REMOVAL OF ORGANIC POLLUTANTS FROM AQUEOUS SOLUTIONS USING NATURAL AND MODIFIED JORDANIAN BENTONITE

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INTRODUCTION

The optimization of wastewater purification process requires a development of new operations based on low cost raw materials, with high pollutant removal efficiency. The unique structure of bentonite gives rise to remarkable physical and chemical properties, which have allowed it to play a vital role in many industrial and agriculture technologies. Bentonite is a kind of expandable clay composed of primarily of montmorillonite with permanent negative charges on its surface resulting from the isomorphous substitution on central atoms in the octahedral/tetrahedral by cations of lower valence. Such structure enables bentonite to be intercalated by organic and inorganic cations, and the resulting material has high specific surface areas associated with their small particle size. These modified calys can be used as efficient adsorbents for many organic and inorganic contaminants in water. (Jianfa Li, et al., 2010).

According to Namasiavayam and Thamaraiselvi,1998,(Gupta, et al., 2009), The major sources of water pollution can be classified as municipal, industrial and agricultural. The environmental pollution by organic compounds has been of growing concern due to their widespread utilization by industrial, agriculture and domestic uses.

Organic pollutants are generally classified as suspended matter. This use is now discouraged due to its high toxicity, including carcinogenicity (Stolkoff, 1988). Naturally Pyridine is found among the volatile components of black tea (Vitzthum, et al., 1975) and in the leaves and roots of Atropa belladonna (Burdock, 1995). Most of the toluene entering the environment is released directly to the atmosphere, as it is a volatile aromatic chemical with low water solubility. It high affinity for lipid-rich tissue, including those in the central nervous system (Arnold, et al., 1994).

Toluene has toxic effects to the central nervous system (CNS), cardiovascular, hematopoietic, reproductive, and respiratory systems, as well as it has to the liver, kidneys, skin, and sensory organs have been reported for toluene (Fishbein, 1988). Biodegradable, high priority pollutants (carcinogens, high acute toxins), refractory (resistant to biodegradation), volatile, and malodoros compounds (Rajeshwar, et al., 1997). As water of good quality is a precious commodity and available in limited amounts, it has become highly imperative to treat wastewater for removal of pollutants (Is, F. Thorikul , et al., 2013), (Yuening, L., et al., 2014). Many researches and studies have been applied to treat and solve environmental problems resulted from the industry to remove pollutants. One branch of these researches is water purification by using surfactant-modified bentonite to remove the toxic organic compounds. The surfactant like Hexadecyltrimethylammonium (HDTMA) increases the surface area of the bentonite and accordingly increases the ability of the adsorption (Rawajfih, et al., 2006).

In this work the Jordanian natural benonite was chemically modified by Hexadecyltrimethylammonium chloride (HDTMA-Cl). The capacity of natural and surfactant-modified bentonite to remove benzene, pyridine and toluene form water were investigated.

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MATERIALS AND METHODS

Raw Sample Preparation

Samples of Jordanian bentonite from Q'a Al Azraq region were donated by Natural Resources Authority. These natural bentonite samples of particle size less than 250 μm were mixed with distilled water and then shaken at 25°C and 150 rpm for 24 hr on a thermostatic shaker, filtered it is dried in an oven at 105°C, then kept in a desiccator at room temperature for further use labeled NB.

Preparation of organobentonite

The organobentonite was prepared according to the following procedure: 30 g of raw bentonite were mixed with 90 mL of 67 mmol/L of hexadecyltrimethylammonium chloride (HDTMA Cl) 96% from Fluka) 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 labeled NBS.

Cation Exchange Capacity (CEC)

The method adopted in this study is the Modified-Kjeldahl Method without Digestion (Schollenberger, et al., 1945). 5.0 grams of bentonite types were added into 500 mL Erlenmeyer flask with 150 mL distilled water, swirl and discarded, filtered and dried; the remaining washed bentonite was dried at 100°C for three hours.

