SYNTHESIS AND CHARACTERIZATION OF ORGANOPHILIC BENTONITE FOR PRODUCED WATER TREATMENT

ABSTRACT

This study investigates the synthesis and characterization of organophilic bentonite,from natural organophobic bentonite from Ebenebe Anambra State, Nigeria. The clay was used after milling and drying at $110^{o}C$ overnight. The natural bentonite was then converted to sodium bentonite via ion exchange process using sodium carbonate. The Sodium exchanged bentonite (SEB) was modified through incipient wetness impregnation and ion exchange technique with dimethyldioctadecylammonium bromide (DMDOA) to obtain organophilic bentonite. The mineralogical characteristic of the clays was determined before and after modification using Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Fluoresence (XRF). Different organic solvents, namely kerosene, diesel, gasoline, xylene, ethyl benzene and toluene, were used to investigate the organophilic nature as well as the adsorption capacity of the modified bentonite. The XRF result showed from the Si/Al ratio that modification did not affect the basic structure of the bentonite. The FTIR result showed bands which are attributable to asymmetric and symmetric stretching vibration of CH_2 group of the alkyl chains present in DMDOA. Another band was also assigned to the asymmetric angular deformation of the CH_3 group of dimethyl ammonium quaternary group. The modified samples showed higher affinity as well as higher sorption capacity to organic solvents compared to SEB and the order of adsorption capacity for these organics are diesel > kerosene > gasoline and toluene > ethylbenzene > xylene. The results show that the organophilic bentonite clay has potential for the removal of organics in produced water.

Keywords: Bentonite clay, Organophilic, Dimethyldioctadecylammonium bromide, Adsorption

INTRODUCTION

The quest for cleaner industrial effluent has been of concern to industries, regulatory and non-governmental organizations. Also, there is a quest for increased local content in the oil and gas sector in oil producing nations like Nigeria. Natural Bentonite, a smectite clay, is a hydrophilic mineral which consist mainly of montmorillonite, and possesses a 2:1 layered structure with a single octahedral aluminum layer sandwiched between two layers of tetrahedral silicon, and has a chemical formula of $(Na,Ca)_{0.33}(Al_{1.67},Mg_{0.33})Si_4O_{10}(OH)_2.nH_2O$, which varies depending on the source of clay [1-3]. A tetrahedron is composed of central silicon surrounded by four oxygen ions in a tetrahedral coordination whereas an octahedron is composed of central aluminium surrounded by six oxygen or hydroxyl ions in an octahedral coordination [4-6]. Upon isomorphous substitution from Si^{4+} to Al^{3+} in the tetrahedral sheet, or from Al^{3+} to Mg^{2+} or Fe^{2+}, or from Mg^{2+} to Li^+ in the octahedral sheet, a negative superficial charge is generated on the clay. This unbalance of charges is compensated by the cations Na^+ or Ca^{2+} exchanged on the surface of the clay, which is hydrophilic and therefore ineffective for adsorption of organic compounds. Thus, they are good adsorbents for ionic and polar compounds but not non ionic and hydrophobic compounds [5,6,7,8,9,10]. Smectites are valuable mineral class for industrial applications because of their high cation exchange capacities, surface area, surface reactivity and adsorptive properties. When large organic cations (derived from organic surfactants) of the form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$, where R is a long alkyl group (with 12 or more carbon atoms), accommodate on the exchanging sites of the bentonite, the surface properties change from hydrophilic to hydrophobic

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character. The combination of the hydrophobic character and the layer-like layer structure of the silicates lead to these singular physico-chemical properties, and the behavior and properties of the organoclays depend on their structure and which organic molecules can be found inside their galleries [11]. The cationic molecule portion of quaternary salts occupies the sites previously occupied by sodium cations, while the long organic chain remains intercalated in the clay lamellae [12]. The organically-modified clays turn into organophilic clays, whereby their surface energy is decreased with more affinity to organic liquids [13]. Several organophilic clays have proved to be highly efficient in removing organic contaminants from water, adsorb oil and fuel spills, industrial wastes, and so on [12, 13, 14]. Organoclays remove oil and grease from water at a rate, seven times that of activated carbon [15]. The objective of this work is to prepare and characterize organophilic bentonite clay suitable for the removal of organic contaminants in an aqueous system.

