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# Characterization of Jordanian Raw Bentonite and Surfactant-Modified Bentonite and their Use in the Removal of Selected Organic Pollutants from Aqueous Solutions

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## ABSTRACT

*Adsorption of aniline, N-methyl aniline and N, N – dimethyl aniline from aqueous solution was investigated using raw and modified Jordanian bentonite. The modification was done using hexadecyltrimethylammomium chloride (HDTMA-Cl),* $C_{19}H_{42}N\,Cl$*. The raw and the modified bentonite (organobentonite) were characterized using X-Ray fluorescence spectroscopy (XRF), X-Ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), UV/VIS spectroscopy and cation exchange capacity (CEC) methods. The adsorption studies were performed in batch system, and the effect of various experimental parameters such as solution PH, initial concentration of pollutants were evaluated upon the aniline and its derivatives adsorption onto raw and organobentonite. It is found that removal of aniline from aqueous solution using raw bentonite ranges from 29.5% to 40.6% while for organobentonite ranges from 60.2% to 88.0%, for N-methylaniline from 19.0% increased to 69.5% and for N,N-dimethyaniline the adsorption increase from 19.4% to 96.4%. Maximum achievement was found to be in the range PH 3.1 to 4.2 for the organobentonite samples. The parameters indicated that organobentonite was feasible and has a significant potential as an adsorbent for removal of aniline and its derivatives from aqueous solutions.*

**Keywords:** Raw Bentonite; Cationic Surfactant; Organic Pollutants; Surfactant-Modified Bentonite.

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## INTRODUCTION

The term “bentonite” is a rock formed of highly colloidal and plastic clays composed mainly of montmorillonite which is a hydrous aluminum silicate containing small amounts of alkali and alkaline-earth metals. The montmorillonite lattice is negative in charge; this negative character is balanced by cations which are held on the surface of the flakes. Cations held in this fashion by the clay can be readily exchanged. [1]

Bentonite deposits were first reported in Q'a Al Azraq 70 Km east of Amman. After that many authors and researchers have studied bentonite ores in Jordan, they found that the major constituent of the clay minerals are mixed layer illite/smectite, montmorillonite, palygorskite and kaolinite. Bentonite whose main component is montmorillnite, is potentially important adsorption material because of its large surface area, large number of inter layer exchangeable inorganic cations and abundance in nature. [2] Aniline is usually used by the chemical industry in many processes such as the synthesis of dyes and several pesticides. It is also a common by-product from paper and textile industries. Aniline and its derivatives are known to be toxic water pollutants and their persistence in wastewater even in very low concentrations has been shown to be harmful to aquatic life [3].moreover, aniline can be easily adsorbed in sediments, fact that can extend its persistence in the aquatic environment [4]. There are many processes, including biodegradation [5], oxidation by ozone [6], lignad exchanger [7], adsorption [8 ]and some other processes that can be used for the removal of aniline from wastewater. These processes can decompose or remove aniline in wastewater to some extent, but it is very difficult to decompose aniline completely [9].

In this work the Jordanian natural bentonite was chemically modified by hexadecyltrimethyammonium chloride (HDTMA-Cl).The capability of natural bentonite and surfactant-modified bentonite to uptake aniline, N-methylaniline, N,N-dimethylaniline from water were investigated.

## MATERIALS AND METHODS

**Sample Preparation:** Samples of Jordanian bentonite from Q'a Al Azraq were obtained from BT-14 borehole by Natural Resources Authority. These natural bentonite samples were crushed gently using glass rod, then sieved to remove particles greater than 120 mesh (<250 µm). The bentonite portions of particle size less than 120 mesh were used in further purification this purifications process was done using the following procedure: A samples of particle size less than 250 µm were mixed with distilled deionized water (conductivity=0µs/cm) and then shaken at 25° C and 150 rpm for 24 hr on a thermostatic shaker (kühner/ISF-1-W), after samples were filtered it is dried in an oven (Mido/1/SS / Dis) at 105$^o$ C, then kept in a desiccators at room temperature for further use and labeled (NB).

**Surfactant Modification:** Natural Jordanian-bentonite was modified by hexadecyltrimethyammonium chloride (HDTMA-Cl, 96%, from Fluka) at 100% of ECEC. 100% represent monolayer coverage. About 30 g of raw bentonite were mixed with 90 mL of 67 mmol/L of HDTMA-Cl to obtain 100% of its ECEC. Bentonite mixture was shaken for 8 hr at 25°C and 150 rpm on a thermostatic shaker, followed by centrifuging and washing with two portions of distilled water. The surfactant-modified samples were then air dried prior to further use, [10] showed that final HDTMA surface coverage for surfactant-modified - bentonite prepared in this manner was 98-100% of the target values and labeled (SMB).