The solid samples were added to a 800 mL Kjeldahl flask and then mixed with 25 mL of 0.1 N NaOH, and distilled 50 mL of 2% H3BO3. The boric acid solution was titrated with standard O.1 N H2SO4. Cation exchange capacity experiment was made twice and determined according to the following equation:

\[ \text{CEC meq / 100g} = \frac{A*N}{g} \]  

Where: A: volume of H2SO4 used for sample in ml, N: normality of NaOH.

Characterization Methods

The raw and modified bentonite were characterized by ascertaining their chemical composition by X-ray fluorescence technique. The operation method were followed as presented by the manufacturer. Thus, 0.8 g of the sample was thoroughly mixed with 7.2 grams of lithium tetra borate (Li2B4O7) in platinum crucible, which was introduced into an automatic fluxer (Leco Corp, model FX-200) where a temperature program was affected starting from room temperature to 1200°C. The melts was then poured into casting dish to cool, the resultant glassy disc was used for XRF analysis. Mineral constitution was determined by powder X-ray diffraction technique using X, pert instrument fitted with Co Kα radiation at λ = 1.7889 Å at 40 KV and 40 mA.

Bentonite samples were analyzed using FTIR technique. The infrared spectra of the samples were determined by grinding about 1.0 mg of each sample with 300 mg KBr in a clean mortar. The resulting homogenous mixture was pressed to ten thousand psi into a pellet, and then mounted in a double beam FTIR instrument (Gadsenden, 1975).

Analytical Measurements

The prepared concentrations of organic pollutants in this study range between 5-200 mg/L (ppm). Absorbance measurements were done by UV/VIS spectrophotometer type, the wavelength corresponding to maximum absorbance (λmax) of organic pollutants was determined by scanning a standard solution of known concentration at different wavelength. Absorbance values were recorded at the wavelength of maximum absorbance. (λmax) of Benzene, Pyridine and Toluene was 254, 270, and 210 nm respectively. These wavelengths were found to be used for preparation of calibration curves, and the calibration curves were prepared with standard solution as shown in Figures 1 and 2.

Adsorption study

The adsorption process of benzene, pyridine and toluene was carried out with batch experiments. Several variables, including initial concentration, pH and contact time were studied in this work.

Effect of Initial Concentration on Pollutants Uptake

To study the effect of initial concentration on pollutants uptake by NB and SMB, one gram of dried NB/SMB was mixed with 10.0 ml of either, Benzene, Pyridine and Toluene Solution (initial concentrations was 5, 15, 25, 50, 100, and 200 ppm); Sivamani et al.(2009); Rajeshkannan et al.(2010),Jayaraj et al.(2011) the samples were Shaken at 25°C and 150 rpm for 24 hr 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 of by UV/VIS spectrophotometer (thermo scientific evolution 160) at λmax for benzene, pyridine and toluene respectively.

Effect of pH on solution

The pH of a solution is one of the most important parameters
affecting the adsorption process. Hu et al., (1989) and Ornek et al., (2007) reported that pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbent. Punjohharn et al. (2008), Cengiz and cavas (2008). Moreover a 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.

To study the effect of the solution pH on the adsorption of some organic pollutants, batch test was carried out. 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 from 3-6 was controlled using CH₃COOH/ CH₃COONa buffer solutions and for the pH from 8-10 was controlled using Na₂CO₃/NaHCO₃ buffer solutions. 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 at temperature 25°C for 24 hr. After that samples were filtered using 0.45 µm syringe filter and the supernatants were analyzed by UV/V is spectrophotometer.

Effect of contact time
Adsorption was carried out for both natural and surfactant-modified bentonite clay, by adding 0.2 g to 50 mL solution of benzene, pyridine and toluene as pollutants with fixed OF 200 ppm. The suspension was shaken at 25°C using a thermostatic shaker. The % of removal of the organic compounds studied at different contact time from 8 to 32 hours.