2. EXPERIMENTLS
2.1. Materials
Natural bentonite, was obtained from Ebenebe in Anambra State, Nigeria and was converted to sodium bentonite. Dimethyldioctadecylammonium bromide (DMDOA; $C_{38}H_{80}BrN$) at 98% purity was obtained from Sigma-Aldrich, Co (Switzerland), while Sodium Carbonate (Na_2CO_3) was purchased from Gauteng, South Africa. Toluene, ACS grade was from HACH Company USA. Xylene and ethyl benzene from Aldrich USA. Kerosine, gasoline and diesel oil were obtained from NNPC filling station, Port Harcourt, Nigeria. All reagents were used without further purification.

2.2. Modification of the Samples

Preparation of Sodium bentonite

This analysis was done following a method described in Yildiz et al, 2002 [16]. 10 g of natural bentonite was dispersed in 250 ml of deionized water and stirred using magnetic stirrer for 15 minutes. A pre-dissolved amount of sodium carbonate (Na_2CO_3) was added slowly to the clay suspension at 65^0 C. The suspension was stirred slowly and continuously with magnetic stirrer under reflux for 4 hrs. The mixture was filtered and washed thoroughly using filter press (API standard) to remove the carbonate. The sodium bentonite cake was collected and dried in an oven at 110^0 C. The dried sample was ground and sieved through a 200 mesh sieve and stored for experimental use.

Preparation of Organoclay by incipient wetness (IW) impregnation technique

10 g of the sodium exchanged bentonite was first dispersed in 200 ml of deionized water then stirred with magnetic stirrer for 10 minutes. A pre-dissolved amount of DMDOA solution was added to the clay suspension at 65 ^{0}C. The reaction mixtures were stirred to a point of near dryness at the same temperature. The organophilic clay was dried in oven at 110 ^{0}C. Finally, the organophilic clay was ground and sieved through a 200 mesh sieve and then stored in an air tight container for further characterization.

Preparation of Organoclay by ion exchange (IE) method

10 g of the sodium bentonite was first dispersed in 200 ml of deionized water then left under magnetic stirring for 10 minutes. A pre-dissolved amount of DMDOA solution was added to the clay suspension at 75 ^{0}C. Concentrations of DMDOA used ranged from 0.008 to 0.06 moles/dm^3. The reaction mixtures were stirred for 5 hours at the same temperature. The organophilic clay was filtered and washed with deionized water repeatedly to remove sodium and bromide ions. The cake was collected using filter press (API standard) and dried in an oven at 110 ^{0}C. Finally, the organophilic clay was ground and sieved through a 200 mesh sieve and then stored in an air tight container for further characterization.

2.3. Characterization of the Samples

The sodium exchanged bentonite and the organophilic bentonite clays were characterized through the following methods:

X-Ray Fluorescence (XRF)

The X-ray fluorescence was performed using Spectro Xepos – Amakek – 11001700 to determine the elemental composition of the samples.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used for the determination of the framework vibrations and the organic functionalities. The samples were subjected to a physical treatment using the KBr disc method, which consists of mixing 0.001 g of the sample and 0.1 g of KBr, grinding and pressing the solid mixture to 5 ton within 30 s in order to form a pellet that allows the passage of light. The FTIR characterization was done using Shimadzu IR Prestige 21 FTIR, A210042 ranging in wavelengths from 4000 to 400 cm^{-1}, with increments of 500 cm^{-1} after 16 scans and resolution of 4 cm^{-1} at room temperature.