**Characterization of Bentonite Samples:** Samples NB and SMB were characterized by ascertaining their chemical composition ,mineral constitution and chemical characterization using powder X-ray diffraction (XRD) using a Philips X' Pert Pro PW 304/60 instrument, with operation conditions 45 kv and 40 mA and using copper tube [λ (CuKa) =1.45 nm]. The starting angle is 2.00$^o$ and end angle is 80.00$^o$.The X-ray fluorescence (XRF) data were recorded with Philips Magix PW 2424, operated at 50 KV and 10rn A, and infrared spectroscopy (FT-IR) techniques, besides determining their Cation Exchange Capacity (CEC) by the Modified-Kjeldahl Method without Digestion [11]. The infrared spectra were obtained using a double beam FTIR (Jasco FTIR, 410) with a resolution of 4cm$^{-1}$.

**Pollutants Uptake:** The prepared concentrations of organic pollutants range between 5-200 ppm. Absorbance measurements were done by UV/VIS spectrometer type, the wavelength corresponding to maximum absorbance (λ max) of organic pollutants was determined by scanning a standard solution of known concentration at deferent wavelength. Absorbance values of aniline, N-Methylaniline and N-N Dimethylanililine were recorded at wavelength at maximum absorbance, found to be 254,270,280 nm respectively shown in figures (1, 2).

**Effect of Initial Concentration of pollutant**: A 1.0 g of dried NB/SMB was mixed with 10.0 ml of either aniline, N-Methylaniline and N, N-Dimethylaniline solution (initial concentrations was 5, 15, 25, 50, 100, and 200 ppm); the samples were shaken at 25° C and 150 rpm for 24 hr, on a thermostatic shaker. After that samples were filtered using syringe filter 0.45 µm to yield a clean supernatant for analysis of the equilibrium solute concentration by UV/VIS spectrophotometer (Thermo Scientific Evolution 160) at λmaxfor aniline, N-Methylaniline and N, N-Dimethylaniline respectively

