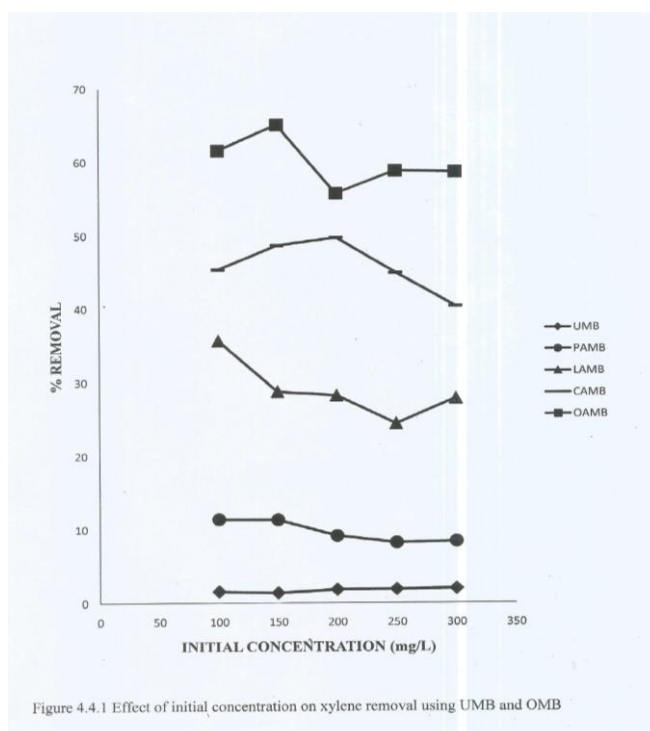

Figure 4.4.1 Effect of initial concentration on xylene removal using UMB and OMB

Table 5: Concentration of Xylene (mg/l) after its adsorption from an aqueous solution using UMB and OMB varying adsorbent concentration.

S/NO	Adsorbate Concentration (mg/l)	UMB	PAMB	LAMB	CAMB	OAMB
1	100	98.43	88.61	64.35	54.70	38.47
2	150	147.91	133.02	106.94	77.13	52.46
3	200	196.33	181.76	143.66	100.67	88.61
4	250	245.28	229.50	189.13	137.94	103.07
5	300	294.03	274.88	216.71	179.22	124.19

Table 6 (a): Effect of Adsorbate Concentration on the Percentage (%) Removal of Xylene from an Aqueous Solution using UMB and OMB.

S/NO.	Adsorbate concentration (mg/l)	UMB	PAMB	LAMB	CAMB	OAMB
1	100	1.59	11.39	35.65	45.30	61.53
2	150	1.39	11.32	28.71	48.58	65.03
3	200	1.84	9.12	28.17	49.67	55.70
4	250	1.89	8.20	24.35	44.82	58.77
5	300	1.99	8.37	27.76	40.26	58.60

OAMB displayed a 65.03% at 150 mg/l adsorption of xylene, which was the highest recorded. CAMB adsorbed 49.67% of xylene at a 200 mg/l concentration, LAMB indicated a 35.65% maximum adsorption percentage at 100 mg/l concentration of xylene. PAMB had the lowest percentage adsorption of xylene for the organo-modified bentonite with 11.39% at 100 mg/l. UMB was ineffective adsorbing a maximum of 1.99% of xylene at 300 mg/l. The trend in figure 4.4.1 indicates a drop in the percentage adsorption of OAMB having the highest adsorption but the lowest pka to PAMB, which had the lowest adsorption and the highest pka. The values in table A4.2 shows a reduction in the concentration of xylene from 294.03 mg/l in UMB to 274 mg/l in PAMB, to 216 mg/l in LAMB, 179.22 mg/l in CAMB and 124.19 mg/l in OAMB. This is an indication of higher adsorption by the adsorbent leading to a lower concentration of xylene in the filtrate. Although the gradual increase and changes in adsorption as the pka decreases within the bentonite clay shows its effect on the adsorption of xylene. The change in the concentration of xylene had little or no effect on its percentage removal from solution. OAMB had 61.53% at 100 mg/l, 65.03% at 150 mg/l, 55.70% at 200 mg/l, 58.77% at 250 mg/l and 58.60% at 300 mg/l and this trend cuts across the rest of the OMB'S and also UMB.

