Modification of Jordanian Diatomite and Its Use for the Removal of Some Organic Pollutants from Water

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ABSTRACT

Jordanian diatomaceous clay modified by some cationic surfactants dodecyltrimethylammonium bromide (DDTMA-Br), tetradecyltrimethylammonium bromide (TDTMA-Br), Hexadecyltrimethylammonium bromide (HDTMA-Br), hexadecyltrimethylammonium chloride (HDTMA-Cl) and octadecyltrimethylammonium bromide (ODTMA-Br) were prepared. The chemical and structural properties of raw and modified samples were studied using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), total organic carbon (TOC), and Fourier transform infrared spectroscopy (FTIR). The adsorption capacities were estimated by methylene blue method. The use of surfactants does not change the mineral structure of the diatomaceous clay. Experiments were done to study the role of surfactants modified diatomaceous clay in the removal of phenol, 4-chlorophenol, and 4-nitrophenol from their aqueous solutions at different pH ranges. The removal of phenol was up to 75% at pH equal to 10.5, for 4-chlorophenol 95% at pH equal to 8.0 and 4-nitrophenol is 98% at pH equal to 6.5. The adsorption isotherm of modified surfactants diatomaceous clay indicates that phenol and its derivatives follow type 1, which is the Langmuir isotherms. The results have revealed that the modified diatomaceous clay improve the adsorption of phenols from aqueous solutions better than the raw ones.

Key words: Jordanian diatomaceous clay, Surfactants, Adsorption, Phenols.

INTRODUCTION

Diatomite is a chalk-like, soft, friable, earthy, very fine grained, siliceous sedimentary rock. Diatomaceous silica is regarded as mineral of organic origin. Where the silica of fossilized diatom skeleton resembles opal or hydrous silica in composition: \( \text{SiO}_2 \cdot n\text{H}_2\text{O} \). The diatomite occurs mainly at A Azraq area, approximately 110 km northeast of Amman, covered an area of more than 150 km². Diatomite reserves in Jordan are found to be more than one thousand million tons.

Diatomite could be noticed to have very low density, fine particles, high absorbance ability, high porous and high surface area properties. The
Diatom cells contain an internal, elaborate siliceous skeleton consisting of two valves (frustules) that vary in size from less than one micrometer (µm) to more than one millimeter in diameter.

Due to high surface area, diatomite has a high absorptive capacity and can absorb up to 2.5 times its weight of water, (4). Improvement in filtration characteristics of diatomite were studied.

Synthetic chemicals can cause water pollution; the great majority of commercial synthetic chemicals are organic compounds, where diatomite may be used as filter aid for all these chemicals. Organoclays form important type of modified clay minerals. Their uses are many including some environmental applications. Organoclays are useful in water purification by removing oil and toxic chemicals from water. Remediation of industrial waste waters is enabled through the use of organoclays.

Surfactants are compounds that have an amphiphilic nature, as their molecular structure contains parts with different polarity, a hydrophobic (non-polar) part and a hydrophilic (polar) part. The hydrophobic part is commonly a hydrocarbon (branched or linear) which may contain aromatic structures. This part of the surfactant is soluble in oils (non-polar solvents) but is not very soluble in water and other polar solvents. Diatomite may be modified chemically in number of ways.

Phenols are organic compounds that are naturally occurring and manufactured chemically are widely distributed in environment. They have been detected in surface waters, rainwater, sediments, drinking water, groundwater, industrial effluents, urban runoff, and at hazardous waste sites.

This paper reports on work on cataionic surfactants treated Jordanian diatomaceous clay and their possible use in removal of phenol, chlorophenol, and nitrophenol from water.

MATERIALS AND METHODS

Sample Preparation
Diatomite sample was supplied by the Jordanian Natural Resources Authority (NRA) brought from "Qa‘ Al Azraq area.

The sample was crushed at NRA and sieved in Al-Balqa Applied University using vibrating sieve shaker to different particle sizes < 0.5, 0.5-1.0, and > 1.00 mm. The portion < 0.5 mm was washed with distilled water (DW) three times to remove any insoluble contaminants. Then dried overnight in an oven at 110 °C, stored in desiccators after being put in polyethylene bottles, and coded Raw-D.