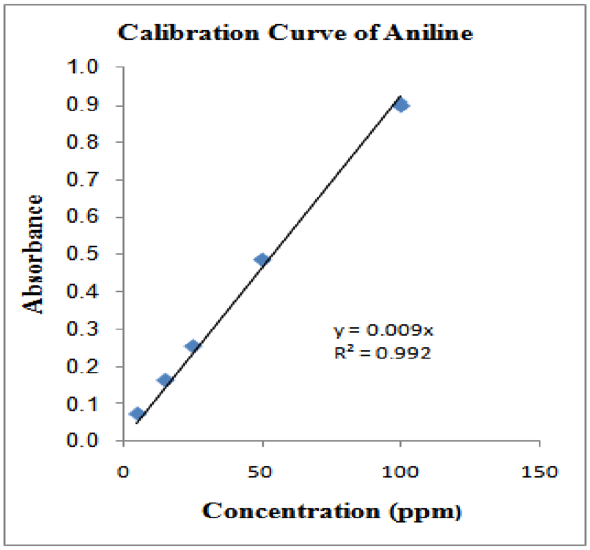

**Figure 1:** Calibration Curve of Standard Aniline Solution at 254 nm

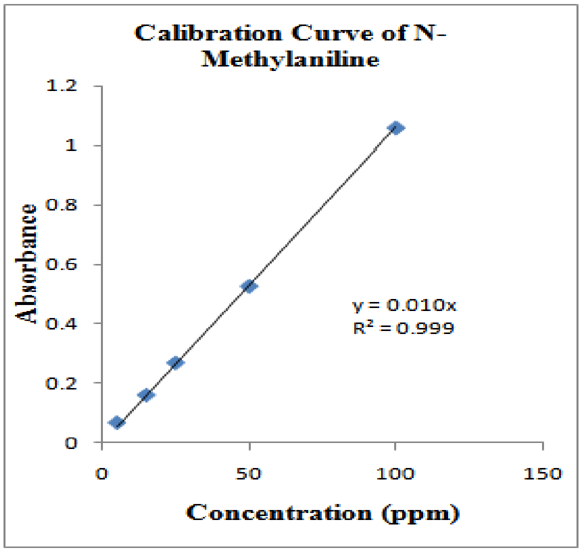

**Figure 2**: Calibration Curve of Standard N-Methylaniline Solution at 270 nm.

**Effect of pH on Adsorption:** The pH of a solution is one of the most important parameters affecting the adsorption process .It was reported that pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbent [12, 13]. To study the effect of the solution pH on the adsorption of some organic pollutants, batch test was carried out according to the following procedure. A 1.00 g of the adsorbent (NB/SMB) was contacted with 10 mL of 100 ppm solution of each pollutant at a different pH ranges from 3 to 10 for 24 hr, The PH 3 to pH 6 was controlled using $CH_3COOH$/ $CH_3COONa$ buffer solutions while for pH 8 to pH 10 was controlled using $Na_2C0_3$/$NaHC0_3$ buffer solutions. Consort-C933 pH meter with a combination of glass electrode with accuracy of ± 0.003 pH units was used . NB/SMB was equilibrated with distilled water to yield a pH of 7. The samples were shaken on a thermostatic shaker at 150 rpm and the supernatants were analyzed by UV/VIS spectrophotometer.

**Adsorption Isotherm:** The Freundlich isotherm is considered as an empirical formulation, which represents the adsorption equilibrium over a limited range in solute concentration [14]' Furthermore this isotherm implies that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations [15].

Freundlich isotherm is given by: $Qe = K_f \ C_e^{1/n}$

Where Qe is the equilibrium amount of solute per unit mass of adsorbent (mg/g), $K_F$ is a constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and the constant 1/n indicates the intensity of the adsorption. The equation can be linearized as follow by plotting $\ln Q_e$ versus $\ln C_e$, $K_F$ and n can be estimated from the intercept and the slope, respectively. The % removal can be calculated from the equation: $\text{Removal\%} = \frac{C0 - Ce}{C0} * 100$ , $C_0$ is the initial concentration of the adsorbate in the solution in (mg/L). Surfactant has distinctive features such as, they have surface and interfacial tension depression in very dilute solution due to the adsorption and orientation of molecules as interface, they form micelle above the critical micelle concentration (CMC), and they are soluble in water-insoluble substances [16].

Studies [17, 18] indicate that quaternary ammonium cations such as hexadecyltrimethyammonium (HDTMA) interact with clays and replace the exchangeable inorganic cations on their surfaces, thus forming a stationary phase in the clay particles. As a result of these changes in the structure of the clay particles, these minerals adsorb fewer water molecules; and their nature is changed from a hydrophilic to an organophilic state.

**Batch Method:** All adsorption experiments in this work were performed by batch technique. Aniline and N-methylaniline were prepared in distilled water, N, N-Dimethylaniline was dissolved in organic solvent (Ethanol).One gram of dried NB or SNB was mixed with 10.0 ml of pollutants with different concentrations, and the samples were shaken in thermostatic shaker and filtered to clear solution which is analyzed by UV/VIS spectrophotometer.

## RESULTS AND DISCUSSION

**Mineral Content :** The X-ray diffraction analyses for natural bentonite (NB) and surfactant-modified bentonite (SMB) samples are tabulated in Table 1.

**Table 1.** Mineral content of natural Jordanian Bentonite sample.

| Sample / Mineral | Smectite (S) | Quartz (Q) | Dolomite (D) | Feldspar (F) |
|---|---|---|---|---|
| Natural Bentonite (NB) | *** | *** | ** | * |
| Surfactant Natural Bentonite (SNB) | *** | ** | ** | * |

*** : Major ,**: Minor , * : Trace

The mineral content of natural bentonite was found to be smectite Ca/Mg type and quartz as a major content. The dolomite is minor while feldspar is trace. The modification of bentonite by cationic surfactant indicates no change in the mineral content, which means that surfactant, is loading on the surface.

**Chemical Composition:** In order to investigate the chemical composition, the X-ray fluorescence (XRF) analyses for natural bentonite (NB) and surfactant-modified bentonite (SMB) were performed. The results of oxide's percentage are shown in Table 2.

**Table 2.** Chemical Composition of Natural Bentonite (NB) and Surfactant-Modified Bentonite (SMB).

| Major Oxides % | Natural Bentonite (NB) | Corrected Values * | Surfactant-Modified Bentonite (SMB) | Corrected Values* |
|---|---|---|---|---|
| $SiO_2$ | 60.33 | 67.03 | 49.36 | 60.40 |
| $TiO_2$ | 1.25 | 1.39 | 0.68 | 0.83 |
| $Al_2O_3$ | 12.80 | 14.22 | 14.53 | 17.78 |
| $Fe_2O_3$ | 6.37 | 7.07 | 7.46 | 9.13 |
| MnO | 0.02 | 0.02 | 0.02 | 0.02 |
| MgO | 2.68 | 2.98 | 3.63 | 4.44 |
| CaO | 1.44 | 1.60 | 2.03 | 2.48 |
| $Na_2O$ | 1.68 | 1.87 | 0.16 | 0.20 |
| $K_2O$ | 3.27 | 3.63 | 3.03 | 3.70 |
| $P_2O_5$ | 0.15 | 0.17 | 0.82 | 1.01 |

* Corrected values based on 10.01 % loss on ignition for bentonite and 18.28% for surfactant modified bentonite.

