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 surfactantsdodecyltrimethy-lammoniumbromide (DDTMA-Br), tetradecyltrimethylammonium bromide (TDTMA-Br) , Hexadecyltrimethylammonium bromide(HDTMA-Br), hexadecltrimethylammonium 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 isothermsof 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[1]. Diatomaceous silica is regarded as mineral of organic origin. Where the silica of fossilized diatom skeleton resembles opal or hydrous silica in composition: $SiO_2 \cdot nH_2O$.

The diatomite occurs mainly at A Azraq area, approximately 110 km northeast of Amman, covered an area of more than 150 km[2]. 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[2]. 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[3].

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[5].

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[7,8]. Organoclays form important type of modified clay minerals .Their uses are many including some environmental applications[9-12].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[13].

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[14-18].Diatomite may be modified chemically in number of ways[19,20].

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[21].

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 >1.00mm. The portion <0.5mm was washed with distilled water (DW) three times to remove any insoluble contaminants. Then dried overnight in an oven at 110 °C, stored indesiccators 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(22). Raw-D sample (200g)was immersed in 1.333Lof 6 MNaOH 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 MNaOH 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 (23). 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 shaked (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 Rawand 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-Dwere 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, 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 (2θ). A (2θ) interval between 5° and 60° 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 is emitted as X-ray photons with $\lambda = 1.78897$ Å. A monochromator removes X-rays of undesired wave lengths so that only Co Kα1 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 ($Li_2B_4O_7$) 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 usingFTIR 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].

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 >1.0 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.

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.

Analysisofadsorbate solution was carried out by UV/VIS spectrophotometer at λ_{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 λ_{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 λ_{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 (12mM Na_2CO_3/1 mM $NaHCO_3$), diluted acetic acid, or sometimes both of them. All samples were shaken in the table shaker at 25 ÚC 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 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) l-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**

Phenol solution	pH
Phenol	9.3, 10.5
4-chlorophenol	8, 9.3, 10
4-nitrophenol	6.5, 9.3

X-Ray Fluorescence (XRF)

All diatomite samples, Raw-D, D-S1, D-S2, D-S3, D-S4and D-S5 were analyzed using XRF technique and tabulated in Tables 3.3.

Table 3.3 shows the trend of loss on ignition in diatomite samples which indicates the amounts of surfactants loaded on diatomite samples as follows: D-S2>D-S4>D-S3>D-S5>D-S1>Raw-D.

Table 3.2: Mineral content of diatomite samples

Halite	Anorthite	Muscovite	kaolinite	Quartz	Sample
*	-	*	**	***	Raw-D
*	*	*	*	***	D-S1
*	*	**	*	***	D-S2
*	*	*	**	***	D-S3
*	*	*	**	***	D-S4
*	*	*	*	***	D-S5

*** 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.

Oxide	Diatomite samples										
%	Raw -D	D-S1	D-S1*	D-S2	D-S2*	D-S3	D-S3*	D-S4	D-S4*	D-S5	D-S5*
Fe_2O_3	7.57	8.09	8.15	6.92	7.68	7.19	7.71	7.00	7.72	5.81	5.93
MnO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02
TiO_2	1.12	1.15	1.16	0.99	1.10	1.07	1.08	0.70	0.77	0.76	0.78
CaO	1.41	0.77	0.78	0.70	0.78	0.72	0.73	0.71	0.78	0.45	0.46
K_2O	2.69	2.79	2.81	2.39	2.65	2.51	2.53	2.42	2.67	2.06	2.10
P_2O_5	0.29	0.28	0.28	0.23	0.26	0.26	0.26	0.26	0.28	0.14	0.14
SiO_2	56.60	55.85	56.24	50.95	56.55	52.85	53.22	51.00	56.23	45.00	45.92
Al_2O_3	16.80	16.95	17.07	15.00	16.65	15.90	16.01	15.45	17.03	17.80	18.16
MgO	2.17	1.83	1.84	1.72	1.91	1.76	1.77	1.69	1.86	0.94	0.96
Na_2O	0.58	0.58	0.58	0.41	0.46	0.35	0.36	0.31	0.35	14.10	14.39
L.O.I[a]	10.70	11.40	11.48	20.60	22.86	17.40	17.52	20.00	22.05	12.70	12.96

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})

S1	S2	S3	S4	S5	Assignment
730	731	729	730	729	rocking [CH$_2$] (729)*
1466	1465	1463	1464	1464	scissoring [CH$_2$] (1465)*
2851	2849	2848	2849	2850	υ_{sy}[CH$_2$] (2850)*
2917	2916	2915	2915	2917	υ_{as} [CH$_2$] (2916)*