Adsorption Capacity

Kerosene, gasoline, diesel oil, xylene, ethyl benzene and toluene sorption capacities were measured following a method based on the "Standard Methods of Testing Sorbent Performance of Adsorbents" [17-18]. In this method, the adsorbent sample was weighed and the exact value recorded. The test cell was filled with the test liquid and the adsorbent sample placed in a 200-mesh stainless steel basket and lowered into the test cell. The sample was allowed to float freely within the test cell. After 1 hr $\pm$ 0.33 minute, the basket with the adsorbent was removed manually in a vertical direction and allowed to drain for 15 seconds $\pm$ 3 seconds. A weighing support was placed under the adsorbent sample/mesh basket set to catch any additional drips and the entire system finally weighed. All the tests were conducted in duplicate with a minimum of two runs used for calculations. Based on the data obtained, the adsorbed solvent was calculated as the weight ratio of adsorbed solvent to dry adsorbent. The results of the adsorption capacity are reported in grams of solvent adsorbed per gram of clay using equation 1 below:

$$AC = \frac{P_1 - P_2}{P_2} \times 100 \qquad (1)$$

Where:
P_1- weight of the material after adsorption, in g;
P_2– weight of dry adsorbent material, in g;
AC – efficiency of adsorption to adsorbent tested, in %.

3. Results and Discussion

3.1. X-Ray Fluorescence (XRF)

The X-ray fluorescence (XRF) technique was used to determine the chemical composition of the clay and presented in Tale 1. Table 1 shows a characteristic elementary composition of the clays. It was observed that Silicon, Aluminium and Iron are present in more amounts while other elements are in lesser amounts, which are in agreement with the work by Maria et al. [18], Araujo et al. [20] and Regina et al [21]. The untreated clay (SEB) result shows the presence of sodium and bromine residues. While the organophilic

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clays prepared by ion exchange technique, shows the absence of sodium due to ion exchange of sodium with the quaternary ammonium cation (DMDOA) and the presence of bromine is more significant especially at high concentration of the ammonium salt which could indicate that washing process was not efficient. The silicon to aluminum ratio remained constant for all the samples, this clearly indicates that modification did not affect the basic structure of the bentonite clay. The presence of Bromine and Sodium in the organophilic clay prepared by incipient wetness impregnation technique can be attributed to no filtering or washing after modification.

Table 1. Chemical composition of sodium exchanged bentonite (SEB) and organophilic clays (DMDOA) prepared by ion exchange and incipient wetness impregnation techniques.

Mineral Composition (%)										
Clay Type	Si	Al	Fe	Mg	Ca	Ti	Na	K	Br	Si/Al
SEB	52.71	21.16	15.73	6.21	0.11	1.68	4.12	1.22	0.0003	2.49
DMDOA-0.008M-IE	53.25	21.08	15.50	6.17	0.18	1.65	-	1.30	0.09	2.51
DMDOA -0.02M-IE	53.10	21.06	15.60	6.13	0.16	1.62	-	1.22	0.23	2.52
DMDOA -0.04M-IE	54.17	19.61	15.51	6.53	0.12	1.65	-	1.20	0.39	2.76
DMDOA -0.06M-IE	53.68	19.56	15.09	6.60	0.14	1.63	-	1.16	1.42	2.74
DMDOA -0.02M-IW	54.14	19.59	15.39	6.57	0.18	1.60	4.10	1.24	11.01	2.76