The SiO2% decrease from 60.33 to 49.36, TiO2 from 1.25 to 0.68 and $Na_2O$ from 1.44 to 0.16 %. This can attributed to the cation exchange that occurred between surfactant and the exchangeable cations on the external surface of bentonite. The major increase in composition was for aluminum oxide from 12.80 to 14.53%, iron oxide 6.37 to 7.46%and MgO by 1.0%. The change in chemical composition indicates that the( HDTMA-Cl) surfactant was loaded on the natural bentonite.

The indicator ratio in Table 3,for $SiO_2$ /($Al_2O_3$+$Fe_2O_{3)}$ decrease from 3.15 to 2.24 and $SiO_2/Al_2O_3$ decrease from 4.71 to 3.40 for surfactant modified bentonite, while the indicator ratios (Si+Al)/O increased from 0.91 to 0.93 and ( $MgO+CaO+K_2O)/Al_2O_3$ from 0.58 to 0.61 for modified sample.
Loss on ignition (LO.I) in modified sample was increased relative to the raw samples is due to the loaded surfactant on bentonite, the loading of surfactant was estimated to be 8.16 %.

**Table 3.** Indicator Ratio of Elements.

| Indicator Ratio | Natural Bentonite (NB) | Surfactant-Modified Bentonite (SMB) |
|---|---|---|
| $SiO_2$ / $Al_2O_3$ + $Fe_2O_3$ | 3.15 | 2.24 |
| Si + Al /O | 0.91 | 0.93 |
| $SiO_2$ / $Al_2O_3$ | 4.71 | 3.4 |
| MgO+ CaO+ $K_2O$/ $Al_2O_3$ | 0.58 | 0.60 |

**Cation Exchange Capacity (CEC):** The cation exchange capacity of natural bentonite (NB) and surfactant-modified bentonite (SMB) samples were calculated according to the following equation:
CEC meg/100g = A*N/g (sample) ,where A: volume of $H_2SO_4$ used in ml, N: normality of NaOH. The average results are shown in Table 4.

**Table 4.** Cation exchange capacity (CEC) of natural bentonite (NB) and surfactant-modified bentonite and (SMB).

| Sample | CEC (meg/100g) |
|---|---|
| Natural bentonite | 27.00 |
| surfactant-modified bentonite | 25.60 |

**Infrared Spectroscopy (FTIR):** Bentonite and surfactant-modified bentonite were characterized by FTIR. This technique could be used to identify the major functional groups consisting bentonite. From the wave number of the molecular vibrations modes, a good explanation of the chemical structure could be obtained. As shown in Figures 3 and 4 the modification of bentonite by cationic surfactant did not change the main structure of bentonite, so the main absorbance bands which are 1431.92, 1640.40, 2341.65 and 3374.56 $cm^{-1}$ of bentonite appeared in both modified and unmodified bentonite samples with some shifts in some of them due to the loading of surfactant on bentonite samples. This means that surfactant is loading on the surface. Peaks of the surfactant has been shown at $\upsilon$ = 2834.41 $cm^{-1}$ and $\upsilon$ = 2919.70 $cm^{-1.}$ These bands are referred to the $CH_2$ asymmetric and symmetric stretching frequencies [19, 20].

