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Competitive adsorption of organic solvents using modified and unmodified calcium bentonite clay mineral

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ABSTRACT

Dodecyltrimethylammonium bromide (DTAB)-modified and unmodified calcium bentonite were both used for the competitive adsorption of aromatics (xylene, ethylbenzene and toluene) and petroleum products (gasoline, dual purpose kerosene and diesel) from their aqueous solution. Infrared spectroscopy (IR) and expansion tests (adsorption capacity and Foster swelling) measurement were performed in order to evaluate the performance of the adsorbents. The Foster swelling index and adsorption capacity of the DTAB modified calcium bentonite in the organic solvents follow the trend: xylene > ethylbenzene > toluene > gasoline > dual purpose kerosene (DPK) > diesel > water. However, the adsorption capacity of the adsorbent in diesel outweighed the adsorption capacity in DPK at high concentration of DTAB indicating that diesel has higher affinity for high DTAB concentration than DPK. The percentage removal of the solvent is directly proportional to the concentration of DTAB used in modifying the bentonite as well as the contact time between the adsorbent and the solvent, hence modified calcium bentonite adsorbed a higher percentage of organic solvents than the unmodified calcium bentonite. The adsorption characteristics of both adsorbents improved remarkably after proper agitation of the organic solvents, the unmodified calcium bentonite however adsorbed more water than the modified bentonite. Data obtained from adsorption isotherm models confirms that Freundlich adsorption isotherm model was favored more than Langmuir adsorption isotherm model with the correlation factor (R^2) of the former tending more towards unity. The adsorption of ethylbenzene using DTAB modified and unmodified calcium bentonites follow a pseudo second order kinetics mechanism, suggesting that the rate determining step of adsorption involves both the adsorbent and the organic solvent.

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Capsule Summary: DTAB modified calcium bentonite has a higher adsorption capacity than the unmodified calcium bentonite as such can be deployed in the adsorption of aromatics (xylene, ethylbenzene and toluene) and petroleum products (gasoline, dual purpose kerosene and diesel) from waste water and effluents thereby protecting the environment and humans from their hazardous effects.

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INTRODUCTION

The introduction and injection of harmful waste such as aromatics and petroleum products to the environment due to the current increase in petrochemical, agro-allied and petroleum industries has indeed constituted a severe threat to humans and animals. Steady and continual release of industrial effluent and waste into water bodies (oceans, rivers, seas, lake, and streams), results in the accumulation of pollutants and contaminants in sediments which are natural habitats of most aquatic lives (Aisien et al., 2013). Most of these toxins (pollutants) are also found in effluents released into the environment. Most aromatic compounds such as ethylbenzene, toluene and xylene are quite harmful and detrimental to humans, animals and the environment. The ingress of these aromatics into the water bodies make them unsuitable for consumption and also leads to total destruction of aquatic lives (Senturk et al., 2009). These aromatics especially ethylbenzene has the tendency to cause some adverse effect to human health such as mucous membranes irritation, impairment of the central nervous system, kidney impairment diseases, human liver disruption, skin irritation, eye irritation, destruction or total damage to the nervous system and also respiratory diseases (Berenjian et al., 2012). Petroleum products such as gasoline also known as petroleum motor spirit (PMS), dual purpose kerosene (DPK) and diesel also contain appreciable concentration of these aromatics as well as other harmful components making them also dangerous to humans and environment. Humans and environment gain undue exposure to petroleum products during oil spillage (Goncharuk et al., 2002). Owing to the aforementioned effects and the non-degradable properties of aromatics, there is an urgent need to adsorb aromatics such as ethyl benzene, xylene and toluene from wastewater before discharging to the surrounding (environment) in order to curtail and avert health implications. This can be achieved through the use of a locally available adsorbent with a relatively high surface area such as bentonite (Aisien et al., 2013). Bentonite is an alumina-silicate mineral clay that occurs naturally, it is primarily composed of montmorillonite mineral with a distinctive alumina octahedral sheet existing in between two tetrahedral sheets of silicon and it is globally found in most countries (Shen, 2000). Bentonite is a hydrophilic compound which swells when it absorbs water however several studies have been carried out on how to change the hydrophilic property of bentonite to organophilic property in order to make it a suitable adsorbent for organic compounds (Osalo et al., 2013). Organophilic bentonite or organo-modified bentonite can be synthesized by the exploitation of an organic acid and a quaternary ammonium compound (QAC) which are good modifying agents (Apemiye and Obi, 2010). Senturk et al., 2009 removed phenol from an aqueous solution with the aid of organophilic bentonite modified with cetyltrimethylammonium bromide (Senturk et al., 2009). The adsorption efficiency of bentonite can also be enhanced when treated with an acid, Obi and Okoye, 2014 utilized an

acid modified bentonite for the removal of naphthalene from an aqueous solution (Obi and Okoye, 2015). The structure of bentonite is illustrated in Figure 1.

There are several ways through which water contaminant and environmental pollutant such as ethylbenzene can be removed from petrochemical wastewater which include the utilization of modified zeolite, exploitation of organokaoline (Egbuchunam et al., 2016). Other means for ethylbenzene removal includes; the utilization of biological method, the use of physical method, the exploitation of chemical method, the application of catalytic oxidation, the employment of Ultraviolet (UV) oxidation, the utilization of bioscrubbers and the use of bio filters (Apemiye and Obi, 2010). However, this study is specifically on adsorption method using modified and unmodified calcium bentonite. Adsorption is a removal process in which an ion, atom or molecule known as the adsorbate from a liquid or gas adhere or attach itself to a liquid or solid surface called adsorbent. It can also be regarded as the concentration of adsorbate molecules on a molecular surface of a highly porous material such as bentonite, kaolin, activated charcoal, carbonized agro-waste material, zeolite and pillared clay (Mebrek and Derriche, 2010). During the adsorption process, the adsorbate particles are attracted and held on the adsorbent's surface by a weak force basically known as intermolecular force (Kralik, 2014).