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR studies of the sodium exchanged bentonite SEB and the organophilic bentonite DMDOA clays were conducted and reported in Figures 1 a, b, c, d, e and f. From Figure 1, FTIR spectra of the sodium exchange bentonite (SEB) and organophilic bentonite clays (DMDOA) prepared by ion exchange and incipient wetness impregnation techniques confirmed the nature of modification and functional group attachment. The bands at 1035.77 and 904.61 cm^{-1} correspond to the bending vibrations of Si–O and Al–O, respectively. This agrees with previous studies [22,23]. The bands at 464.84, 509.21 and 3620.39 cm^{-1} are due to the stretching vibrations of Al–O–Si and OH groups in bentonite. The bands at 1467 cm^{-1} (Fig. 1b), 1467 cm^{-1} (Fig. 1c), 1485 cm^{-1} (Fig. 1d), 1463 cm^{-1} (Fig. 1e), and 1467.83 cm^{-1} (Fig. 1f) correspond to asymmetric angular deformation of the CH_3 groups from the ammonium cation, suggesting that the ammonium ion has been intercalated into the interlayer galleries of the organophilic clay. The bands at 2922 to 2850 cm^{-1} (Fig. 1b), 2920 to 2850 cm^{-1} (Fig. 1c), 2927 to 2848 cm^{-1} (Fig. 1d), 2968 to 2839 cm^{-1} (Fig. 1e) and 2920.23 to 2850.79 cm^{-1} (Fig. 1f), are due to the stretching vibrations of symmetric and asymmetric CH_2 groups [24]. The band at 1629 cm^{-1} (Fig. 1a-f), indicates the presence of adsorbed water within the interlayer of bentonite. It was also observed that the peaks were sharper and more intense as the concentration of the surfactant increases. Nevertheless, most bands are identical after modification, suggesting that the core crystal structure of SEB and the organophilic clays remains. The presence of CH_2 and CH_3 groups in the infrared spectra of the organophilic clays is good evidence that the quaternary ammonium cation has been intercalated into the interlamellar spaces of the organophilic clays. These observations are in agreement with recent work by Hongping et al. [25] and Pereira et al. [12].
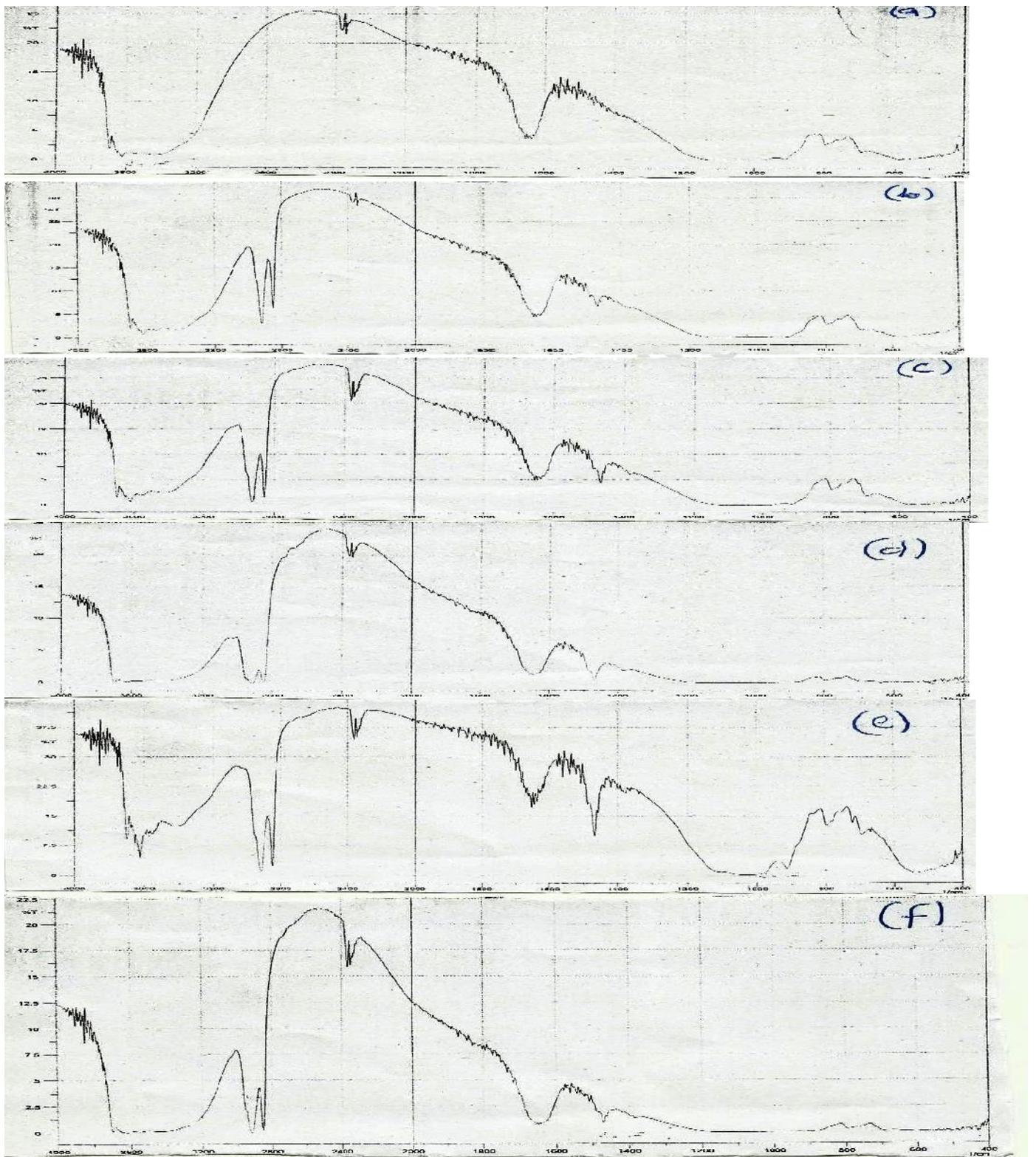
Figure 1: Infrared spectra of, a) SEB; b) DMDOA-0.008M-IE; c) DMDOA-0.02M-IE; d) DMDOA-0.04M-IE; e) DMDOA-0.06M-IE; f) DMDOA-0.02M-IW