* (Reference 28). $\upsilon_{as:}$ asymmetric stretching vibration; υ_{sy}: symmetric stretching vibration

Table 3.5: Infrared absorption bands (cm⁻¹) of raw diatomite sample (Raw-D)

Wave number (cm⁻¹)	shape of the peak	Assignment
467	M	β[Si-O-Si] of diatomite (466)[1]
538	W	β[Si-O-Si] of diatomite (532) [1], kaolinite (539)[2], and muscovite (535)[2].
694	w,br	υ_{sy}[Si-O-Si] of diatomite (697-692) [2]
781	Sh	O-H vibration of SiO-H of diatomite (786)[1]
797	M	Si–O stretching of [Si-O-Si] of diatomite (800)[3]
912	M	Si-O stretching of (Si-OH) of diatomite (910)[1,4]
1110	Sh	(Si-O-Si) stretching of diatomite (1113)[2]
1032	s,br	υ_{as}[Si-O-Si] of diatomite (1026)[1]
1626	w,br	β(H_2O) of diatomite (1630)[2]
3437	w,br	OH-stretching vibration of SiO-H (3435)[2]
3620	M	OH-stretching vibration of SiO-H of muscovite (3614) [1]
3696	M	OH-stretching vibration of SiO-H of kaolinite (3695) [2]

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

Table 3.6

Raw-D	D-S1	S1	D-S2	S2	D-S3	S3	D-S4	S4	D-S5	S5	Assignment
467	463		463		463		463		463		shifted from Raw-D band 467
538	538		538		538		538		538		no shift
694	694		694		694		694		694		no shift
	730	730	730	731	730	729	730	730	730	729	shifted from surfactants band 730
781	781		781		781		781		781		no shift
797	797		797		797		797		797		no shift
912	912		912		914		912		912		no shift
1110	1111		1111		1112		1110		1113		shifted from Raw-D band 1110
1032	1032		1032		1032		1035		1034		no shift
	1465	1466	1465	1465	1465	1463	1465	1464	1465	1464	no shift
1626	1625		1625		1625		1625		1625		no shift
	2855	2851	2853	2849	2853	2848	2851	2849	2855	2850	shifted from surfactants band 2849
	2928	2917	2926	2916	2926	2915	2924	2915	2926	2917	shifted from surfactants band 2916
3437	3440		3440		3439		3439		3440		shifted from Raw-D band 3437
3620	3618		3618		3619		3618		3619		no shift
3696	3696		3698		3698		3698		3696		no shift

**Table 3.7: Values of pH used
for the removal of phenols**

phenol solution	pKa[a]	pH used
Phenol	9.89	9.3
		10.5
4-chlorophenol	9.20	8.0
		9.3
		10.0
4-nitrophenol	7.15	6.5
		9.3

[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_2O_5 and Na_2O. The Fe_2O_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[27].

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 (υ_{sy}), and asymmetric

stretching vibration (υ_{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

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_2O 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 (SiO-H) vibration, 538 and 467 cm^{-1} absorption bands are due to bending vibration of (Si-O-Si) of diatomite[29,30].

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 $\upsilon_{sy}(CH_2)$ group of the tail moietyhas 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.
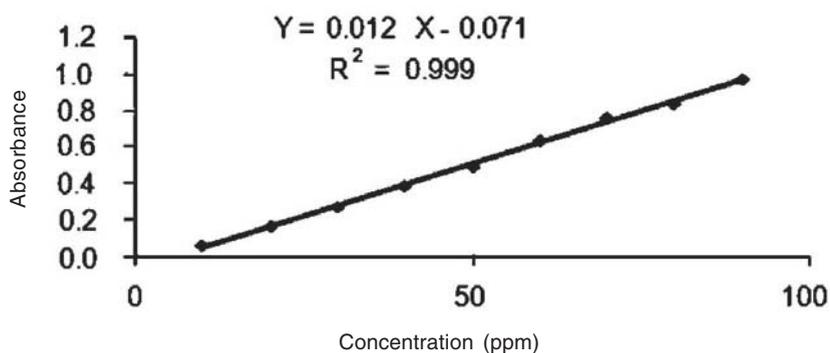

