RESEARCH ARTICLE

REMOVAL OF PHENOLS FROM AQUEOUS SOLUTIONS USING BI MODIFIED JORDANIAN DIATOMACEOUS CLAY

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ARTICLE INFO	ABSTRACT
	Modification of Jordanian diatomitaceous clay by aluminum chloride followed by treatment with cationic surfactants was carried out to enhance its capacity to remove phenols and its derivatives as organic pollutants from their aqueous solutions. The original sample and the modified derivatives were thoroughly characterized to check for the modification process by X-ray diffraction, X-ray fluorescence, scanning electron microscopy, total organic carbon, and Fourier transform infrared spectroscopy. The surface area for all studied samples was also estimated using methylene blue method. Experiments were performed to study the role of modified diatomite and surfactants treated modified diatomite samples in the removal of phenol, 4-chlorophenol, and 4-nitrophenol from their aqueous solutions. The results has revealed, in general, that efficiency of diatomite to remove organic pollutants form aqueous solution is higher than efficiency of the unmodified ones, and the efficiency of the treated modified diatomite samples are higher than the untreated samples.

INTRODUCTION

Diatomaceous clay with moderate silica content similar to the composition of Molar of Denmark occurs in Al Azraq area about 110 km northeast of Amman (Alali J. and Qararah, 1995). The diatoms are of the discs and pinnate forms (Khoury, 2004). Besides alumina, iron oxides are also found to be 2.3-8.5% in the samples (Alali, 1991). The unique combination of physical and chemical properties of diatomite has made it suitable material for a wide range of industrial and agricultural applications (Burrnett, 1991). Among its various uses, that of adsorbent is of special interest in the treatment of wastewaters, particularly from heavy metals cations and organic pollutants. Phenols are widely used in production of resins for various applications (Roostaei and Tezel, 2004). They have been detected in surface waters, rainwater, sediments, drinking water, groundwater, industrial effluents, urban runoff, and at hazardous waste sites. It generally does not adhere very strongly to soils and tends to filter rapidly through soil, which may account for the lack of monitoring data, since any phenol released to soils is likely to move to groundwater. It is degraded rapidly in air (half-life of approximately 15 hours), but may persist in water for a somewhat longer period. In soil, phenol will biodegrade rapidly; the half-life in soil is generally short period (few days) (Roostaei and Tezel, 2004). Phenols presence in polluted waters is of concern to many countries including Jordan, and always there some interest in the development of local methods in water remediation. Therefore, the removal of phenols from industrial effluents is required before sewage disposal. For this purpose, various (more or less) environment-friendly methods have been suggested (Wang *et al*., 2013; Min Wang *et al*., 2013; Peng Yuan *et al*., 2013; Angela F. Danil de Namor *et al*., 2012). Surfactants are chemicals that exhibit ability to a dsorb at surfaces. They 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. The hydrophilic part on the other hand has a great affinity to water but it is not very compatible with non-polar solvents. The hydrophilic Part is an ionic or strongly polar group (for instance ethylene oxide) (Porter, 1994; Pilemand, 2002; Landgren, 1990). The hydrophobic part of the surfactants is often referred to as the hydrocarbon tail, whereas the polar part is referred to as the head-group. More than one hydrophilic or hydrophobic group can be present in a surfactant molecule. The purpose of the present work is modifying the Jordanian diatomaceous clay with aluminum chloride followed by modification with different surfactants to improve their surface properties that could enhance their use as agents for the removal of phenols from water. The cationic surfactants are dodecyltrimethyl ammonium bromide

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(DDTMA-Br) coded (S1), tetradecyltrimethyl ammonium bromide (TDTMA-Br) coded (S2), hexadecyltrimethyl ammonium bromide (HDTMA-Br) coded (S3), and octadecyltrimethyl ammonium bromide (ODTMA-Br) coded (S4). Many studies were carried out to study the Jordanian diatomite. For example, the effect of initial concentration, particle size, mass of the adsorbent, pH and agitation speed on adsorption behavior of methylene blue (MB) onto Jordanian diatomite has been investigated by Al-Ghouti *et al.* (2009). The maximum adsorption capacity, q, increased from 75 to 105 mg/g when pH of the dye solution increased from 4 to 11. The feasibility of using diatomite and Mn–diatomite for remediation of Pb^2, Cu^2, and Cd^2 from water was studied by Al-Degs *et al.* (2000) Khraisheh *et al.* (2005) studied the effect of OH and silanol groups in the removal of dyes from aqueous solution using diatomite.

MATERIALS AND METHODS

Sample preparation

Diatomite sample was brought from borehole MQ/BH-8 from depth of 18-22 m drilled by the Jordanian NRA. The sample was crushed at the 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 over night in an oven at 110 ˚C, stored in a desiccator after being put in polyethylene bottles, and coded Raw-D.

Pretreatment of raw diatomite (Raw-D) with AlCl₃/NaOH

Pretreatment of Raw-D sample with $AlCl_3$ and NaOH was done according to Khraisheh *et al.* (2005). Raw-D sample (200 g) was immersed in 1.3 L of 6 M NaOH at 90 ˚C for 2 hours. Then the mixture was placed in one liter 2.5 M $AlCl_3$ (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 1.3 L 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 Al-D.