Adsorption isotherm
The adsorption of benzene, pyridine and toluene on organobentonite was investigated through batch process. For adsorption experiments, 10 mL of benzene, pyridine or toluene solution in the concentration range of 5-200 ppm was mixed with 1.0 gram of NB/NBS samples. The mixture was shaken at 25°C and 150 rpm for 24 hours, on a thermostatic shaker, after reaching equilibrium the suspension was filtered through 0.45um nitrocellulose membrane and the filtrate was analyzed by UV-vis spectrophotometer at certain wave length. The amount adsorbed by the organobentonite was calculated as following equation:

\[ Q_e = \frac{C_i - C_f}{C_i} \times 100 \]

\( C_i \) (ppm ) is the initial concentration of benzene, pyridine and toluene, \( C_f \) (ppm) is the equilibrium concentration in aqueous solutions and \( m \) (ppm) is the organobentonite concentration, \( Q_e \) is the amount of calculated organic pollutant onto 1.0 g of organobentonite.

RESULTS AND DISCUSSIONS

Mineralogical Study (XRD)
Bentonite samples was analyzed for its mineral composition using XRD technique and tabulated in table 3.1.

As shown in table 3.1, the major content in bentonite is quartz. The smectite, anothite, microcline and muscovite are trace. The modification of bentonite by cationic surfactant indicates some change in the mineral content. Smectite and quartz appears to be major minerals, while muscovite, microcline and kaolinite appears to be trace minerals which show that surfactant (HDTMA-Cl), was loaded on the surface.

Chemical Composition
Determination of chemical composition of natural bentonite (NB) and surfactant-modified bentonite (SMB) using XRF instrument is shown in Table 2.

<table>
<thead>
<tr>
<th>Major Oxides %</th>
<th>Natural Bentonite (NB)</th>
<th>Corrected Values</th>
<th>Surfactant Modified Bentonite(SMB)</th>
<th>Corrected values</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>57.43</td>
<td>64.05</td>
<td>51.36</td>
<td>60.37</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.04</td>
<td>1.16</td>
<td>1.03</td>
<td>1.21</td>
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<tr>
<td>Al₂O₃</td>
<td>12.50</td>
<td>13.94</td>
<td>14.20</td>
<td>16.70</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.23</td>
<td>6.95</td>
<td>7.16</td>
<td>8.42</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>3.81</td>
<td>4.25</td>
<td>3.96</td>
<td>4.66</td>
</tr>
<tr>
<td>CaO</td>
<td>3.48</td>
<td>3.88</td>
<td>3.98</td>
<td>4.67</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.12</td>
<td>2.36</td>
<td>0.51</td>
<td>0.60</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.95</td>
<td>3.28</td>
<td>2.76</td>
<td>3.25</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.08</td>
<td>0.09</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>LOI</td>
<td>10.30</td>
<td>11.47</td>
<td>14.95</td>
<td>17.58</td>
</tr>
</tbody>
</table>

Corrected values based on 10.31% loss on ignition for Bentonite and 14.95% for surfactant modified Bentonite.

The investigation of the chemical composition of the natural bentonite and the surfactant modified bentonite as oxide percentage shows that the SiO₂% decrease from 57.43 to 51.36, Al₂O₃ increase from 12.5 to 14.2%, Fe₂O₃ from 6.23 to 7.16%, and Na₂O from 2.12 to 0.51%, this can be attributed to the cation exchange that occurred between the surfactant and the exchangeable cations on the surface of bentonite. The change of chemical composition indicates that HDTMA-Cl surfactant was loaded on the bentonite.

Cation Exchange Capacity
The cation exchange capacity of natural bentonite (NB) and surfactant-modified bentonite (SMB) samples were calculated in Table 4.1 which represents the average of three trials.