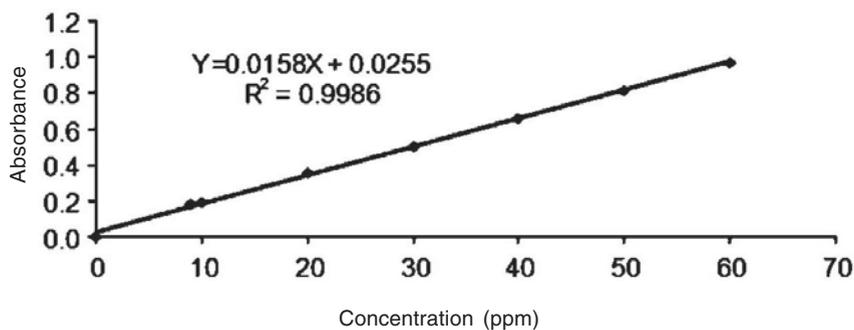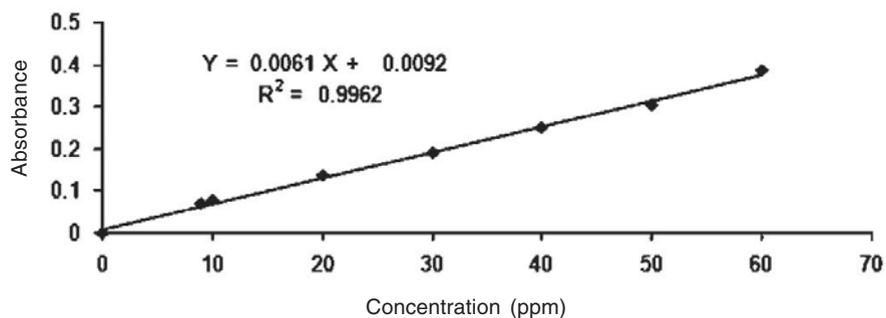**Fig. 2.1: Calibration curve of MB solutions at λ_{max} = 664.4 nm**

Fig. 2.2: Calibration curve of phenol solutions at λ_{max} = 270 nm
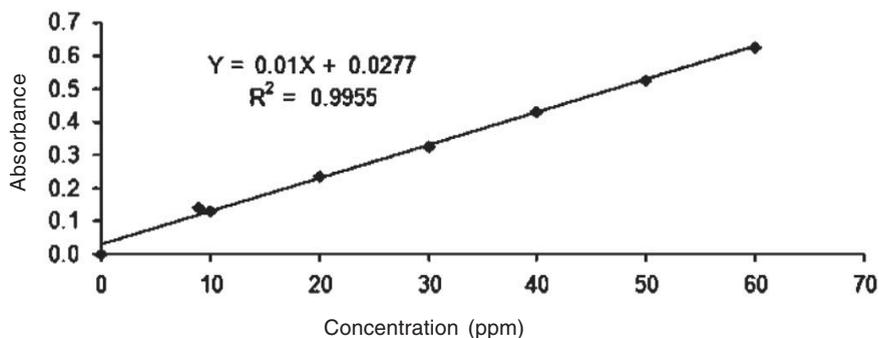
Fig. 2.3:Calibration curve of 4-chlorophenol solutions at λ_{max} = 280 nm

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_2) 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 $\upsilon_{sy}(CH_2)$ 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

Fig. 2.4: Calibration curve of 4-nitrophenol solutions at λ_{max} = 318 nm
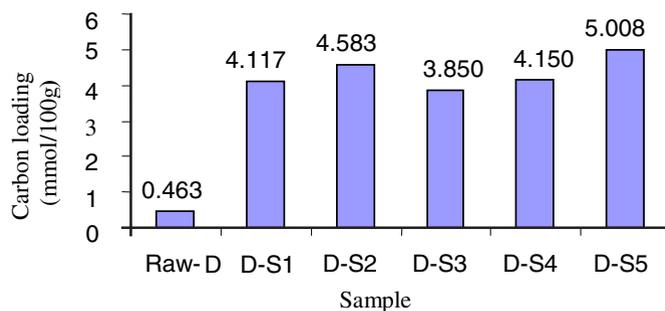
Fig. 3.1: Amounts of organic carbon content in diatomite samples
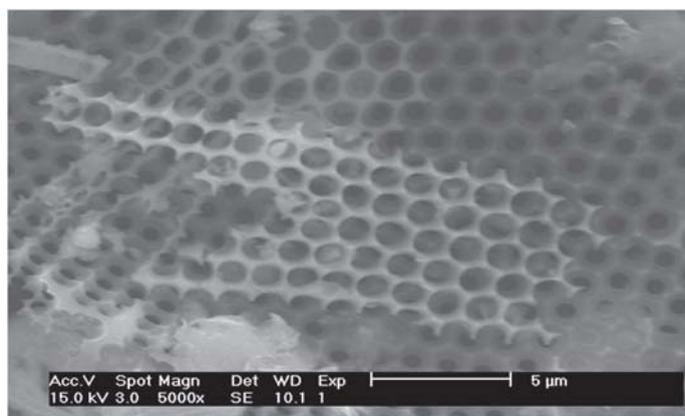
Fig. 3.2: SEM for Raw-D sample