3.3. Adsorption Capacity

Figures 2-5 show the adsorption capacity of sodium exchanged bentonite (SEB) and organophilic clays prepared by ion exchange and incipient wetness impregnation techniques in different organic solvent and water. It was observed that the organophilic clays adsorbed xylene, ethyl benzene, toluene, gasoline, kerosene, and diesel more than the SEB but there is higher affinity for diesel and toluene than other organic solvent. This means that the organic solvent adsorption capacity of the organophilic clays is higher than SEB and this agrees with previous studies on organoclays used to remove petroleum hydrocarbons [26, 12]. The adsorption capacity follows the order: Toluene > Ethyl benzene > Xylene in figures 2 and 4 while figure 3 and 5 follows the order: diesel > kerosene > gasoline. The study demonstrates that the organophilic bentonite clays are more efficient material for the removal of hydrocarbons.
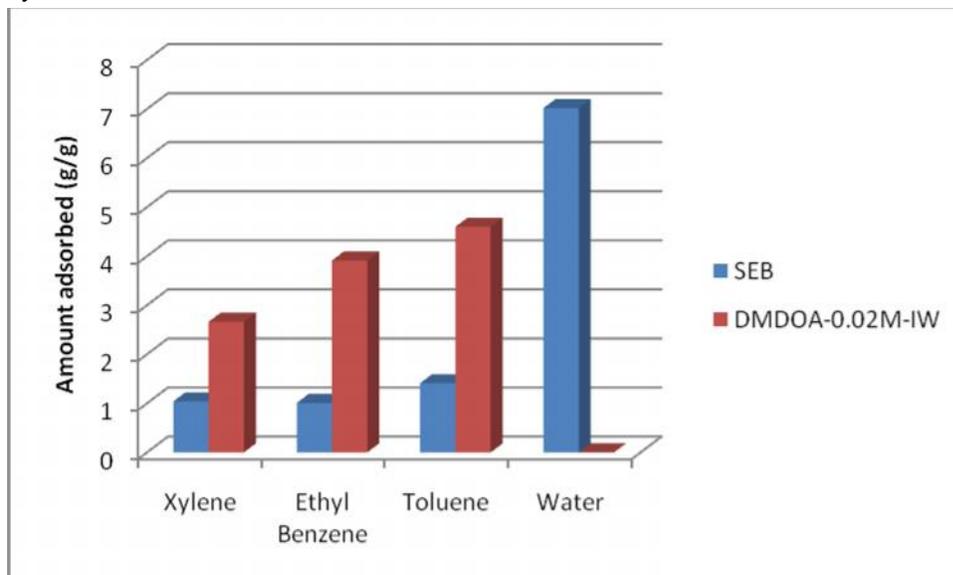