Effect of Contact Time on the Adsorption of Xylene: Figure 4.4.2 and tables 6 and 7 illustrate the effects of contact time on the elimination of xylene from an aqueous solution.

Figure 4.4.2 Effect of contact time on xylene removal using UMB and OMB

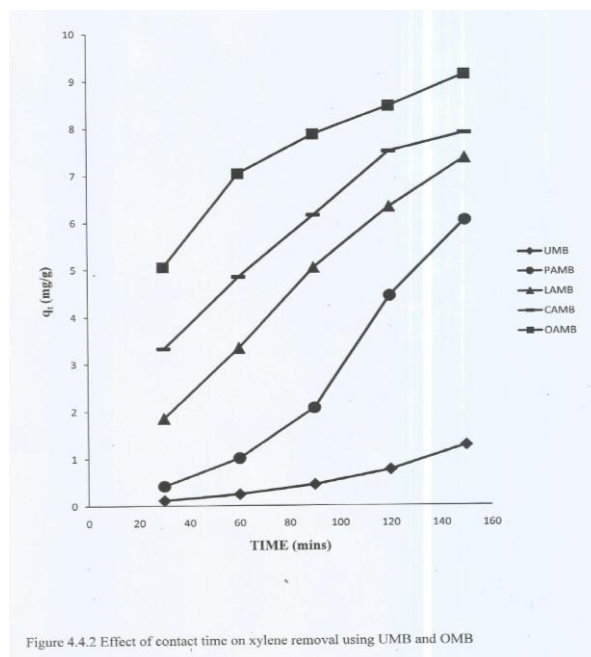**Table 6 (b): Concentration of Xylene (mg/l) after its adsorption from an aqueous solution using UMB and OMB varying Contact Time.**

S/NO.	Time (min)	UMB	PAMB	LAMB	CAMB	OAMB
1	30	297.34	289.67	253.88	217.13	173.97
2	60	294.03	274.88	216.71	179.22	124.19
3	90	288.11	248.53	174.37	146.43	103.55
4	120	281.11	189.38	141.93	112.68	88.61
5	150	268.29	149.26	116.18	102.87	71.94

Table 7: Effect of Contact Time on the Equilibrium (q_t) Removal of Xylene from an aqueous Solution using UMB and OMB.

S/NO.	TIME (min)	UMB	PAMB	LAMB	CAMB	OAMB
1	30	0.1064	0.4132	1.8448	3.3148	5.0412
2	60	0.2388	1.0048	3.3316	4.8312	7.0324
3	90	0.4428	2.0588	5.0252	6.1428	7.858
4	120	0.7556	4.4248	6.3228	7.4928	8.4556
5	150	1.2684	6.0296	7.3528	7.8852	9.1224

The percentage removal of xylene was directly proportional to the contact time, indicating that increase in contact time increases the percentage removal of xylene. The hydrophilicity of UMB greatly reduced its ability to adsorb xylene and therefore is the reason for the low removal of xylene from the solution The OMB's showed a higher percentage removal of xylene than the UMB clay, indicating the effective conversion of the clay from hydrophilic to organophilic, in agreement with the work reported by Abbas *et al.*,(2017) and Nourmoradi *et al.*,(2012). The percentage removal of xylene by UMB ranged between 0.887-10.570%; 3.443-50.247% was the range for PAMB; 27.623-65.71% for CAMB; 42.010-70.020% for OAMB. This shows that OAMB was the most efficient in the removal of xylene from the aqueous solution and therefore the best modified clay.

Effect of Adsorbent Weight on the Adsorption of Xylene: The variation of the weight of bentonite used for the removal of xylene from an aqueous solution was studied and the results presented in figure 4.4.3 and tables 8 and 9.

Figure 4.4.3 Effect of adsorbent weight on the removal of xylene using UMB and OMB

Table 8: Concentration of Xylene (mg/l) after its adsorption from an aqueous Solution using UMB and OMB varying adsorbent weight.