Fig. 3.3: SEM for D-S1 sample
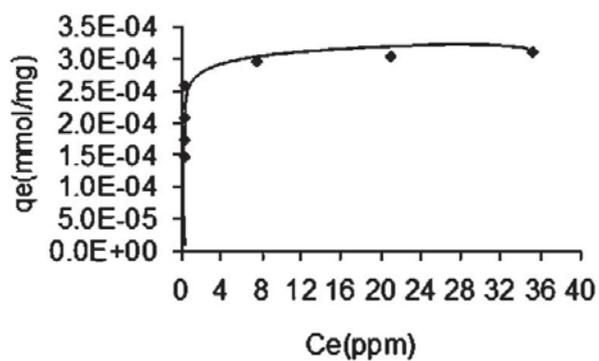
Fig. 3.4: Adsorption of MB on Raw-D sample
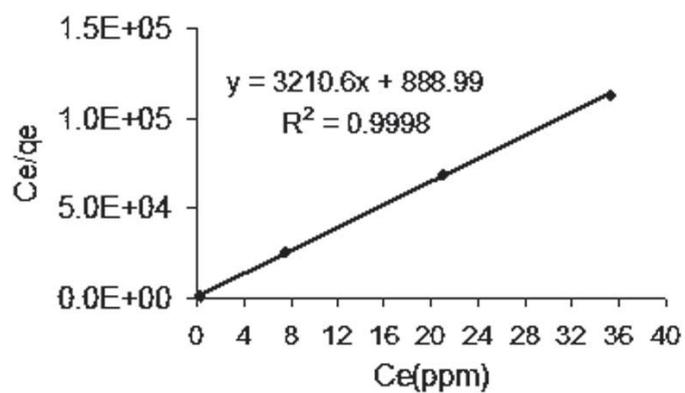
Fig. 3.5: Langmuir adsorption isotherms for Raw-D sample
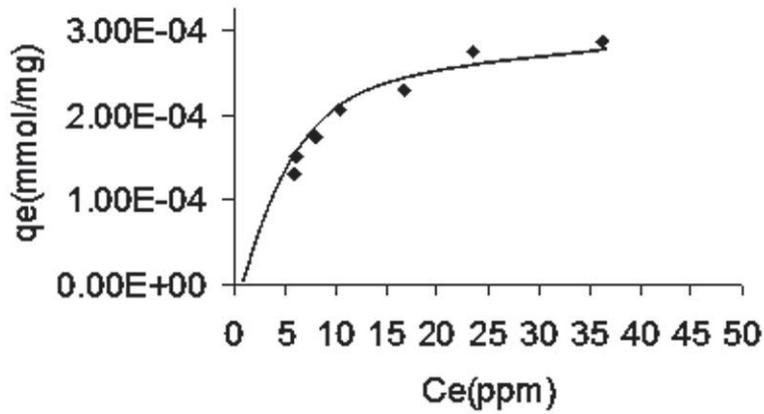
Fig. 3.6: Adsorption of MB on D-S3 sample

$$y = 3728.9x + 24857$$
$$R^2 = 0.9911$$
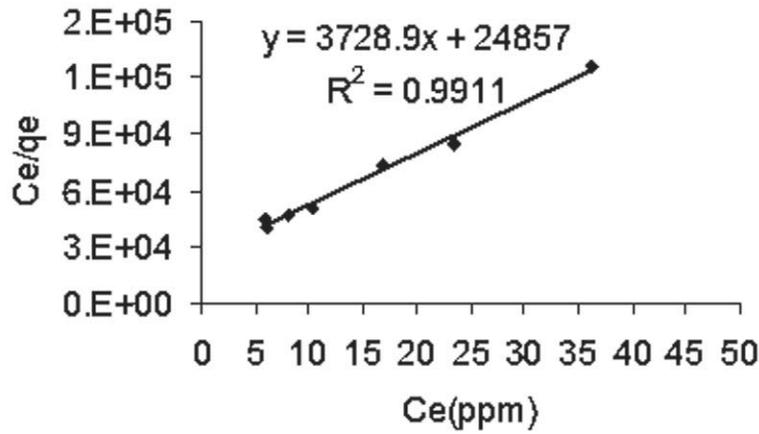
Fig. 3.7: Langmuir adsorption isotherms for D-S3 sample
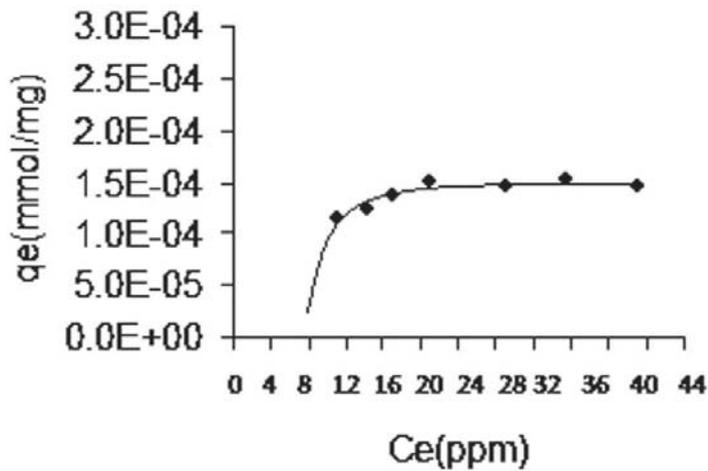
Fig. 3.8: Adsorption of MB on D-S4 sample