Figure 2. Adsorption capacity of sodium exchanged bentonite (SEB) and organophilic clay (DMDOA-0.02M-IW) prepared by incipient wetness impregnation technique in Xylene, Ethyl benzene, Toluene and water

Table 2 gives the hydrocarbon adsorption capacities of SEB and organophilic clays and this clearly shows that the organophilic clays adsorbs more than the SEB. The obtained results compared favorably with previously reported data [26], though slightly lower possibly due to low concentrations of the quaternary ammonium compound used in the present study. In Figures 2-5, the SEB has higher affinity for water than the organophilic clays. However, the amount of water adsorbed reduced significantly upon modification. This is a clear demonstration of change from hydrophilic to organophilic.
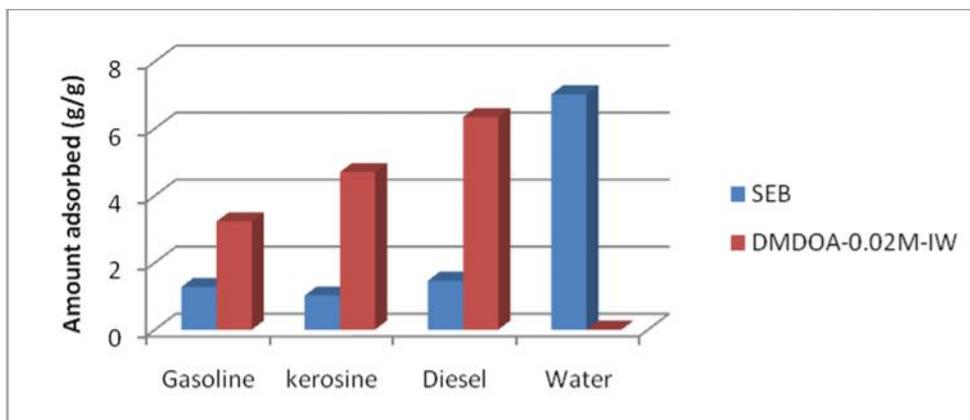
Figure 3. Adsorption capacity of sodium exchanged bentonite (SEB) and organophilic clay (DMDOA-0.02M-IW) prepared by incipient wetness impregnation technique in gasoline, kerosene, diesel and water
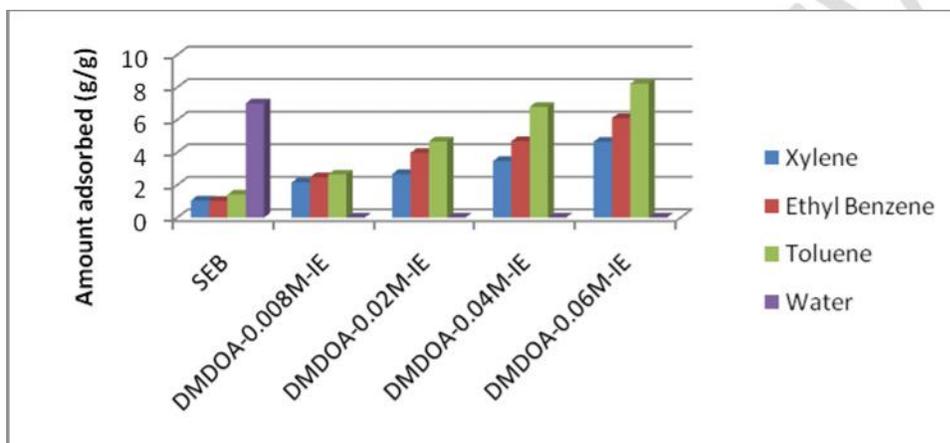