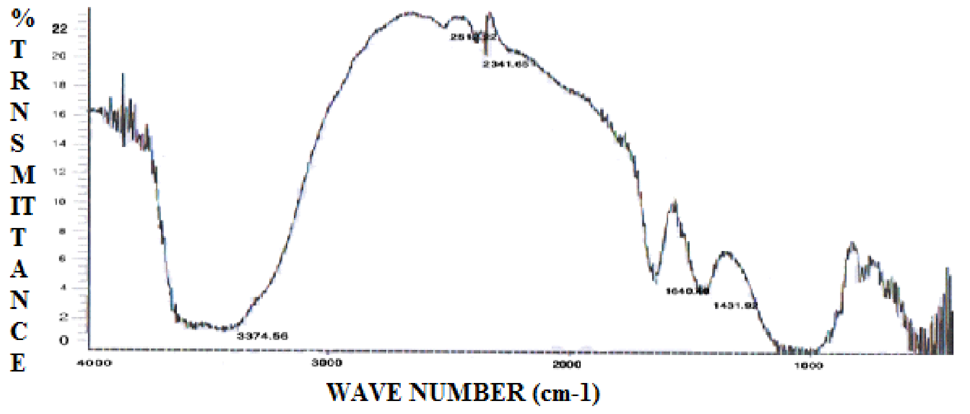

**Figure 3:** FTIR of natural bentonite (NB)

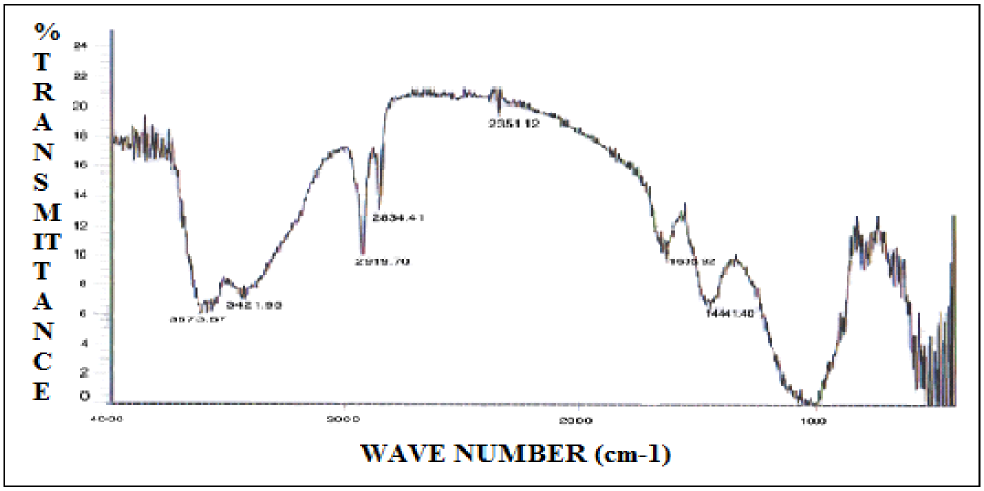

**Figure 4:** FTIR of surfactant-modified bentonite (SMB)

## APPLICATIONS

### Pollutant Uptake

**Effect of Initial Concentration on Pollutant :** Linearized Freundlich adsorption isotherm was applied to analyze the data obtained from the adsorption experiments. Organic pollutants uptake by NB/SMB were fit to Freundlich adsorption isotherm and not applicable to Langmuir, this is due to the fact that the surface of adsorbent is heterogeneous and the adsorption followed a physical adsorption (i.e. vender Waals forces)[21].The pollutants (aniline, N-Methylaniline and N, N-Dimethylaniline) concentration data were used to calculate the % Removal for each one of the pollutants by NB . It was shown that for aniline the mass adsorbed after 24h ranges from 2.0 , 6.0, 10.1, 25, 29 and 74 ppm form the starting solutions 5, 15, 25, 50, 100 and 200 ppm which reflects average removal percentage 39.5% .While for SNB the adsorbed concentration ranges from 4.4, 13, 21, 35, 67 and 121 ppm shows average removal 75.8%. As shown in Fig.5.

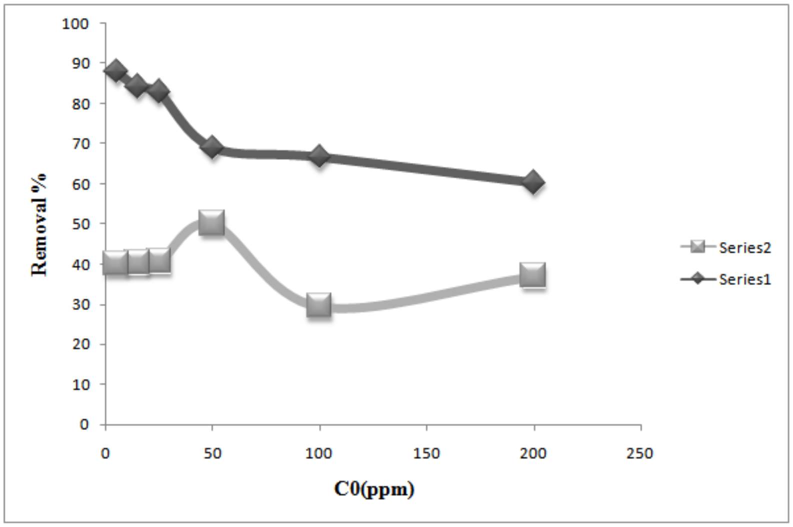

**Figure 5**: Effect of initial aniline concentration on the adsorption by NB (series1) and SMB (series2).

The effect of initial aniline concentration on adsorption by NB and SNB shows that the relationship between $C_e$ and $Q_e$ gives indication of isotherm model which goes to the C-type isotherm that reflects the availability of adsorbing sites is constant with increasing solute concentration due to the increase in sorbent phase. The adsorption isotherm for Aniline on Natural bentonite (series1) and Surfactant modified bentonite (series2) is shown in fig.6.