absorption band appeared at 2916 cm^{-1} that assigned to υ_{as}(CH$_2$) 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
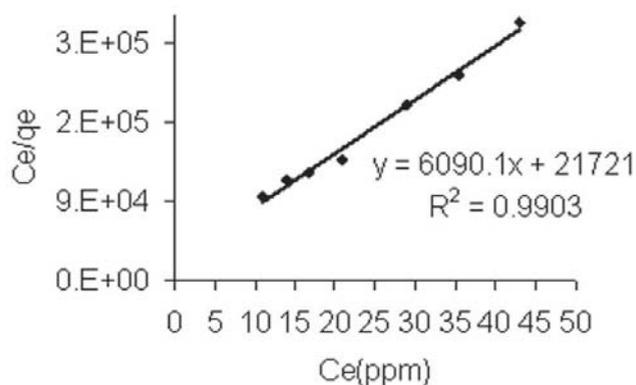
Fig. 3.9: Langmir adsorption isotherms for D-S4 sample
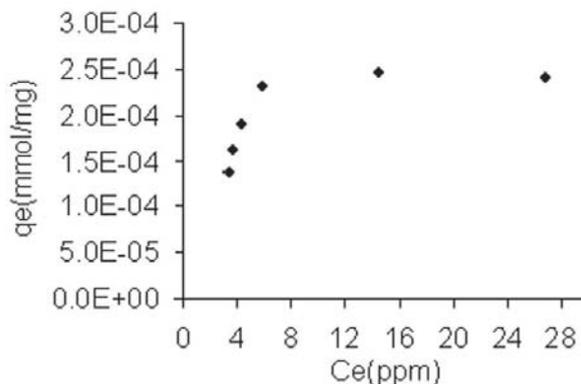
Fig. 3.10: Adsorption of MB on D-S5 sample
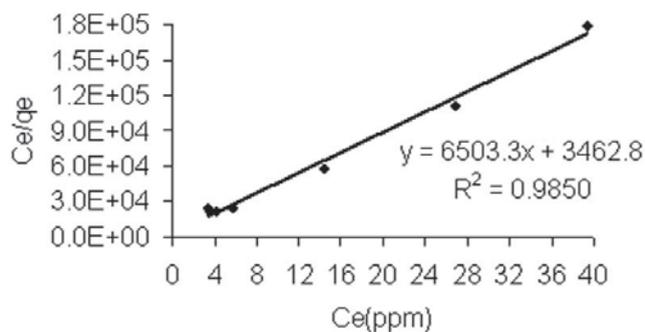
Fig. 3.11: Langmuir adsorption isotherms for D-S5 sample

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):

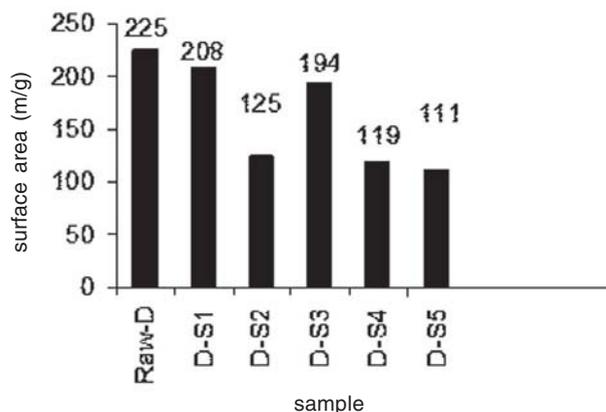[mmol carbon/100g mineral]=[g organic carbon/100g mineral]×[1000/12] …(3.1)