Figure 4. Adsorption capacity of sodium exchanged bentonite (SEB) and organophilic clay in different concentrations of DMDOA prepared by ion exchange technique in Xylene, Ethyl benzene, Toluene and water
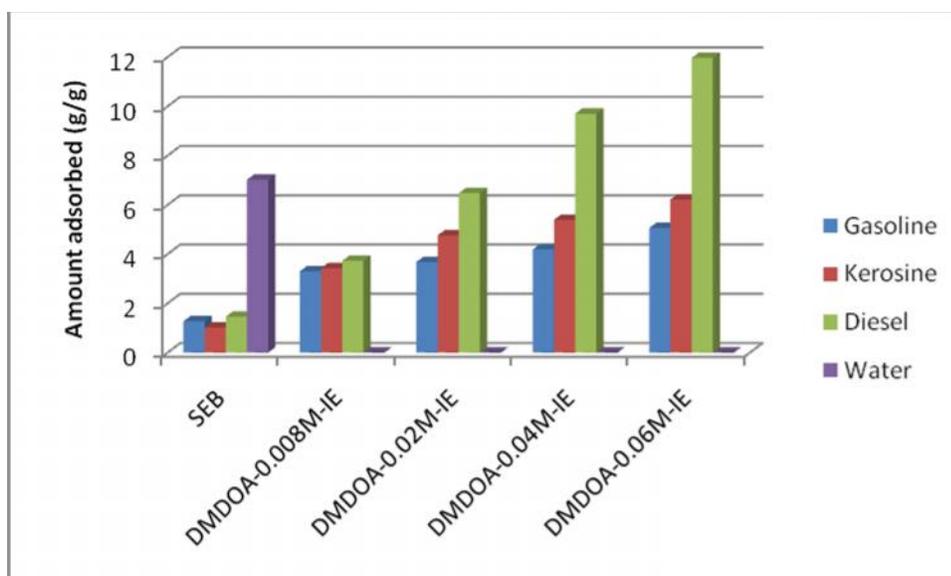
Figure 5. Adsorption capacity of sodium exchanged bentonite (SEB) and organophilic clay in different concentrations of DMDOA prepared by ion exchange technique in gasoline, kerosene, diesel and water

Table 2. Result of adsorption capacities of sodium exchanged bentonite (SEB) and organophilic clays prepared by ion exchange and incipient wetness impregnation techniques

Adsorbent	Xylene	Ethyl Benzene	Toluene	Gasoline	Kerosene	Diesel	Water
SEB	1.04	1.01	1.41	1.27	1.02	1.46	7.02
DMDOA-0.008M-IE	2.15	2.47	2.64	3.30	3.43	3.73	0.01
DMDOA-0.02M-IE	2.68	3.98	4.68	3.68	4.76	6.47	0.01
DMDOA-0.04M-IE	3.47	4.69	6.80	4.19	5.39	9.70	0.01
DMDOA-0.06M-IE	4.66	6.11	8.23	5.06	6.22	11.96	0.01
DMDOA-0.02M-IW	2.66	3.91	4.60	3.23	4.70	6.34	0.01

4. Conclusions

This study shows that the introduction of a new cost effective sorbent material and its modification with two long alkyl chain quaternary ammonium compound through ion exchange and incipient wetness impregnation technique, which are synthesized by introducing organic molecules into the clay structure, could be effective for the removal of organics in produced water before discharge into the sea. The organophilic clays were found to be more effective than sodium exchanged bentonite and could provide a solution for both land and water pollution control.

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