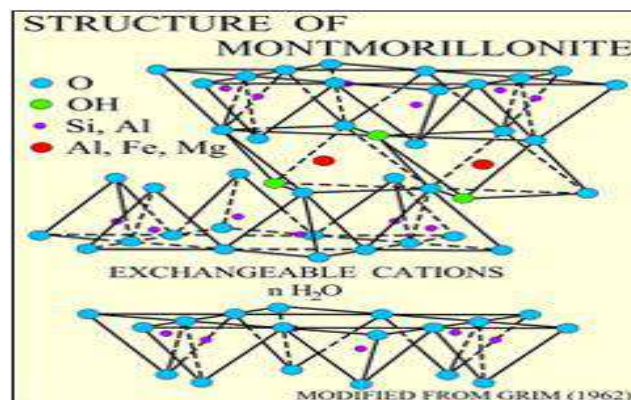


Fig. 1: Structure of bentonite

Exploration and production of crude oil have been the main contributor and the major source of economic growth in Nigeria and the utilization of imported bentonite as a hydrocarbon adsorbent during wastewater treatment has been capital intensive, it is therefore of utmost importance to reduce the importation of bentonite.

Hence the need to explore and provide an alternative adsorbent that is produced locally and is environmentally pleasant and friendly. The aim of this study is to determine the efficiency and effectiveness of modified and unmodified calcium bentonite clay in the removal of organic solvents from aqueous solution through the process of adsorption.

MATERIAL AND METHODS

The calcium bentonite used for this study was obtained from Mansid Nigeria Limited, Port Harcourt Rivers State, Nigeria. Dodecyltrimethylammonium bromide (DTAB), m-xylene, toluene and ethylbenzene were purchased from Sigma-Aldrich Company, Switzerland at >98% purity. The petroleum products were obtained from Nigerian National Petroleum Cooperation (NNPC), Port Harcourt, Rivers State, Nigeria. Equipment used include FT-IR Spectrometer, UV-Visible Spectrometer, electrical oven, magnetic stirrer / hot plate, mechanical shaker, auto sieve machine and weighing balance

Preparation of calcium bentonite

The calcium bentonite sample was crushed and thereafter sieved using a 150 μm sieve to obtain a homogenized powdered mixture. The powdered form was completely used for the study.

Modification of calcium bentonite

A measured amount of 10g of the milled calcium bentonite was soaked in 200ml of distilled water for 24 hours after which the bentonite-water mixture was properly stirred for 30 minutes before 0.8M of dodecyltrimethylammonium bromide (DTAB) was gradually added to the bentonite-water mixture and was subsequently stirred, heated and refluxed for two hours at temperature of 75°C. Upon the completion of the process of modification, filtration was carried out and the organo-modified bentonite was oven dried at a temperature of 110 °C. The dried DTAB modified bentonite was properly stored and preserved in a sample tube for characterization and batch adsorption. The whole process was repeated for different concentration of DTAB (Tina and Robin, 2014).

Characterization of calcium bentonite

The test samples (calcium bentonite) were characterized using a number of techniques such as FT-IR analyses, foster swelling test, adsorption capacity measurement and batch adsorption experiment using Ultraviolet Spectrometric analyses

FT- IR analysis

The FT- IR analysis was carried out using Fourier transformed infrared spectrometer (model number IR AFFINITY-1) at a range of 400 – 4000 cm^{-1} . The samples were analyzed using potassium bromide (KBr) technique. A sample of 1mg of bentonite was homogenized with 100mg of pure potassium bromide and the mixture was carefully screwed and compressed to form a disc which was afterward placed in the machine and then scanned (Stankovic et al, 2011).

Foster swelling test

Exactly 0.5g of bentonite sample was placed inside a 50ml capacity glass tube, its volume was recorded and 50 ml of water was carefully poured into the glass tube. The set up was allowed uninterruptedly to stand for 24 hours without

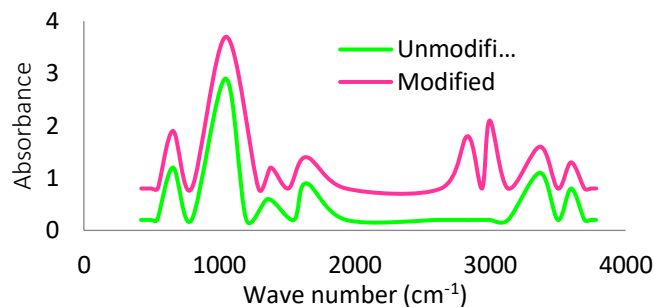


Fig. 2: FT- IR spectral of (green) unmodified and (purple) DTAB modified calcium bentonite

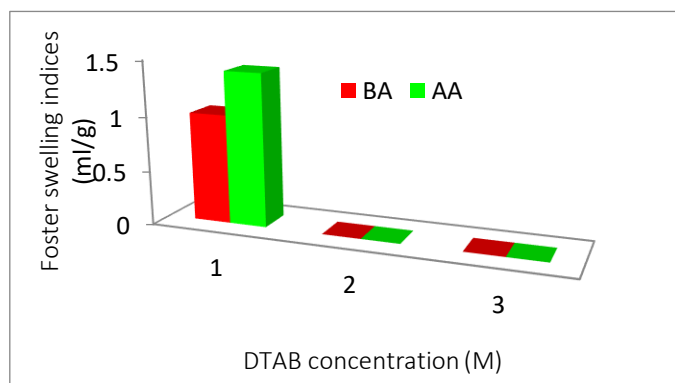


Fig. 3: Foster swelling indices of calcium bentonite at various DTAB concentration in water