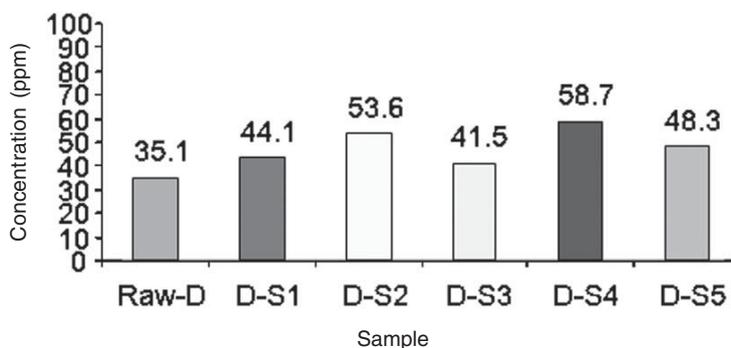**Fig. 3.12: Surface areas for diatomite samples (Raw-D, D-S1, D-S2, D-S3, D-S4, D-S5)**

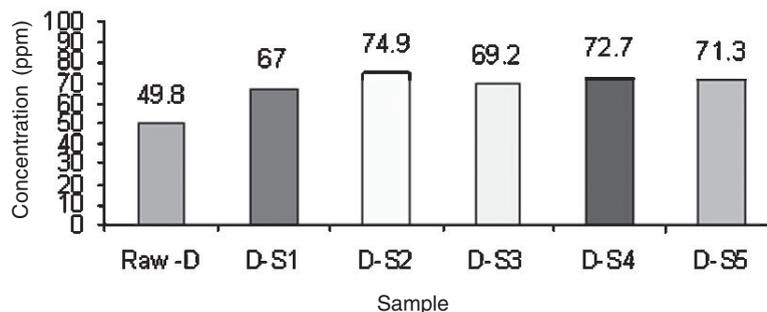**Fig. 3.13: The amount of phenol adsorbed at pH 9.3 on diatomite samples**

Fig. 3.14: Show the amount of phenol adsorbed at pH 10.5 on diatomite samples

As shown in and 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.
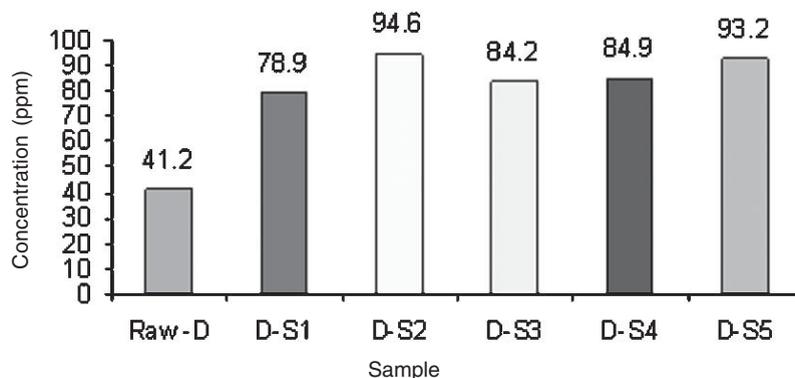

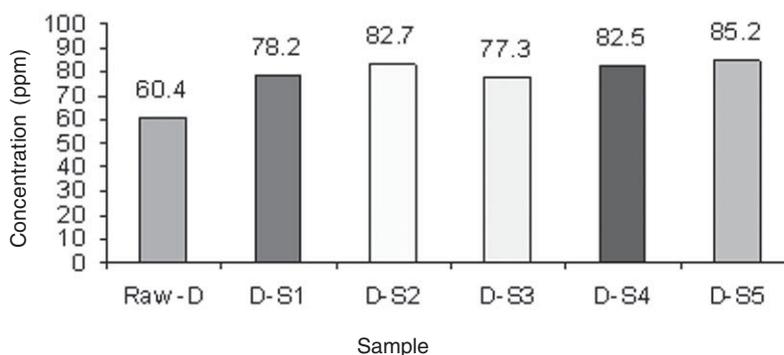**Fig. 3.15: The amount of 4-chlorophenol adsorbed at pH 8.0 on diatomite samples**

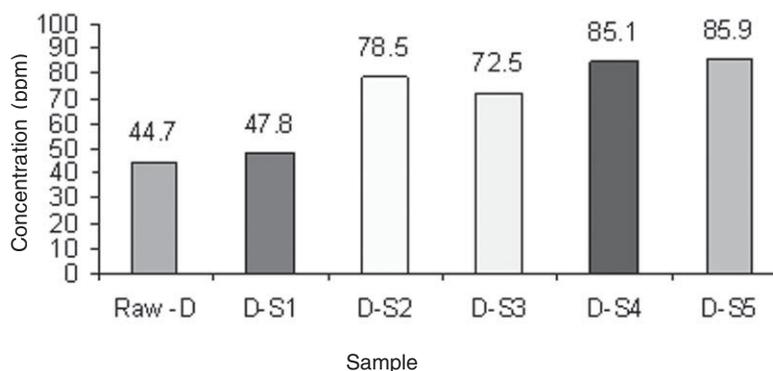**Fig. 3.16: The amount of 4-chlorophenol adsorbed at pH 9.3 on diatomite samples**