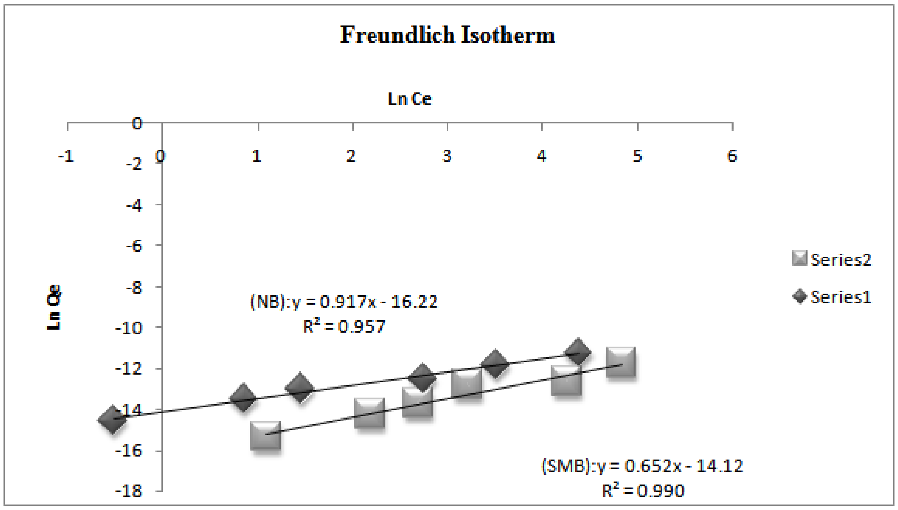

**Figure 6:** Freundlich adsorption isotherm for Aniline on NB (series1) and SMB (series2).

For N-Methylaniline the adsorption on NB ranges from 2.5, 6, 7.6, 13.2, 19, and 43 ppm for the same set of concentrations giving average removal of 31.6% .While for SNB the concentration of the removed pollutant increase to 4.7, 11.3, 21, 38.7, 69.4, and 142.6 ppm. As shown in Fig. 7.

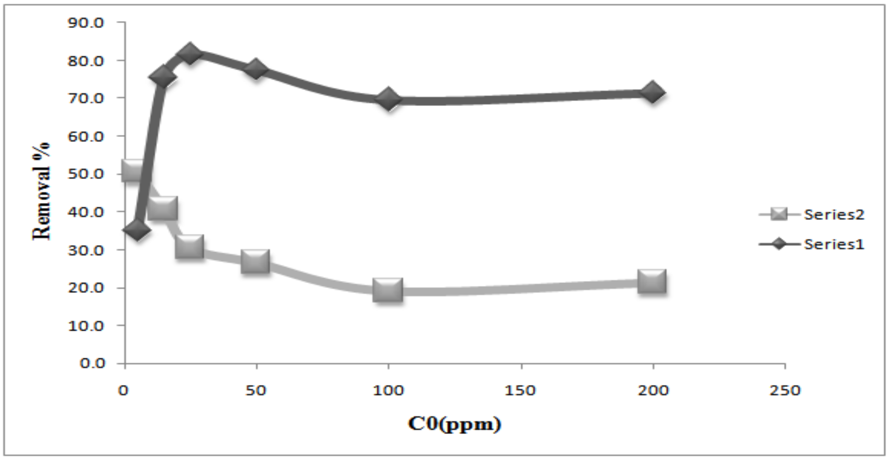

**Figure 7:** Effect of initial N-Methylaniline concentration on the adsorption by NB (series1) and SMB (series2).

The effect of initial concentration of N-Methyl aniline on the adsorption process is shown. Fig.8 gives the $C_e$ and $Q_e$ of NB and SNB samples.