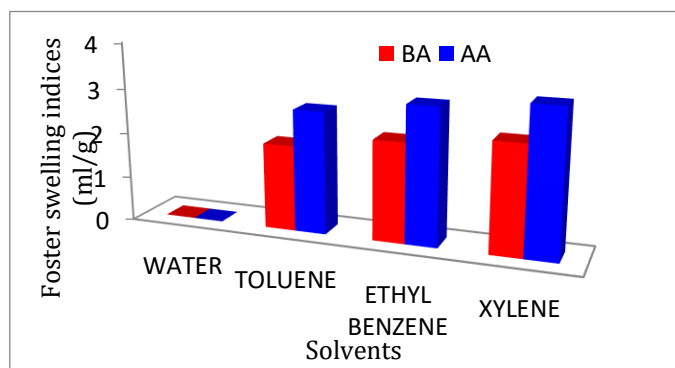


Fig. 4: Foster swelling indices of modified calcium bentonite in aromatic compounds and water

any disturbance and the bentonite's new volume was recorded before subsequent agitation. After the agitation, it was allowed uninterruptedly to stand for another 24 hours and the bentonite's new volume was as well recorded. Both the modified and the unmodified calcium bentonites were used for this analysis. The Foster swelling test was repeated using other solvent (toluene, m-xylene, gasoline, diesel and DPK). The swelling factor (F_s) was calculated using equation 1 and 2.

$$F_{SB} = \frac{V_B - V_I}{V_I} \quad (1)$$

$$F_{SA} = \frac{V_A - V_I}{V_I} \quad (2)$$

F_{SB} and F_{SA} are the foster swelling index before and after agitation respectively, V_B and V_A are the volume of the adsorbent before and after agitation respectively, While V_I is the initial volume of the adsorbent in the glass tube before solvent addition (Apemiye and Obi, 2010).

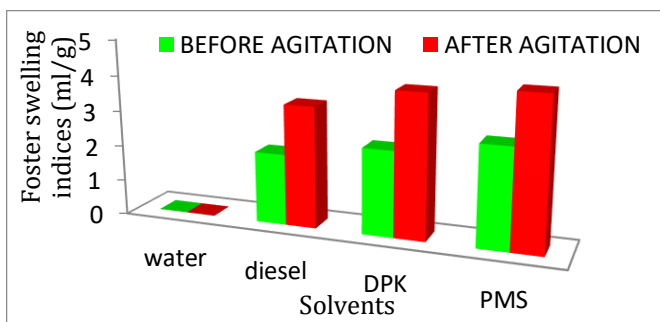


Fig. 5: Foster swelling indices of modified calcium bentonite in petroleum products and water

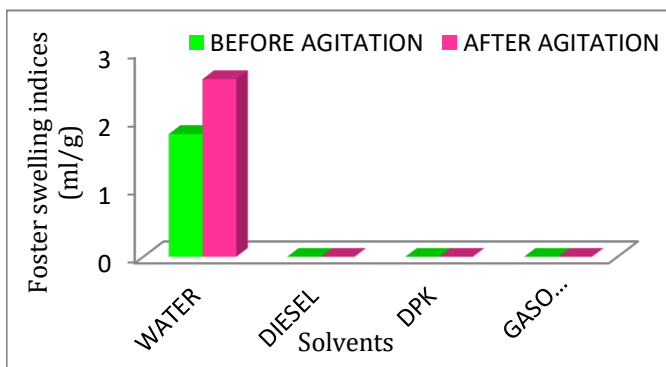


Fig. 6: Foster swelling indices of unmodified calcium bentonite in petroleum products and water

Adsorption capacity measurement in a static condition

Specifically, 0.5 g bentonite sample was carefully weighed and placed in a glass mesh bucket (GMB) which was attached to a retort stand with a white string and the glass mesh bucket was lowered inside a 100ml capacity beaker containing 100ml of water for 30mins. After the allotted time, the glass mesh bucket (GMB) was removed from the solvent and weighed, for the determination of total amount of solvent adsorbed onto the bentonite's surface. The adsorption capacity (AC) in a static condition is calculated using equation 3

$$Ac = \frac{W_F - W_I}{W_I} \quad (3)$$

Where, W_F and W_I are the weight of the adsorbent after adsorption and before adsorption respectively.

Batch adsorption experiment

A measurement of 0.5 g of bentonite sample was placed inside a plastic container of 25 ml capacity and 20 ml of 50 mg/L of ethyl benzene solution was poured into the container containing the bentonite and quickly covered. The mixture was subjected to one hour shaking at 400 rpm using mechanical shaker (model number: J. P. SELECTA, 7000384) and thereafter the supernatant solution was carefully decanted and analyzed using UV - Visible spectrometer (model number: UV 3000). The analysis was repeated by varying adsorbate concentration (100mg/L, 150mg/L, 200 mg/L, and 250 mg/L), time (30 minutes, 90 minutes, 120 minutes and 150 minutes) and adsorbent weight (0.1g, 0.4 g, 0.7 g, 1.0 g and 1.3 g). The blank analysis was subsequently carried out for the determination of the rate of evaporation of the ethylbenzene and also to ensure that no reaction ever occurred between the container and the adsorbate (ethylbenzene). The percentage removal (% R) and the adsorption Capacity (q_e) are calculated using equation 4 and 5.

$$\text{Percentage removal (\% R)} = \frac{C_o - C_e}{C_o} \times 100 \quad (4)$$

$$\text{Adsorption capacity (} q_e \text{)} = \frac{C_o - C_e}{m} \times V \quad (5)$$

Where m is the mass of the adsorbent, V is the volume of the adsorbate, C_o and C_e are the initial and final concentration of the adsorbate, respectively (Chikwe et al., 2018).