Pretreatment of Raw Diatomite
Pretreatment of Raw-D sample with NaOH was done according to Khraisheh. Raw-D sample (200g) was immersed in 1.333L of 6 M NaOH at 90 °C for 2 hours. PH of the mixture was decreased to 1.94 by using HCl at 25 °C for 20 hours. The supernatant was discarded and the solid precipitate was immersed again in 1.333L of 6 M NaOH at 25 °C for another 20 hours.

The solution was decanted off then the precipitate was left exposed to the air before being washed with DW, dried in the oven at 110 °C, and coded raw-D.

Modification of Diatomite Raw-D by Different Cationic Surfactants
Diatomite samples Raw-D were independently modified by five cationic surfactants, i.e., dodecyltrimethylammonium bromide (S1), tetradecyltrimethylammonium bromide (S2), hexadecyltrimethylammonium bromide (S3), hexadecyltrimethylammonium chloride (S4), and octadecyltrimethylammonium bromide (S5) according to a reported procedure. A solution of 67 mM of each surfactant (S1, S2, S3, S4, and S5) was prepared. A volume of 66 mL surfactant solution was added to 20 g of diatomite samples Raw-D in 125 mL polyethylene bottles then shaken (150 rpm, 25 °C) in a thermostatic table shaker for 8 hours. Supernatants were discarded and the precipitates were washed twice with 100 mL DW each time, before drying in the oven at 50 °C overnight and stored in the desiccator. The modified samples of Raw-D were coded D-S1, D-S2, D-S3, D-S4, and D-S5 respectively.

Characterization of Raw and Surfactants Modified Diatomite Samples
The surfactant modified raw diatomite samples (D-S1, D-S2, D-S3, D-S4, and D-S5) and the unmodified sample Raw-D were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), total organic carbon (TOC), and scanning electron microscopy (SEM) techniques.

**X-Ray Diffraction (XRD)**

All diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4, and D-S5) were characterized using XRD technique. During analysis the samples were illuminated by X-ray beams and the intensities of the emerging X-rays were recorded as a function of the deflection angle ($\theta$). A ($\theta$) interval between $5^\circ$ and $60^\circ$ was used with a step size of 0.02 and a step time of 1 second. The distance between the crystal layers, which is specific for each element, can be compared with reference patterns and hence yields information about the crystalline structure of a sample.

XRD-data for the samples were recorded with X’pert instrument powder diffractometer equipped with a cobalt anode, energy emitted as X-ray photons with $\lambda = 1.78897$ Å. A monochromator removes X-rays of undesired wave lengths so that only Co K$_\alpha$1 can be detected which simplifies the evaluation (24).

**X-Ray Fluorescence (XRF)**

All diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4, and D-S5) were analyzed using XRF technique. This type of chemical analysis was done by applying smooth surface of the samples to X-ray radiation. The smooth surface was achieved by taking 0.8 g of each sample and mixing it with 7.2 g of lithium tetra borate (Li$_2$B$_4$O$_7$) in a platinum crucible. Then the crucible was introduced into automatic fluxer, where the temperature programming was started from room temperature to 1200 °C, to finish with glassy discs that are smooth and can be used for XRF analysis (Natural Resources Authority, 2011).

**Fourier Transform Infrared Spectroscopy (FTIR)**

All diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4, and D-S5) 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 mounted in a double beam FTIR instrument with a resolution of 4 cm$^{-1}$ (25).

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**Total Organic Carbon (TOC)**

All diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4 and D-S5) were analyzed for their carbon content using total organic carbon (TOC) analyzer. About 1.0 g of each sample was combusted in the TOC analyzer at a furnace temperature of 1450 °C. The CO$_2$ gas was detected from the flow oxygen gas by thermal conductivity cell detector. The percentage of carbon is displayed on a direct reading digital display (Natural Resource Authority, 2011).