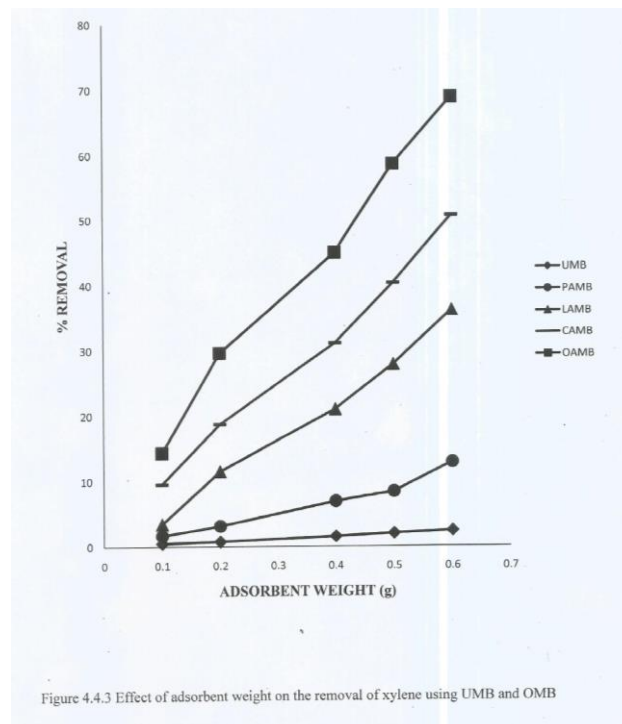| S/NO.	Adsorbent weight(g)	UMB	PAMB	LAMB	CAMB	OAMB
1	0.1	298.62	295.13	289.67	271.44	252.07
2	0.2	297.79	290.62	265.53	243.86	271.32
3	0.4	295.47	279.37	237.13	206.95	165.30
4	0.5	294.03	274.88	216.71	179.22	124.19
5	0,6	292.83	261.54	191.68	148.19	93.55

Table 9: Effect of Adsorbent weight on the Percentage (%) Removal of Xylene from an aqueous Solution using UMB and OMB

S/NO.	Adsorbent weight(g)	UMB	PAMB	LAMB	CAMB	OAMB
1	0.1	0.46	1.62	3.44	9.52	14.31
2	0.2	0.74	3.13	11.49	18.71	29.56
3	0.4	1.51	6.88	20.96	31.02	44.90
4	0.5	1.99	8.37	27.76	40.26	58.60
5	0.6	2.39	12.82	36.11	50.60	68.82

This result clearly indicates the increase in the percentage removal, with the increase in adsorbent weight of both UMB and each of the OMB clays. This shows a directly proportional relationship. When 0.1 g of bentonite was used to adsorb xylene, it was less effective than 0.2 g, which was much less effective than 0.6 g. UMB as indicated in tables 8-9 showed percentage removal values of 0.46-2.39%; PAMB was 1.62-12.82%; LAMB showed a 3.44-36.11% increase; CAMB had the second highest percentage with 9.52-50.60% and OAMB showed a 14.37-68.82% increase as the highest. The extent in percentage of xylene removal increases as the pka of the acids decreases. This was indicated by only a 11.2% change from 0.1-0.6 g of bentonite for PAMB, a 32.67% increase for LAMB, a 41.07% increase for CAMB and a 54.45% change for OAMB.

4. CONCLUSION

The use of unmodified and organo-modified sodium bentonite in the competitive adsorption of xylene was profitable. The alterations of the surface characteristics of the clay by the organic acids indicate an enhancement in the properties of the raw sodium bentonite. This improvement is shown in the surface area, pore size/volume and the number of bronsted and lewis acid sites. The results in the improvement of the adsorptive properties of the clay makes it suitable for the intended purpose. Also the intercalation of organic compounds into the clay interlayer illustrates the conversion from hydrophilic to organophilic.

The variation of pka values of the organo-modified bentonite played an important role in the enhancement of its properties and thereby increased the performance of the clay during adsorption. Oxalic acid modified bentonite having the lowest pka was the most productive in the adsorption of xylene from an aqueous solution. The adsorption capacity for organic solvents, swelling factor, and pore size illustrated a decreased efficiency as the pka of the organic acid increased. In the treatment of petrochemical effluents, the use of organic acids as adsorbent modifiers should be employed as a low cost/easily accessible method. The effectiveness of this method is crucial and depends largely on the pka of the organic acid chosen.

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