RESULTS AND DISCUSSION

The FT- IR spectral result of DTAB modified calcium bentonite and unmodified calcium bentonite is shown in Figure 1. Figures 3 to 6 shows the Foster swelling indices of modified and unmodified calcium bentonite in aromatic compounds, petroleum products and water which is a universal solvent. Figures 7 and 8 showed the adsorption capacity of modified calcium bentonite at various DTAB concentrations in aromatic compounds (ethylbenzene, xylene and toluene) and petroleum products (PMS, DPK and diesel). Figures 9 and 10 showed the impact of contact time and initial concentration on the adsorption of ethylbenzene using modified calcium bentonite. Figure 8 shows the impact of contact time on percentage adsorption while Figure 9 shows the impact of initial concentration on adsorption capacity. Figure 11 is a graph showing the Langmuir isotherm model for ethylbenzene removal using calcium bentonite. Figure 12 is a graph showing the Freundlich isotherm model for ethylbenzene removal using calcium bentonite. Figure 13 is a graph illustrating Lagergren pseudo first-order for ethylbenzene removal using calcium bentonite. Figure 14 is a graph illustrating Lagergren pseudo second-order for ethylbenzene removal using calcium bentonite.

The spectral bands at wavenumbers 3369 cm^{-1} , 3598 cm^{-1} and 3697 cm^{-1} as shown in figure 2 indicates the presence of O-H stretch vibration in the silanol group. The spectral band at 1640 cm^{-1} shows the presence of H-O-H bending vibration whereas the broad band around 1047.1

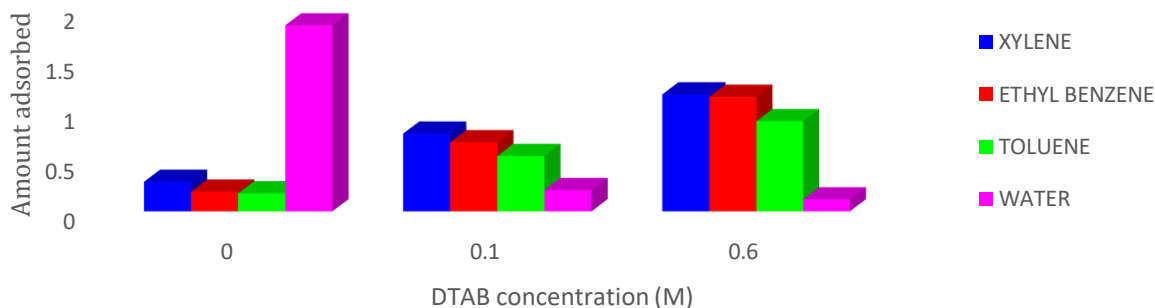


Fig. 7: Adsorption capacity of calcium bentonite in aromatic compounds at various DTAB concentrations

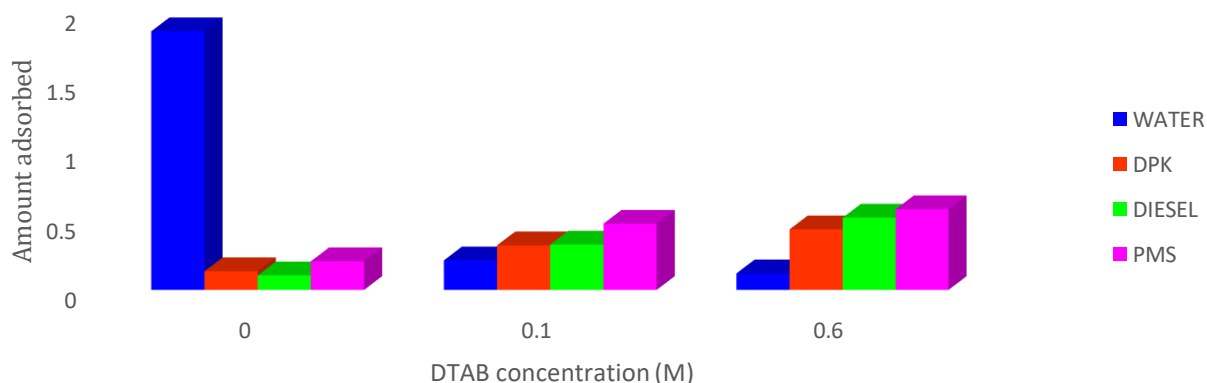


Fig. 8: Adsorption capacity of calcium bentonite in petroleum products at various DTAB concentrations

cm^{-1} and 1051.1cm^{-1} wavelengths are related to the stretch vibration of Si-O-Si groups. The modified calcium bentonite has two prominent peaks at 2834cm^{-1} and at 2997cm^{-1} which indicate the vibrational stretch of $-\text{CH}_2$ and $-\text{CH}_3$ respectively, this reveals the intercalation of dodecyltrimethylammonium bromide (DTAB) in the bentonite sample (Amin et al., 2010).