**Scanning Electron Microscopy (SEM)**

All diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4 and D-S5 were coated with thin layers of carbon on double conductive copper tapes and put on stub. Then they introduced into the scanning electron microscope to be scanned by a beam of highly energetic electrons to give a magnified three dimensional picture to 5000 times of the original size. The cathode used to generate that beam of electrons was made of tungsten element, which has a voltage of 15 kV.

**Surface Area Estimation**

A 100 ppm stock solution of methylene blue (MB) in distilled water (DW) was prepared. Standard solution, 10, 20, 30, 40, 50, 60, 70, 80, and 90 ppm concentrations were prepared from the stock solution to get a calibration line shown in Figure 2.1.
The surface areas for diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4 and D-S5) were estimated using the methylene blue method (26). Masses of 15, 30, 45, 60, 75, 90, and 105 mg of diatomite adsorbent were introduced in 250 mL Erlenmeyer flasks to which 100 mL volumes of 50 ppm methylene blue solutions were added. The mixtures were left at room temperature in darkness for 6 weeks to reach equilibrium.

Analysis of adsorbate solution was carried out by UV/VIS spectrophotometer at $\lambda_{\text{max}} = 664.4$ nm using the calibrated Beer’s law plot shown in Figure 2.1.

**Removal of Phenols from Aqueous Solutions by Diatomite Samples**

The $\lambda_{\text{max}}$ values for phenol, 4-chlorophenol, and 4-nitrophenol were determined by UV/VIS scan to be 270, 280, and 318 nm respectively.

100 ppm stock solutions for phenol, 4-chlorophenol, and 4-nitrophenol were prepared in DW. Standard solutions (2, 5, 7, 9, 10, 20, 30, 40, 50, and 60 ppm) were prepared for each phenol to draw the calibration curves shown in Figures 2.5, 2.6, and 2.7 at $\lambda_{\text{max}}$ 270, 280, and 318 nm, respectively.

The removal of the three selected phenols from water using unmodified diatomite (Raw-D), surfactant modified diatomite (D-S1, D-S2, D-S3, D-S4, and D-S5), was studied. About 1.2 g of each diatomite samples was placed in a different 125 mL polyethylene bottles. A 30 mL of 100 ppm of each phenol (phenol, 4-chlorophenol, and 4-nitrophenol) were added after being adjusted to pH 9.3 using a buffer solution of pH 11 (12 mM Na$_2$CO$_3$/1 mM NaHCO$_3$), diluted acetic acid, or sometimes both of them. All samples were shaken in the table shaker at 25 °C and 150 rpm for 24 hours. The supernatant of each solution was centrifuged and analyzed for their phenols equilibrium concentrations using UV/VIS spectrophotometer, according to the stated calibration curves shown in Figures 2.2, 2.3 and 2.4.

The removal of phenol solutions were further investigated at different pH values, i.e., at pH over and lower the pH$_{\text{pK}_a}$ for each phenol solution as shown in Table 2.1.

**RESULTS AND DISCUSSION**

Raw diatomite (Raw-D) was modified by five cationic surfactants i.e., dodecyltrimethylammonium bromide (S1), tetradecyltrimethylammonium bromide (S2), hexadecyltrimethylammonium bromide (S3), hexadecyltrimethylammonium chloride (S4), and octadecyltrimethylammonium bromide (S5).

The raw diatomite (Raw-D), and their surfactant modified samples (D-S1, D-S2, D-S3, D-S4, D-S5) were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), total organic carbon (TOC), and scanning electron microscopy SEM techniques. Their surface areas were investigated by methylene blue (MB) method. The adsorption capacities of these diatomite samples for phenol, 4-chlorophenol, and 4-nitrophenol were also investigated.

**Characterization of diatomite samples**

**X-Ray diffraction (XRD)**

Diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4, and D-S5) were analyzed for their mineral composition using XRD technique as shown in Table 3.2.

As shown in Table 3.1, the major content in all diatomite samples is quartz. The kaolinite, muscovite, anorthite, and halite are minors and traces in general. The sodalite mineral, did not appear in diatomite samples.

The modification of raw diatomite sample (Raw-D) with the five cationic surfactants (S1, S2, S3, S4, and S5) indicated almost no change in the mineral contents of the diatomaceous clay.