<table>
<thead>
<tr>
<th>Table 3 Indicator Ratio of Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indicator ratio</td>
</tr>
<tr>
<td>SiO₂/Al₂O₃</td>
</tr>
<tr>
<td>Si+Al/Na</td>
</tr>
<tr>
<td>SiO₂/Al₂O₃</td>
</tr>
<tr>
<td>MgO+CaO+K₂O/Al₂O₃</td>
</tr>
</tbody>
</table>

The indicator ratios show that there is significant reduction of SiO₂ / Al₂O₃+ Fe₂O₃ from 3.07 to 2.4 this due to decrease of SiO₂ content in the modified bentonite, SiO₂/Al₂O₃ from 4.59 to 3.62 for modified bentonite samples. Loss on ignition (L.O.I) increase due to loaded surfactant on bentonite which was estimated to be 6.11%.

Table 1 Mineral content of bentonite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Smectite</th>
<th>Quartz</th>
<th>Anorthite</th>
<th>Moscovite</th>
<th>Microcline</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant-modified bentonite</td>
<td>***</td>
<td>***</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Bentonite</td>
<td>*</td>
<td>***</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>-</td>
</tr>
</tbody>
</table>

Major *** Minor ** trace *
Table 4 CEC of NB and SMB

<table>
<thead>
<tr>
<th>Sample</th>
<th>CEC (mEq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Bentonite</td>
<td>52.5</td>
</tr>
<tr>
<td>Surfactant-Modified Bentonite</td>
<td>47.6</td>
</tr>
</tbody>
</table>

**FTIR Technique**

Bentonite and surfactant-modified bentonite were characterized by FTIR. For the organobentonite the bands at 2920 , 2850 cm⁻¹ and between 1520 and 1440cm⁻¹ corresponds to CH₂ asymmetric stretching as (CH₂) and symmetric stretching s(CH₂) vibrations and CH₂ bending vibrations δ(CH₂) of alkyl chains respectively. Lower frequency, and decreasing the intensity of δ (CH₂) indicate reduced interaction between the alkyl chains. The main absorbance bands which are 1432, 1641, 2342 and 3375 cm⁻¹ appeared in both modified and unmodified bentonite samples with small shifts in some of them due to the loading of surfactant.

**Effect of Initial Concentration**

Sorption isotherm studies were conducted on the modified and natural bentonite to measure the adsorption of benzene, pyridine and toluene compounds from aqueous solutions. Linearized Freundlich adsorption isotherms as in figures (3, 4, 5) respectively.

It was noticed that the for benzene the mass adsorbed after 24h ranges from 3.2, 7.6, 8.9, 13.9, 17.6, and 40.9 ppm from the starting concentrations 5, 15, 25, 50, 100, and 200 ppm respectively, reflects average removal of 39.2%. While for modified bentonite (SMB) the removal % increase to 45.9% for the same set of concentration. The removal of pyridine after 24h ranges on natural bentonite was from 1.3, 2.8, 5.3, 9.5, 26, and 65 ppm respectively for the same set of concentration. The relationship between C and Qe (SNB) was 47.3%, while adsorption increase to 65.5%. Freundlich constants on organobentonite (NB) were shown.

For the modified bentonite, however, the average removal % were 45.9, 74.8 and 65.5% respectively, which donates that the organic uptake by modified bentonite decreased in the order toluene > pyridine > benzene as shown in table.

The lower adsorption of benzene may be attributed to the presence of a long alkyl chain of the tailoring agent used to modify the bentonite, The Freundlich adsorption isotherm for Toluene on NB (series1) and SMB (series2). The relationship between C vs. Qe for Benzene, pyridine and toluene adsorption by NB/SMB which goes to C-type isotherm which reflects that the availability of sorbing sites is constant with increasing solute concentration due to the increase in the sorbent phase.