The Foster swelling indices of modified calcium bentonite at various DTAB concentrations in water is shown in figure 3. From the figure, it can be deduced that the higher the DTAB concentration of the bentonite, the lower the foster swelling index. Calcium bentonite with little or no DTAB concentration swell more in water (more hydrophilic) than those at higher DTAB concentration hence unmodified calcium bentonites swells more in water than the modified calcium bentonite. Figure 4 shows the Foster swelling indices of modified calcium bentonite in aromatic compounds and water. From Figure 4 it can be deduced that modified calcium bentonite swells more in aromatic compounds than in water. The swelling is most in xylene and least in toluene with the rate of swelling directly proportional to the DTAB concentration in the calcium bentonite. Figure 5 shows the Foster swelling indices of modified calcium bentonite in petroleum products and water. Just as with aromatic compounds, modified calcium bentonite swells more in

petroleum products than in water with the swelling most in gasoline and least in diesel. It is worthy to note that modified calcium bentonite swells more in aromatic compounds than in petroleum products this may not be unconnected with the fact that the petroleum products contains other hydrocarbon components other than aromatics which may interfere with the swelling tendencies of the bentonites. Figure 6 shows that unmodified calcium bentonite swells more in water (hydrophilic) than in petroleum products and this is to a large extent due to the organophobic nature of Ca-bentonite. DTAB reduces the polarity of the clay by creating a balance between the hydrocarbon solvents of low polarity and its (DTAB) alkyl chains (Stankovic et al., 2011).

Figure 7 and 8 shows the adsorption capacity of the modified calcium bentonite at various DTAB concentration in aromatic compounds and petroleum products. Results show that the adsorption capacity of the modified calcium bentonite increased with increase in DTAB concentration in both aromatic compounds and petroleum products. For the aromatic compounds, the adsorption capacity is highest in xylene and least in toluene whereas for petroleum products the adsorption capacity is highest in gasoline and least in diesel, however figure 8 shows that the adsorption capacity of diesel is at a higher rate at high DTAB concentration than that of DPK hence diesel has higher affinity for high DTAB-

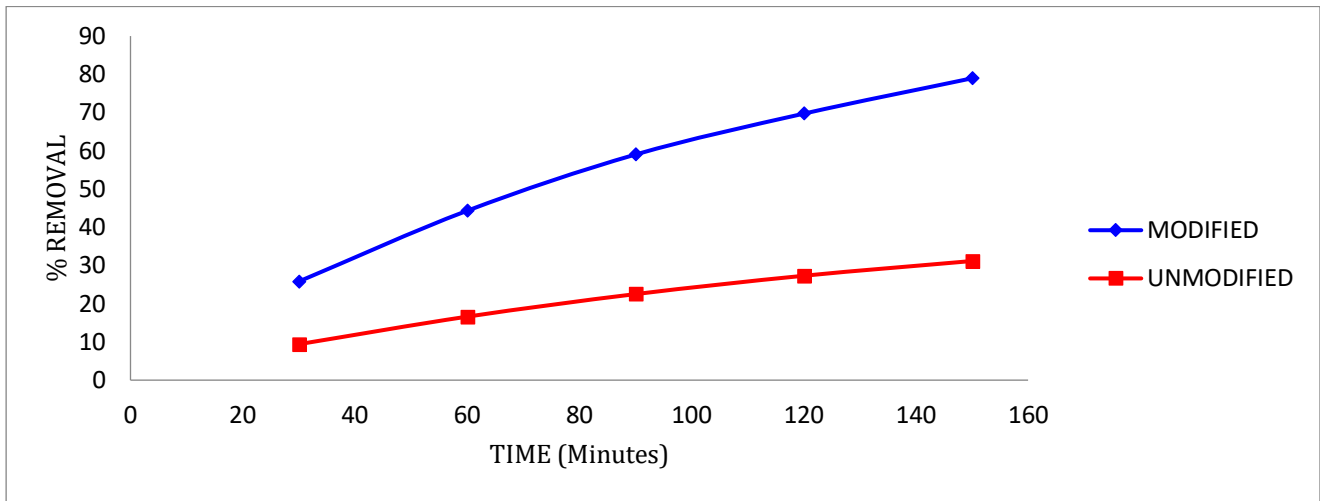


Fig. 9: Impact of contact time on percentage adsorption of ethylbenzene using calcium bentonite

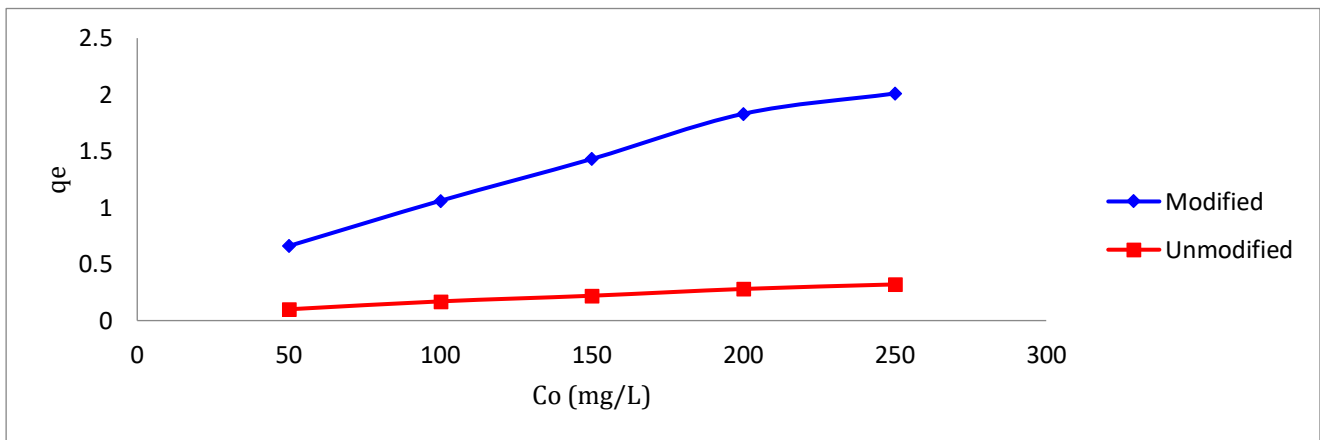


Fig. 10: Impact of initial concentration on adsorption capacity of ethylbenzene using calcium bentonite