**Table 2.1: Values of pH used for the removal of phenols**

<table>
<thead>
<tr>
<th>Phenol solution</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>9.3, 10.5</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>8, 9.3, 10</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>6.5, 9.3</td>
</tr>
</tbody>
</table>
X-Ray Fluorescence (XRF)

All diatomite samples, Raw-D, D-S1, D-S2, D-S3, D-S4 and D-S5 were analyzed using XRF technique and tabulated in Tables 3.3.

Table 3.2: Mineral content of diatomite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Halite</th>
<th>Anorthite</th>
<th>Muscovite</th>
<th>kaolinite</th>
<th>Quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>-</td>
<td>*</td>
<td>**</td>
<td>***</td>
<td>Raw-D</td>
</tr>
<tr>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>***</td>
<td>D-S1</td>
</tr>
<tr>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>D-S2</td>
</tr>
<tr>
<td>*</td>
<td>*</td>
<td>*</td>
<td>**</td>
<td>***</td>
<td>D-S3</td>
</tr>
<tr>
<td>*</td>
<td>*</td>
<td>*</td>
<td>**</td>
<td>***</td>
<td>D-S4</td>
</tr>
<tr>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>***</td>
<td>D-S5</td>
</tr>
</tbody>
</table>

*** major  ** minor  * trace  - does not exist

Table 3.3: Corrected for deposited amount of S1 (0.7%), S2 (9.9%), S3 (6.7%), S4 (9.3%), and S5 (2.0%), the assumption of constant water content of 10.7% as in Raw-D.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Diatomite samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>Raw -D</td>
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<tr>
<td>Fe₂O₃</td>
<td>7.57</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.12</td>
</tr>
<tr>
<td>CaO</td>
<td>1.41</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.69</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.29</td>
</tr>
<tr>
<td>SiO₂</td>
<td>35.60</td>
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<tr>
<td>Al₂O₃</td>
<td>16.80</td>
</tr>
<tr>
<td>MgO</td>
<td>2.17</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.58</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>10.70</td>
</tr>
</tbody>
</table>

Corrected for deposited amount of S1 (0.7%), S2 (9.9%), S3 (6.7%), S4 (9.3%), and S5 (2.0%), the assumption of constant water content of 10.7% as in Raw-D.

a L.O.I.: Loss on ignition.

Table 3.3: Infrared absorption bands (cm⁻¹)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
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<tbody>
<tr>
<td>rocking [CH₂]</td>
<td>730</td>
<td>731</td>
<td>729</td>
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<td>729</td>
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<tr>
<td>scissoring [CH₂]</td>
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<td>1463</td>
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<tr>
<td>v₃as [CH₂]</td>
<td>2851</td>
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<td>v₁as [CH₂]</td>
<td>2917</td>
<td>2916</td>
<td>2915</td>
<td>2915</td>
<td>2917</td>
</tr>
</tbody>
</table>

(Reference 28), v₃as: asymmetric stretching vibration; v₁as: symmetric stretching vibration
Table 3.5: Infrared absorption bands (cm⁻¹) of raw diatomite sample (Raw-D)

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>shape of the peak</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>467</td>
<td>M</td>
<td>β[Si-O-Si] of diatomite (466)¹¹</td>
</tr>
<tr>
<td>538</td>
<td>W</td>
<td>β[Si-O-Si] of diatomite (532)³¹, kaolinite (539)²², and muscovite (535)²².</td>
</tr>
<tr>
<td>694</td>
<td>w,br</td>
<td>νₚ[Si-O-Si] of diatomite (697-692)²²</td>
</tr>
<tr>
<td>781</td>
<td>Sh</td>
<td>O-H vibration of SiO-H of diatomite (786)¹¹</td>
</tr>
<tr>
<td>797</td>
<td>M</td>
<td>Si-O stretching of [Si-O-Si] of diatomite (800)³³</td>
</tr>
<tr>
<td>912</td>
<td>M</td>
<td>Si-O stretching of (Si-OH) of diatomite (910)¹¹,⁴⁴</td>
</tr>
<tr>
<td>1110</td>
<td>Sh</td>
<td>(Si-O-Si) stretching of diatomite (1113)²²</td>
</tr>
<tr>
<td>1032</td>
<td>s,br</td>
<td>νₚ[Si-O-Si] of diatomite (1026)¹¹</td>
</tr>
<tr>
<td>1626</td>
<td>w,br</td>
<td>β(H₂O) of diatomite (1630)²²</td>
</tr>
<tr>
<td>3437</td>
<td>w,br</td>
<td>OH-stretching vibration of SiO-H (3435)²²</td>
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<tr>
<td>3620</td>
<td>M</td>
<td>OH-stretching vibration of SiO-H of muscovite (3614)¹¹</td>
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<td>3696</td>
<td>M</td>
<td>OH-stretching vibration of SiO-H of kaolinite (3695)²²</td>
</tr>
</tbody>
</table>