**Effect of pH on Adsorption**

The effect of pH Benzene solution on adsorption by natural bentonite (NB) and surfactant-modified bentonite (SMB) were studied. The optimum PH is shown in the table.
It is found that the PH is important parameter effecting the adsorption process. Change in PH will effect both aqueous chemistry and surface binding sites of the adsorbant, Vijayaraghavan and Yun,(2008). Moreover change in PH will results in a change in charge profile of a disorbate species, which consequently influence the interaction between the adsorbate species and adsorbent. The of PH on benzene adsorption on NB increase from 22.7% at PH of 3.2 increased to maximum at 4.95. The optimum PH as shown in figures (6, 7, 8), which is the same for organobentonite SMB). The maximum Qe is 9.61E-06 (mmol/mg) at pH 4.949 for adsorption by NB and is 5.88E-06 (mmol/mg) at pH 3.95 for adsorption by surfactant modified bentonite (SMB). For pyridine the optimum PH was 4.45, and the uptake of pollutant was 54.3%, using natural bentonite and 74.9% using surfactant modified bentonite, with optimum PH of 4.985. While the uptake of toluene by natural bentonite (NB) and surfactant-modified bentonite (SMB) shows different optimum PH; this indicate that the maximum Qe is 8.75E-06 (mmol/mg) at pH 9.91 for adsorption by NB and is 1.06E-05 (mmol/mg) at pH 9.91 for adsorption by SMB.

It has been observed that increasing concentration of PH results in a change in charge profile of a dsorbate species, which consequently influence the interaction between the adsorbate species and adsorbent. The of PH on benzene adsorption on NB increase from 22.7% at PH of 3.2 increased to maximum at 4.95. The optimum PH as shown in figures (6, 7, 8), which is the same for organobentonite SMB). The maximum Qe is 9.61E-06 (mmol/mg) at pH 4.949 for adsorption by NB and is 5.88E-06 (mmol/mg) at pH 3.95 for adsorption by surfactant modified bentonite (SMB). For pyridine the optimum PH was 4.45, and the uptake of pollutant was 54.3%, using natural bentonite and 74.9% using surfactant modified bentonite, with optimum PH of 4.985. While the uptake of toluene by natural bentonite (NB) and surfactant-modified bentonite (SMB) shows different optimum PH; this indicate that the maximum Qe is 8.75E-06 (mmol/mg) at pH 9.91 for adsorption by NB and is 1.06E-05 (mmol/mg) at pH 9.91 for adsorption by SMB.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Natural Bentonite (NB)</th>
<th>Surfactant Modified Bentonite (SNB)</th>
<th>Adsorbate concentration (Qe/ug/g)</th>
<th>Adsorbate</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4.949</td>
<td>3.951</td>
<td>9.61E-06</td>
<td>5.88E-06</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>4.123</td>
<td>4.985</td>
<td>1.09E-05</td>
<td>9.49E-03</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>9.907</td>
<td>9.910</td>
<td>8.71E-06</td>
<td>1.06E-05</td>
<td></td>
</tr>
</tbody>
</table>

Effect of contact time

The variation of amount of adsorbent used is constant with different organic pollutants. That is reached within 8 hours. The saturation time is independent on the concentration. Uptake of the pollutants is more effective at low concentrations. The removal of benzene, pyridine and toluene with time is shown in Figure.

In industrial applications, higher removal at low concentration is more important.

CONCLUSION

This work investigates the ability of natural Jordanian bentonite and surfactant–modified bentonite for treatment of waste water from organic pollutants. The surfactant used for this modification (HDTMA-Cl) change some mineral content of the natural bentonite this was shown from XRF and XRD results. The surfactant loading occurs on the surface and some effect the inner layers of the clay. The adsorption was tested to be best fitted with Freundlich isotherms. The efficiency of removal of organic pollutants was higher with surfactant modified bentonite, which means that the adsorption depend on the pollutant itself and the adsorbate as well. The change in PH influences the charge profile of the adsorbate and influence the interacting species. The contact time has almost no effect after saturation time.

Acknowledgements

Authors would like to thank the Natural Resources Authority for giving the samples chemical facilities, and colleagues of chemistry Department at Petra University for their help.

References


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