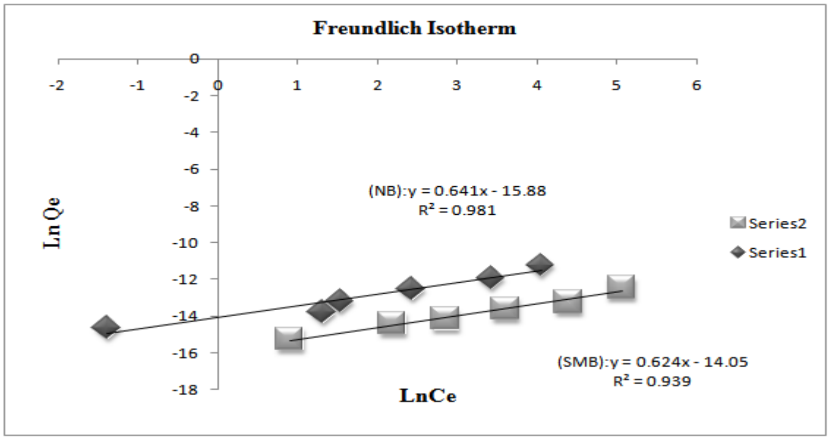

**Figure 8**: Freundlich adsorption isotherm for N-Methylaniline on NB (series1) and SMB (series2).

The result illustrated from the adsorption isotherm reveals that maximum adsorption is 80 % for NB as shown in Table 5. For N, N- Dimethylaniline the adsorption on NB the adsorption after 24h ranges from 3.9, 9,11.8, 20, 26.5, and 38.8 ppm while for SNB the adsorption increase to 0.2, 13.7, 23.4, 47.5, 95.6, and 192 ppm respectively as shown in Fig. 9.

The removal % of the pollutant is shown indicates that the maximum adsorption reaches almost 97% for higher concentrations.

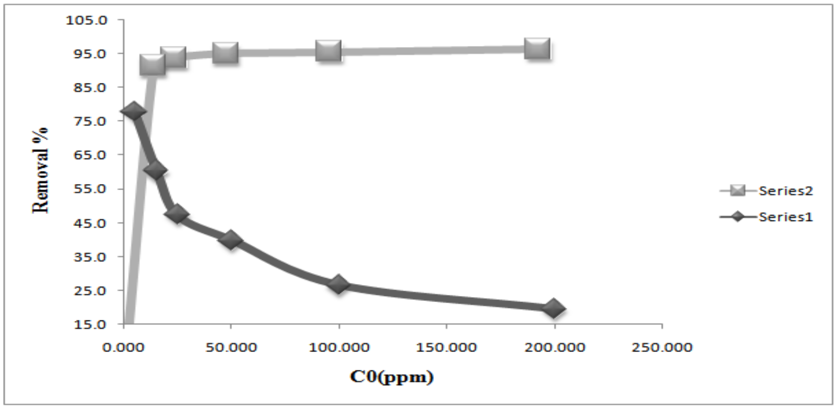

**Figure 9:** Effect of initial N,N-Dimethylaniline concentration on the adsorption by NB (series1) and SMB (series2).

The freundlich adsorption isotherm for pollutant on NB and SNB is shown in Fig.10.

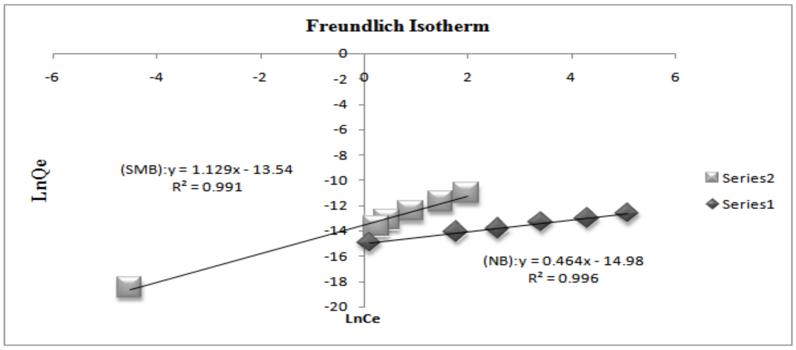

**Figure 10**: Freundlich adsorption isotherm for N,N-Dimethylaniline on NB (series1) and SMB (series2).

The relative adsorption capacity of the adsorbent (Kf) mg/g and the intensity of the adsorption (1/n) were calculated from the data obtained in table 5.

**Table 5.** The % Removal of pollutants.

| Pollutants | Natural Bentonite (NB) | Surfactant-Modified Bentonite (SMB) |
|---|---|---|
| Aniline | 50.0 | 88.0 |
| N-Methyl aniline | 50.6 | 88.0 |
| N,NDimethylaniline | 77.8 | 96.4 |

The fruendlich constants for aniline and its derivatives were shown in table 6-A and 6-B.