(1) References(30-33)m: medium; w: weak; br: broad; sh: shoulder; s: strong.

Table 3.6

<table>
<thead>
<tr>
<th>Raw-D</th>
<th>D-S1</th>
<th>S1</th>
<th>D-S2</th>
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<th>S3</th>
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<td>3618</td>
<td>3619</td>
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<td>3618</td>
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<td>3619</td>
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<td>3619</td>
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</tr>
<tr>
<td>3696</td>
<td>3696</td>
<td>3698</td>
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<td>3698</td>
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<td>3696</td>
<td>3696</td>
<td>3696</td>
<td>3696</td>
<td>no shift</td>
</tr>
</tbody>
</table>
Table 3.7: Values of pH used for the removal of phenols

<table>
<thead>
<tr>
<th>phenol solution</th>
<th>pKa$^a$</th>
<th>pH used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>9.89</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.5</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>9.20</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>7.15</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.3</td>
</tr>
</tbody>
</table>

$^a$ From Solomons, 1996.

Which means that the surfactants were loaded on diatomite samples in the following order: S2 > S4 > S3 > S5 > S1. For Raw-D, the loss on ignition means that the Raw-D contains carbon and this is related to the biological origin of the diatomite.

In addition, it could be shown from Table 3.3 that the silica content decreased in modified samples relative to Raw-D. The same observed for CaO, MgO, P$_2$O$_5$, and Na$_2$O. The Fe$_2$O$_3$ was increased in all modified diatomite samples relative to Raw-D.

Fourier Transform Infrared Spectroscopy (FTIR)

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an unknown with previously recorded reference spectra.

Surfactants

The results of infrared study for the five cationic surfactants used in the modification process of diatomite samples (DDTMA Br (S1), TDTMA Br (S2), HDTMA Br (S3), HDTMA Cl (S4), and ODTMA Br (S5)) are shown in Table 3.4

Table 3.4 shows the main absorption bands for the five cationic surfactants S1, S2, S3, S4, and S5. They are found at about (729-731), (1463-1466), (2848-2851), and (2915-2917) cm$^{-1}$, which are assigned for rocking, scissoring, symmetric stretching vibration ($\nu_{sy}$), and asymmetric stretching vibration ($\nu_{as}$) of CH$_2$ group of the tail moiety, respectively.

Raw Diatomite (Raw-D)

The results of infrared study for the Raw-D sample are shown in Table 3.5

Some of the main absorption bands of diatomite occur at 3437, 1032, and 912 cm$^{-1}$. The absorption bands at 3696 cm$^{-1}$ and 3620 cm$^{-1}$ are assigned to terminal Si-OH, the band at 1626 cm$^{-1}$ is due to bending vibration of H$_2$O found within diatomite structure. Some of the main absorption bands of diatomite occur at 3437, 1032, and 912 cm$^{-1}$. The band at 3620 cm$^{-1}$ is due to the free silanol group (SiO-H), the band at 1032 cm$^{-1}$ reflects the siloxane (Si-O-Si) group stretching, and the band at 912 cm$^{-1}$ corresponds to (Si-O) stretching of silanol group, 781 cm$^{-1}$ band represents (Si-O-H) vibration, 538 and 467 cm$^{-1}$ absorption bands are due to bending vibration of (Si-O-Si) of diatomite.