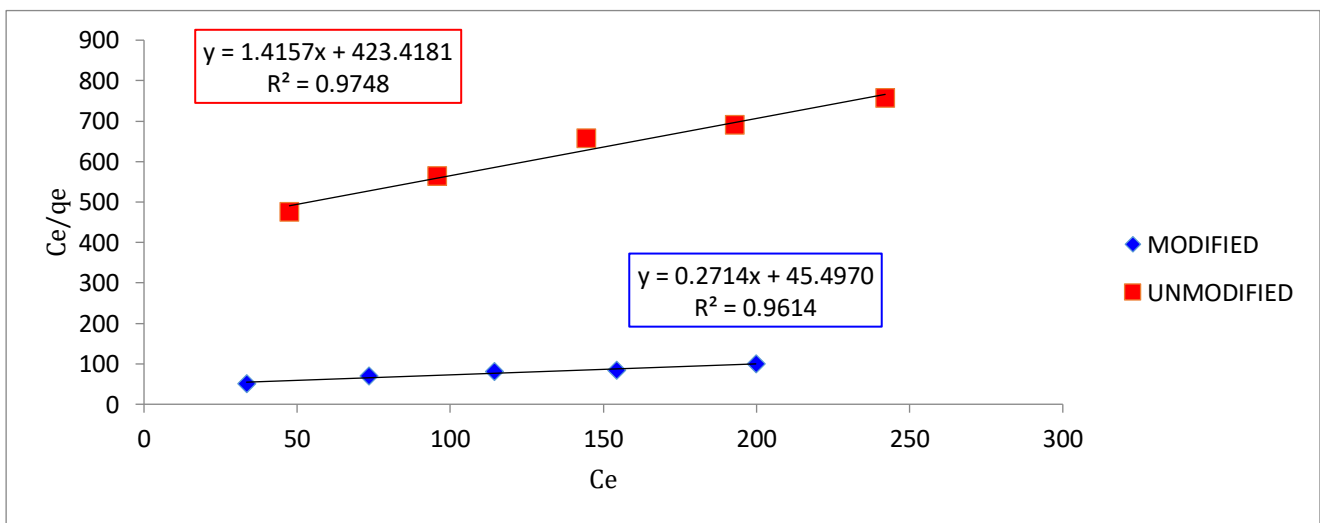


Fig. 11: Langmuir isotherm model for ethylbenzene removal using calcium bentonite

Table 1: Parameters obtained from Langmuir and Freundlich adsorption isotherm models

| Ethylbenzene | | | |
|----------------|----------------|-----------|---------|
| Isotherm Model | | MCB | UCB |
| | | Co (mg/L) | 250.000 |
| Langmuir | Qe (mg.g) | 2.0100 | 0.3200 |
| | K _L | 0.0060 | 0.0033 |
| | R _L | 0.4010 | 0.5460 |
| | R ² | 0.9214 | 0.9588 |
| | K _F | 0.0700 | 0.0065 |
| Freundlich | I/n | 0.6432 | 0.714 |
| | R ² | 0.9964 | 0.9781 |

MCB = Modified Calcium Bentonite, UCB = Unmodified Calcium Bentonite

Table 2: Parameters obtained from Pseudo first and Pseudo second order adsorption kinetics models

| Ethylbenzene | | | |
|------------------|----------------|-------------------------|-------------------------|
| Kinetics Model | | MCB | UCB |
| | | Co (mg/L) | 250 |
| Pseudo 1st order | qe (mg/g) | 7.89 | 3.12 |
| | K ₁ | 0.017 | 0.016 |
| | R ² | 0.9802 | 0.9709 |
| | qe (mg/g) | 7.89 | 3.12 |
| Pseudo 2nd order | K ₂ | 3.85 x 10 ⁻⁴ | 6.14 x 10 ⁻⁴ |
| | R ² | 0.9997 | 0.9988 |

MCB = Modified Calcium Bentonite, UCB = Unmodified Calcium Bentonite

concentration than DPK. Navigating through figures 3 through 8 it can be deduced that both parameters (Foster swelling index and adsorption capacity) are higher after agitating the test samples than before agitation, this affirms that homogenizing the samples during experiment is key to achieving optimum results. S

Figures 9 and 10 showed that both the contact time and initial concentration are directly proportional to the adsorption capacity of the adsorbents. Figure 9 shows that the higher the contacts time between the adsorbents and the organic solvent (ethylbenzene), the higher the percentage removal of the organic solvent. Figure 10 shows that the higher the initial concentration of DTAB which in this case is used to modify the calcium bentonite, the higher the adsorption capacity of the adsorbents.

The Langmuir isotherm model is based on the assumption that adsorbate adsorption occurs at a homogeneous specific site on the adsorbent's surface. According to this model, adsorption ceases to occur once the adsorbent sites are occupied by the adsorbate's molecules (Kumar et al., 2010). Mathematically, the Langmuir adsorption isotherm model is expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (6)$$

Where, C_e is the concentration (mg/L) of the adsorbate at equilibrium while q_e, which is the adsorption capacity, refers to the quantity or amount of adsorbate removed or adsorbed from the solution per unit weight of the adsorbent. K_L is the langmuir constant while q_m is the maximum capacity of the adsorbent. The values of K_L and q_m are obtained from a linear