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.
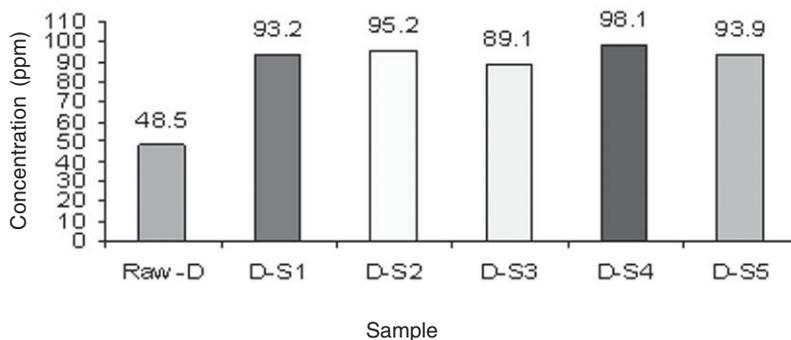

Fig. 3.18: The amount of 4-nitorphenol adsorbed at pH 6.5 on diatomite
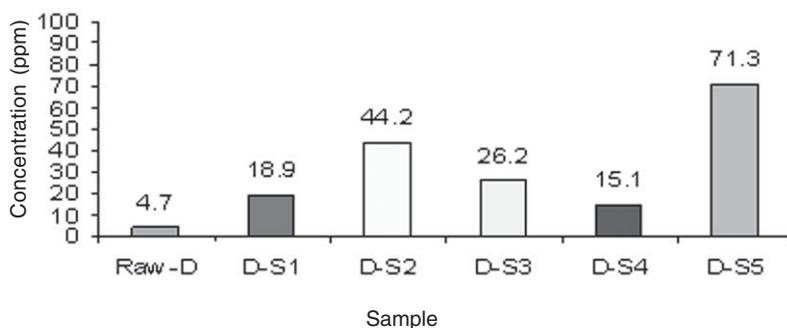

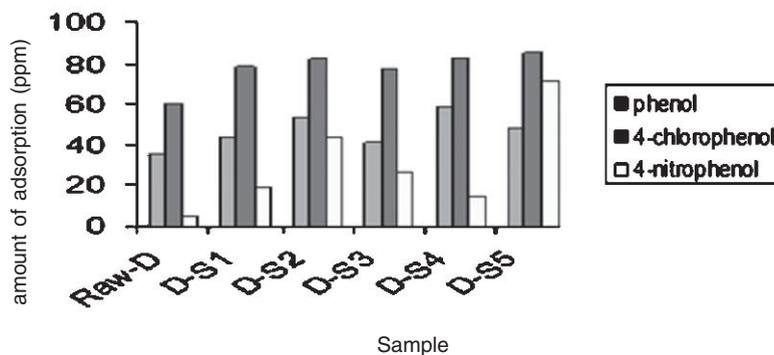**Fig. 3.19: The amount of phenol adsorbed at pH 9.3 on diatomite samples**

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).

$$S = X_m . N . A_m \qquad ... (3.2)$$

Where; S: surface area (m^2/g), N: Avogadro's number (molecule/mol), A_m: molecular cross sectional area (m^{2-}/molecule) (1.2 m^2/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:

$$C_6H_5OH \text{ (phenol)} \qquad C_6H_5O^- \text{ (phenolate ion)} + H^+$$
$$\qquad\qquad\qquad .... (3.3)$$

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:

D-S4>D-S2>D-S5>D-S1>D-S3>Raw-D.

At pH 10.5 adsorption capacity of diatomite samples decreases in the order: D-S2>D-S4>D-S5>D-S3>D-S1>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-S4>D-S1>D-S3>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-nirophenol 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-clorophenol 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 Langmiur.

REFERENCES

1. Kadey, J."Diatomite", Industrial minerals and rocks, **267**: 677-707.(1973)
2. Al'ali, J., and Qaqr'a, M.,Diatomite in Jordan. Arabic Edition(1995).
3. Dolley, P., and Moyle, R., History and overview of the U.S. diatomite mining industry, with emphasis on the Western United States. Geological Survey Bulletin, pp 2209. E1-E8(2003)
4. Baird, C., Environmental Chemistry, pp215-325(2001).
5. Al-Rashdan, Z.,Investigation of Natural Zeolite Tuffs on Their Ability for Sewage Cleaning purposes. PhD thesis, Oldenburg University, Germany (2001).
6. Al-Degs Y., Tutunju M., ShawabkehR. The Feasibility of Using Diatomite and Mn–Diatomite for Remediation of Pb^{2+}, Cu^{+2}, and Cd^{2+} from Water. *Separation Science and Technology.* **35**(14): 2299-2310 (2000).
7. Xi,Yunfei and Martens , Way de and He ,Hongping and Frost ,Ray, *Journal of Thermal Analysis and Calorimetry* **81**: 91-97 (2005).
8. Guodong Sheng ,Jun Hu,Xiangke Wang ,Applied Radiation and Isotopes , **66**: 1313-1320 (2008).
9. Noemie Van Garderen , Frank J. Clemers, Matheus Mezzomo Perez Bergmann,

Thomas Graule, *Applied Clay Science,* **52** (1-2): 115-121 (2011).