Some of the main absorption bands of diatomite occur at 3618, 1032, and 911 cm$^{-1}$. The band at 3618 is due to the free silanol group (SiO-H), the band at 1032 reflects the siloxane (Si-O-Si) group stretching, and the bands at 911 cm$^{-1}$ and 798 cm$^{-1}$ correspond to (Si-O) stretching of silanol group, 530 and 465 cm$^{-1}$ absorption bands are due to bending vibration of (Si-O-Si) of diatomite.

The appearance of the band at 1465 cm$^{-1}$ for the modified diatomite which is assigned to scissoring (CH$_2$) group of the tail moiety of the surfactants confirms the modification process. The absorption band appeared at 730 cm$^{-1}$ that is assigned to rocking (CH$_2$) group of the tail moiety of the pure surfactant has shifted to 720 cm$^{-1}$ in all modified -D samples. The absorption band appeared at 2849 cm$^{-1}$ that is assigned to $\nu_{sy}$(CH$_2$) group of the tail moiety has shifted to 2855, 2851, 2851, 2851, and 2853 cm$^{-1}$ in -D-S1, D-S2, D-S3, D-S4, and D-S5 samples, respectively.

Surfactant Modified Raw Diatomite Samples

The results of the infrared study for the surfactant modified raw diatomite samples compared with raw-D sample are shown in Table 3.6.

From Table 3.6, we can conclude that the
modification of diatomite with different cationic surfactants did not change the main structure of diatomite, so that the main absorption bands which are 467, 538, 694, 781, 797, 912, 1110, 1032, 1626, 3437, 3620, and 3696 cm$^{-1}$ of diatomite appeared in both modified and unmodified samples with some shift in some of them due to the loading of surfactant on diatomite samples.
The appearance of the band at 1465 cm\(^{-1}\) which assigned to scissoring (CH\(_2\)) group of the tail moiety in the surfactants for the modified diatomite reveals the success of modification process. The absorption band appeared at 730 cm\(^{-1}\) that assigned to rocking (CH\(_3\)) group of the tail moiety of the surfactants showed almost shift in some modified diatomite samples. The absorption band appeared at 2849 cm\(^{-1}\) that assigned to \(\nu_s(\text{CH}_2)\) group of the tail moiety of the surfactants has shifted to 2855, 2853, 2853, 2851, and 2855 cm\(^{-1}\) in D-S1, D-S2, D-S3, D-S4, and D-S5 samples, respectively. The

![Graph](image1.png)

**Fig. 2.4:** Calibration curve of 4-nitrophenol solutions at \(\lambda_{\text{max}} = 318\) nm

![Bar Chart](image2.png)

**Fig. 3.1:** Amounts of organic carbon content in diatomite samples

![SEM Image](image3.png)

**Fig. 3.2:** SEM for Raw-D sample
Fig. 3.3: SEM for D-S1 sample

Fig. 3.4: Adsorption of MB on Raw-D sample

Fig. 3.5: Langmuir adsorption isotherms for Raw-D sample
Fig. 3.6: Adsorption of MB on D-S3 sample

Fig. 3.7: Langmuir adsorption isotherms for D-S3 sample

Fig. 3.8: Adsorption of MB on D-S4 sample
absorption band appeared at 2916 cm\(^{-1}\) that assigned to \(\nu_{as}(\text{CH}_x)\) group of the tail moiety has shifted to 2928, 2926, 2926, 2924, and 2926 cm\(^{-1}\) in D-S1, D-S2, D-S3, D-S4, and D-S5 samples, respectively.

**Total organic carbon (TOC)**

To check the amount of cationic surfactant loaded on the surface of diatomite samples, the TOC analysis technique have been selected, because it gives accurate results for the real surfactant.

![Graph of Langmir adsorption isotherms for D-S4 sample](image)

**Fig. 3.9: Langmir adsorption isotherms for D-S4 sample**

![Graph of Adsorption of MB on D-S5 sample](image)

**Fig. 3.10: Adsorption of MB on D-S5 sample**

![Graph of Langmuir adsorption isotherms for D-S5 sample](image)

**Fig. 3.11: Langmuir adsorption isotherms for D-S5 sample**
coverage on the samples. Table 3.7 represents the carbon content in all diatomite samples.