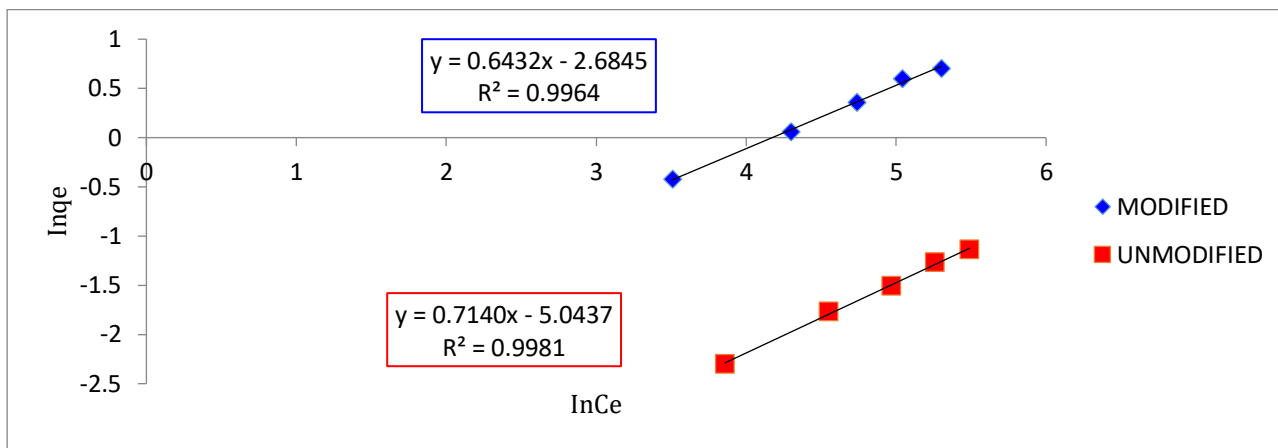


Fig. 12: Freundlich isotherm model for ethylbenzene removal using calcium bentonite

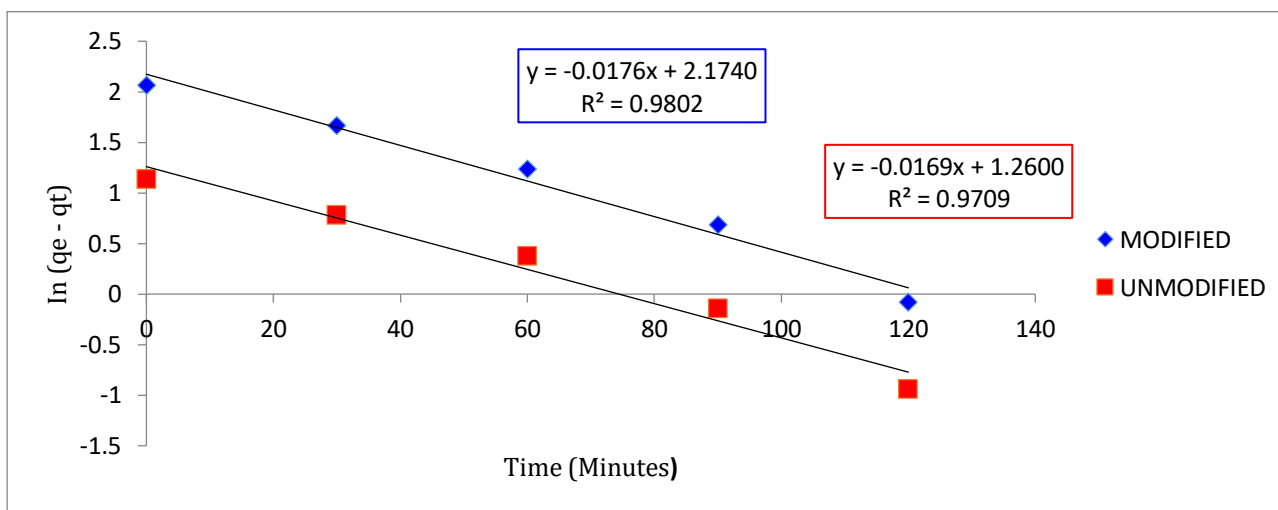


Fig. 13: Lagergren pseudo first-order for ethylbenzene removal using calcium bentonite

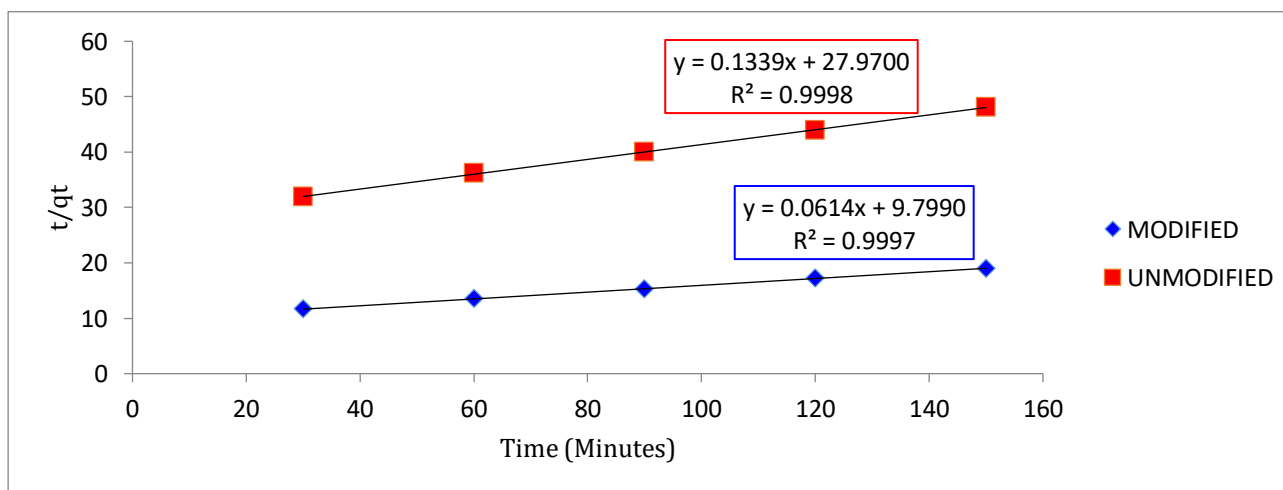


Fig. 14: Lagergren pseudo second-order for ethylbenzene removal using calcium bentonite