10.   Ali Ergun ,Construction and Building Material , Vol 25, issue 2, 806-812(2011)

11.   NurhayatDegirmenci , ArinYilmaz ,*Construction and Building Materials ,* **23**(1): 284-288 (2009)

12.   G.R. Alther, *Fluid/Particle Separation Journal* **13**: 146 (2000).

13.   NezahatEdiz Ismail Bentli, Liknur Tatar, *International journal of Menar Processing* ,**94**(28):129-134 (2010).

14.   Reckweg Anders, BASF – personal communication 21st January (2000)..

15.   Porter, R.,"The Handbook of Surfactants" ; 2. Edition, Chapman & Hall(1994).

16.   Falbe, J.,"Surfactants in Consumers Products"(1987).

17.   Landgren, M.,"ThermodynamicModelling of Ionic Surfactant Systems", A doctoral dissertation, Lund University(1990).

18.   Porter, R., "The Handbook of Surfactants" ; 2. Edition, Chapman & Hall(1994)..

19.   Al-Degs Y., Tutunju M., ShawabkehR.,The Feasibility of Using Diatomite and Mn–Diatomite for Remediation of Pb^{2+}, Cu^{+2}, and Cd^{2+} from Water. Separation Science and Technology. 35(14), pp. 2299–2310(2000).

20.   Li , Z ., Anghel, I., Bowman, S.,Sorbtion of Oxyanionsby Surfactant-Modified Ziolite, 19,843-857(1998).

21.   Lide, R., CRC Handbook of Chemistry and Physics. 73rd edition. CRC Press(1993).

22.   Khraisheh, M., Al-Degs, Y., Mcminn, W., Remediation of wastewater containing heavy metals using raw and modified diatomite. *Chemical Engineering Journal*, **99**: 177-184 (2005).

23.   Li, Z., Alessi, D., Allen, L.,Influence of Quaternary Ammonium on Sorption of Selected Metal Cation onto ClinoptiloliteZiolite, *Journal of Environmental Quality,* **31**: 1106-1114 (2002).

24.   He, M., Wu, C., Zhang, J., Ran Y.,Removal of Aniline and Phenol from Water Using Raw and Aluminum Chloride-Modified Diatomite. *Journal   of   Environmental Management*(2005).

25.   Gao, B., Jiang, P., An, F., Zhao, S., and Ge, Z., *Applied Surface Science*, **250**(1-4): 273-279 (2005).

26.   Porter, R., "The Handbook of Surfactants" ; 2. Edition, Chapman & Hall(1994)

27.   Cutler, G., &Cavis, C.**,**"Detergency. Theory and test methods", Surfactant Science Series, vol 5(1981).

28.   Farmer, V. C.,"The Infrared Spectra of Minerals," 1st ed. Mineralogical Society, London (1974).

29.   Reckweg Anders, BASF – personal communication, Presentation at the Danish Varnish and Paint Chemist Association (DLFF) (1999).

30.   HellstenM.**,**"Industrial Applications of Nonionic Surfactants", Industrial Applications of Surfactants I, Royal Society of Chemistry, Special publication no. **39**: 179-194 (1987).

31-   Marel, W., Beutelspacher, H.,*Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures,* Elsevier Scientific Publishing Company, Amesterdam(1976).

32-   Wu, J., Yang, S., Lin, J.,Advanced tertiary treatment of municipal wastewater using raw and modified diatomite(2005).

33-   Gaiabeh, S., Rawejfeh, Z., Water Treatment and Energy Source in Jordan Developing Country study. *Water Resources*, **79**(9): 458-463(1989)

34.   Ibrahim I. Bazbaz ,Roshdi I. Yousif and Salem M. Musleh , *Asian Journal of Chemistry* .**22**, Part 2 ,(2011)

35.   Gao, B., Jiang, P., An, F., Zhao, S., and Ge, Z., *Applied Surface Science,* **250**(1-4): 273-279 (2005).

36.   Schuler, F., and Ghosh, M." Diatomaceous Earth filtration of Cysts and other Particulates Using Chemical Additives " , Journal of AWWA, **82**: 67-75(1990)