TOC percentages of the samples were converted into (mmol carbon/100 g mineral) according to the following equation (34):

\[ \text{mmol carbon/100g mineral} = \left( \frac{\text{g organic carbon/100g mineral}}{12} \right) \times 1000 \]

... (3.1)

Fig. 3.12: Surface areas for diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4, D-S5)

Fig. 3.13: The amount of phenol adsorbed at pH 9.3 on diatomite samples

Fig. 3.14: Show the amount of phenol adsorbed at pH 10.5 on diatomite samples
As shown in Figures 3.1 and 3.2, Raw-D sample has a very low amount of organic material due to the origin of diatomite which is a sedimentary rock composed principally of silica microfossils of aquatic unicellular algae (35). All modified diatomite samples showed higher TOC values than the raw samples (Raw-D). This trend confirms the loading of surfactants on diatomite samples. The highest TOC content in diatomite samples was found in D-S5.

Figure 3.1 showed that the trend for the organic carbon content in diatomite samples is as follows: D-S5>D-S2>D-S4>D-S1>D-S3>>Raw-D.

Fig. 3.15: The amount of 4-chlorophenol adsorbed at pH 8.0 on diatomite samples

Fig. 3.16: The amount of 4-chlorophenol adsorbed at pH 9.3 on diatomite samples

Fig. 3.17: The amount of 4-chlorophenol adsorbed at pH 10.0 on diatomite samples
The difference between TOC contents in all diatomite samples compared to raw diatomite (Raw-D) confirm the loading of the cationic surfactants on diatomite samples which is in agreement with the loss on ignition values determined by XRF analysis in the same samples.

**Fig. 3.18:** The amount of 4-nitrophenol adsorbed at pH 6.5 on diatomite

**Fig. 3.19:** The amount of phenol adsorbed at pH 9.3 on diatomite samples

**Fig. 3.20:** Comparison among the adsorption of phenol, 4-chlorophenol, and 4-nitrophenol on diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4 and D-S5 at pH 9.3
**Scanning electron microscopy (SEM)**

SEM is used to obtain structural and analytical information about minerals (36). The SEM pictures for Raw-D, and their S1-modified samples are shown in Figures 3.2 and 3.3.

Figures 3.2 and 3.3 show obvious partial coverage for the diatomite pores, which indicates the loading of cationic surfactants on the surface of the diatomite samples. Sodalite was appeared as revealed by XRD measurements as a major mineral constituent.

**Surface Area Estimation**

The results of Langmuir adsorption isotherms for methylene blue (MB) adsorption on diatomite samples are summarized in Tables (3.12-3.17). The saturation level of MB adsorption and its adsorption isotherms for all diatomite samples are illustrated in Figures (3.7-3.18).

\[ S = X_m \cdot N \cdot A_m \]  

... (3.2)

Where: S: surface area (m²/g), N: Avogadro’s number (molecule/mol), A_m: molecular cross sectional area (m²/molecule) (1.2 m²/molecule), X_m: monolayer capacity.

Monolayer capacity X_m is estimated according to the Langmuir equation (3.2) and the surface areas (S) are also estimated. The results are summarized in Figure 3.12.

The raw diatomite samples (Raw-D) have higher surface areas than their surfactant modified samples. Thus, the modification of Raw-D and by cationic surfactants decreases the surface area.

It has been noticed from the general trend of TOC in diatomite samples that the more TOC value means the more loading of the surfactant on the diatomite samples, and that may be noticed in general from the surface areas estimated in Table 3.18. Since D-S5, which has the largest TOC value, it has the smallest surface area, and Raw-D, which has the lowest amount of TOC, has the largest surface area.