plot of C_e/q_e against C_e . K_L is the slope of the graph while q_m is the y-axis intercept. Langmuir separation factor, R_L is an important equilibrium parameter which helps to analyze the properties of the Langmuir isotherm model. The mathematical expression of the Langmuir separation factor, R_L is given as;

$$R_L = \frac{1}{1 + (K_L C_0)} \quad (7)$$

Where, K_L and C_0 are Langmuir constant (L/mg) and the adsorbate's initial concentration (mg/L) respectively. If the separation factor, $R_L = 0$, adsorption is considered to be irreversible, if $R_L = 1$, it is considered to be linear but if $R_L > 1$, it is considered to be unfavorable. Adsorption is only considered to be favorable if $1 > R_L > 0$. (Chikwe et al., 2018).

The correlation factors (R^2) obtained from Langmuir model for the removal of ethylbenzene using modified and unmodified calcium bentonite are 0.9214 and 0.9588 respectively as shown in Table 1. The Langmuir separation factors (R_L) for ethylbenzene removal using modified and unmodified calcium bentonite are less than unity but greater than zero as shown in Table 1. This indicates that the adsorption bonds between the adsorbent and the adsorbate are very strong and adsorption is highly favored.

The Freundlich isotherm model assumes that adsorbate adsorption occurs on the heterogeneous adsorbent's surface, thereby resulting to the emergence of multiple layers on the surface. It is an empirical adsorption isotherm model which describes the equilibrium relationships that exist between the adsorbate and the adsorbent molecules and assume multi-layer adsorption on the heterogeneous site of the adsorbent unlike the Langmuir model which assumes formation of a single layer or monolayer (Kumar et al., 2010). The Freundlich isotherm model is mathematically represented as

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (8)$$

Where, q_e and C_e are the adsorption capacity (mg/g) and the concentration (mg/L) of the adsorbate at equilibrium. The values of $1/n$ and k_F are obtained from the linear plot of $\ln q_e$ against $\ln C_e$. $1/n$ is the slope of the graph while k_F is the intercept on y-axis (Chikwe et al., 2018).

The correlation factors, R^2 obtained from Freundlich isotherm model for modified and unmodified calcium bentonite are 0.9964 and 0.9781 respectively as shown in Table 1. Table 1 shows that the Freundlich constant ($1/n$) with respect to the heterogeneous surface is less than unity this indicates that the adsorption is favorable.

Adsorption kinetics is a very useful tool which gives a better comprehension of adsorption processes and mechanism. It also helps to examine the adsorbent's performance. The three kinetics models commonly used are Lagergren pseudo-first-order kinetics, pseudo second-order kinetics and intra particle diffusion kinetics (Kumar et al., 2010). In order to investigate the adsorption kinetics of the hydrocarbons onto the adsorbents, Lagergren's pseudo first

and second order were applied to the experimental data. The linearized form of the pseudo first order can be mathematically represented as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

Where, q_e and q_t are the amount of the hydrocarbon adsorbed at equilibrium (mg/g) and time t (min), respectively, and k_1 is the rate constant of the equation (min^{-1}) which can be obtained by plotting $\ln(q_e - q_t)$ versus t . The plot of $\ln(q_e - q_t)$ versus t as shown in Figure 12 reveals that the data obtained from the hydrocarbon adsorption using unmodified and DTAB – modified calcium bentonite are not well fitted with pseudo first order kinetics. The linearized form of pseudo second order equation is expressed as;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where, k_2 ($\text{mg.g}^{-1} \text{min}^{-1}$) is the rate constant for the second order equation, q_t (mg/g) is the amount of hydrocarbons adsorbed at a particular time t (min) and q_e (mg/g) is the amount of hydrocarbons adsorbed at equilibrium. A plot of t/q_t versus t as shown in Figure 12 gives a linear relationship, from which q_e and k_2 can be obtained from the slope and intercept of the plot respectively. Linear plots were obtained with high correlation coefficients (R^2), which are far closer to unity compared to pseudo first order as shown in Table 2, suggesting that the interaction between the adsorbent and the adsorbate (ethylbenzene) follow second order mechanism. From this observation it can be deduced that the rate determining step for the adsorption of ethylbenzene using DTAB modified calcium bentonite is bimolecular involving the adsorbents and adsorbates (Chikwe et al., 2018).

CONCLUSIONS

The adsorption of organic solvents such as aromatic compounds (xylene, ethylbenzene and toluene) and petroleum products (gasoline, DPK and diesel) were successfully carried out using unmodified and DTAB modified calcium bentonites. Modified calcium bentonite has a higher percentage removal and higher adsorption capacity for the organic solvents than raw or unmodified calcium bentonite with the adsorption capacity and percentage removal directly proportional to the concentration of the DTAB modifier and contact time between the adsorbents and adsorbates. Characterization of the bentonites using Foster swelling test and adsorption capacity measurement revealed that the raw unmodified calcium bentonite showed a higher level of hydrophilicity than the DTAB modified bentonite. Data obtained from adsorption isotherm for ethylbenzene removal by batch adsorption technique affirms that Freundlich adsorption isotherm was more favored than Langmuir isotherm while data obtained from adsorption kinetics affirms the suitability of pseudo second order kinetics over pseudo first order kinetics. DTAB modified calcium bentonite has proven to be an effective adsorbent for

removal of organic solvents (aromatic compounds and petroleum products) from their aqueous solution, hence water treatment and petrochemical industries can utilize this adsorbent for the removal of aromatics such as xylene, ethylbenzene and toluene from waste water and effluents, Petroleum industries can also take advantage of it during clean up exercises after oil spillage.

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