**Table 6- A:** Freundlich Constant for Pollutant Uptake by Natural Bentonite (NB).

| Pollutant | Freundlich Constant | | |
|---|---|---|---|
| | $K_f$ | N | $R^2$ |
| Aniline | 90.6E-9 | 1.06 | 0.957 |
| N-Methylaniline | 1.27E-7 | 1.56 | 0.981 |
| N,N-Dimethylaniline | 3.12E-7 | 2.16 | 0.996 |

**Table 6- B:** Freundlich Constant for Pollutant Uptake by Surfactant-Modified Bentonite (SMB).

| Pollutant | Freundlich Constant | | |
|---|---|---|---|
| | $K_f$ | N | $R^2$ |
| Aniline | 551.8E-9 | 1.02 | 0.99 |
| N-Methyl aniline | 7.91E-7 | 1.6 | 0.939 |
| N,N-Dimethylaniline | 1.40E-6 | 0.88 | 0.991 |

**Effect of pH on Adsorption:** The effect of pH on the pollutants adsorption (aniline, N-Methylaniline and N, N-Dimethylaniline) by NB/SMB vary with changing the pH values. Samples of 100 ppm concentration of the analyst were taken for this purpose. For aniline it is found that the adsorption on NB ranges from 7.9, 57.9, 36.3, 14.6, 47.4 and 17.9% for PH 3.1, 4.14, 5.01, 5.7, 8.01, and 9.87 respectively. While for SNB using the same concentration of aniline, the removal was 80.3, 74.2, 54.1, 31.1, 8.1 and 22.1% or the same PH values respectively. The optimum PH is found to be 4.14. For N-Methyl aniline the same concentration of 100 ppm is taken to measure the optimum PH on NB, it is found that the removal % were 80.0, 30.4, 39.5, 20.7, 33.2, and 20.3% at PH 3.1, 4.1, 4.9, 6.3, 7.9, and 9.8 respectively, while the effect of PH using SNB is 60.0, 48.3, 17.9, 46.2, 33.8, and 38.2% for the same PH values. The effect of PH on N,N-Dimethylaninline adsorption by NB shows that removal % is 80.0, 73.3, 97.0, 41.8, 14.7,and 37.5% for the same PH values respectively, while the adsorption using SNB was 80.1, 66.7, 29.5,30.3 ,30.8, and 63.3% for the same pollutant concentration. In table 7 the optimum PH and the amount of adsorbate concentration are tabulated.

**Table 7.** The optimum pH and the maximum solid phase concentration ($Q_e$ mg/g)

| Pollutants | Optimum pH | | Adsorbate concentration ($Q_e$ mmol/mg). | |
|---|---|---|---|---|
| | (NB) | (SMB) | (NB) | (SMB) |
| Aniline | 4.15 | 3.18 | $6.21E^{-06}$ | $8.71E^{-06}$ |
| N-Methyl aniline | 3.18 | 3.18 | $7.5E^{-06}$ | $5.66E^{-06}$ |
| N,N-Dimethylaniline | 4.98 | 3.01 | $8.12E^{-06}$ | $5.56E^{-06}$ |

The change in pH also results in a change in charge profile of adsorbate species, which consequently influences the interactions between the adsorbate species and adsorbent [22]. The pollutants (aniline, N-Methylaniline and N, N-Dimethylaniline) concentration data were used to calculate the % Removal for each one of the pollutants by NB/SMB at the optimum pH is shown in Table 8.

**Table 8.** The % Removal of the pollutants at optimum pH.

| Pollutants | Natural Bentonite (NB) | Surfactant-Modified Bentonite (SMB) |
|---|---|---|
| Aniline | 57.9 | 80.3 |
| N-Methylaniline | 80.0 | 60.0 |
| N,N-Dimethylaniline | 97.0 | 80.0 |

## CONCLUSIONS

This research investigated the performance of natural bentonite and surfactant-modified bentonite for the treatment of waste water from organic pollutants.

The type of the cationic surfactant used for modification of bentonite did not change the mineral content of the natural bentonite, which was clear from the XRD and FTIR results.

This is because the surfactant loading was occurred only on the bentonite surface. The results also show that the adsorption of tested organic pollutants by surfactant modified-bentonite was best fitted to Freundlich adsorption isotherm more than Langmuir and the removal efficiency of organic pollutants by surfactant modified-bentonite was higher than that of natural bentonite, which means that the adsorption depends on the pollutants itself and on the adsorbent as well, the change in pH also results in a change in charge profile of adsorbate species, which consequently influences the interactions between the adsorbate species and adsorbent which is shown in our results.

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