**Removal of Phenol, 4-Chlorophenol, and 4-Nitrophenol from Their Aqueous Solutions**

Phenols exist in solution as both protonated and deprotonated species, with the proportions being a function of pH as in the following equation:

\[ \text{C}_6\text{H}_5\text{OH} \text{ (phenol)} \rightarrow \text{C}_6\text{H}_4\text{O}^- \text{ (phenolate ion)} + \text{H}^+ \]  

... (3.3)

Removal of phenols was studied at pH 9.3. In order to compare the amounts of phenols removal, experiments were conducted at different pH values (higher and lower than the pKa ) of each phenol, as shown in Table

**Removal of Phenol**

The removal of phenol was investigated at pH values 9.3 and 10.5, the former is lower than pK_a (phenol) = 9.89 and the latter is higher than pK_a. Thus, the effect of pH on the adsorption of phenol was investigated. Tables 3.15-3.22 and Figures 3.16-3.19 show the amounts of phenol adsorbed at pH 9.3 and 10.5 on all diatomite samples, respectively.

General trends could be obtained from Figures 3.14. The adsorption of phenol at pH 10.5 is greater than that at pH 9.3 for all diatomite samples. The surfactant modified diatomite samples showed higher adsorption capacities than unmodified samples. Thus, the adsorption capacity at pH 9.3 decreases in the order:

\[ \text{D-S4}\text{>}\text{D-S2}\text{>}\text{D-S5}\text{>}\text{D-S1}\text{>}\text{D-S3}\text{>}\text{Raw-D}. \]

At pH 10.5 adsorption capacity of diatomite samples decreases in the order: \text{D-S2}\text{>}\text{D-S4}\text{>}\text{D-S5}\text{>}\text{D-S1}\text{>}\text{Raw-D}.

**Removal of 4-Chlorophenol**

The removal of 4-chlorophenol on diatomite samples was investigated at pH 8.0, 9.3, and 10.0. Tables 3.17-3.20 and Figures 3.18-3.23 show the amount of 4-chlorophenol adsorbed at pH 8.0, 9.3, and 10.0, respectively.

General trends could be obtained from Figures 3.17. The adsorption of 4-chlorophenol at pH 8.0 is greater than that at pH 9.3 and 10.0. The surfactant modified diatomite samples showed higher adsorption capacities than unmodified samples.
For modified diatomite samples, the adsorption capacity at pH 8.0 decreases in the order: D-S2>D-S5>D-S4>D-S3>D-S1>>Raw-D.

At pH 9.3 diatomite samples have an adsorption capacity decreases in the order: D-S5>D-S2>D-S3>D-S1>D-S4>>Raw-D.

At pH 10.0 diatomite samples have an adsorption capacity decreases in the order: D-S5>D-S4>D-S2>D-S3>D-S1>Raw-D.

Removal of 4-nitrophenol

The removal of 4-nitrophenol was investigated at pH 6.5 and 9.3 by diatomite samples. Table 3.31 and Figures 3.42 show the amount of 4-nitrophenol adsorbed at pH 6.5 and 9.3, respectively.

General trends could be obtained from Figures 3.18-3.19. The adsorption of 4-nitrophenol at pH 6.5 is greater than that at pH 9.3 for all diatomite samples. The adsorption of 4-nitrophenol on modified treated samples were found to be higher than unmodified diatomite samples at pH 9.3. The surfactant modified diatomite samples showed higher adsorption capacities than unmodified samples in all PH ranges.

For modified diatomite samples, the adsorption capacity at pH 6.5 decreases in the order: D-S4>D-S2>D-S5>D-S1>D-S3>>Raw-D.

At pH 9.3 diatomite samples have an adsorption capacity that decreases in the order: D-S5>D-S2>D-S3>D-S1>D-S4>>Raw-D.

Comparing the adsorption capacities for phenol, 4-chlorophenol, and 4-nitrophenol at the same pH value (9.3) are shown in Figure 3.19.

Figure 3.20 show that the adsorption amount of 4-chlorophenol on both raw and modified diatomite samples has the highest adsorption properties. Whereas phenol and 4-nitrophenol have different adsorption amounts on diatomite samples.

In general, we can say that modified diatomite samples have better adsorption capacities for phenol, 4-chlorophenol, and 4-nitrophenol than raw diatomite samples. Diatomite samples adsorb phenol better than 4-nitrophenol.

All adsorption follows type one isotherms which is the Langmuir.

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