Modification of diatomite (Al-D) by different cationic surfactants

The sample (Al-D) was independently modified by four cationic surfactants, i.e., (S1), (S2), (S3), and (S4) according to the procedure reported in (Li *et al.*, 2002a). A solution of 67 mM of each surfactant (S1, S2, S3, and S4) was prepared. A volume of 65 mL surfactant solution was added to 20 g of diatomite sample (Al-D) in 125 mL-polyethylene bottles then shaked for 8 hours (150 rpm, 25 ˚C) in a thermostatic table shaker. 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 were coded Al-D, Al-D-S1, Al-D-S2, Al-D-S3, and Al-D-S4 respectively.

Characterization of samples

The modified sample (Al-D), and the surfactants modified aluminum treated diatomite samples (Al-D-S1, Al-D-S2, Al-D-S3, and Al-D-S4) were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and total organic carbon (TOC). The chemical composition was determined using XRF technique by $(Li_2B_4O_7)$ fusion discs (Lodding and Rhett, 1972). The mineral constitution of samples was determined using X'pert XRD instrument equipped with a Co anode operated at 40kV and 40 mA. For the SEM investigation, samples were carbon coated and introduced into the SEM to be scanned by a beam of highly energetic electrons. The cathode used to generate that beam of electrons was made of tungsten element, which has a voltage of 15 kV. FTIR spectroscopy was applied using KBr matrix in a scanning range of 400-4000cm⁻¹. All samples were grinded with dried KBr using agate mortar and pestle. The transparent discs were obtained using hydraulic press at12 tons/m². The carbon content in the samples was determined using total organic carbon (TOC) analyzer. About 0.1 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.

Surface area estimation

The surface area was estimated using the methylene blue method (Potgieter, 1991). A 100 ppm stock solution of methylene blue (MB) in distilled water (DW) was prepared. Standard solutions of 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 1. Masses of 15, 30, 45, 60, 75, 90, and 105 mg of the samples 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 λ_{max} = 664.4 nm using the calibrated Beer's law plot shown in Figure 1.
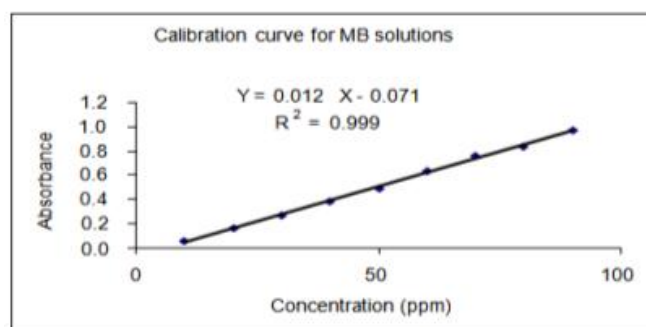

Figure 1. Calibration curve of MB solutions at λ_{max} = 664.4 nm

Removal of phenols from aqueous solutions by diatomite samples

The λ_{max} values for phenol, 4-chlorophenol, and 4-nitrophenol were determined. 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 curve shown in Figure 2. The removal of the three selected phenols from water, using aluminum treated diatomite 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
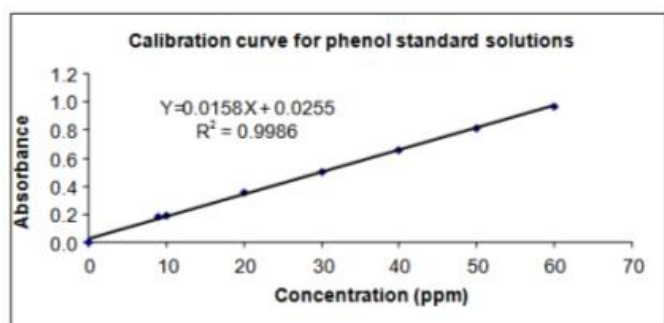
Figure 2. Calibration curve of phenol solutions at λ_{max} = 270 nm

added after being adjusted to pH 9.3 using a buffer solution of pH 11 (12 mM Na_2CO_3/1 mM $NaHCO_3$), diluted acetic acid, or sometimes both of them. Samples were shaken in the table shaker at 25 °C and 150 rpm for 24 hours. The supernatant was centrifuged and analyzed for their phenols equilibrium concentrations using UV/VIS spectrophotometer. 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.

RESULTS AND DISCUSSION

Characterization of diatomite samples

X-Ray fluorescence (XRF)

Chemical composition of the samples is tabulated in Table 1. Result shows that the treatment of the raw diatomite by aluminum increases its ratio by about 1.75%. The loss on ignition in modified aluminum treated (Al-D) samples decreases in the following order: Al-D-S2>Al-D-S4>Al-D-S3>Al-D-S1. Thus, the surfactants were loaded on Al-D samples in the following trend: S2>S3>S4>S1. Indicator ratios are shown in Table 2.

Table 1. Chemical composition of studied samples

Oxide %	Al –D	Al-D-S1	Al-D-S2	Al-D-S3	Al-D-S4
SiO_2	40.75	41.80	37.90	42.35	38.8
TiO_2	0.95	0.98	0.854	0.957	0.901
Al_2O_3	18.55	20.50	17.80	19.65	17.8
Fe_2O_3	6.08	6.28	5.63	6.07	5.96
MnO	0.01	0.01	0.011	0.012	0.017
MgO	1.35	1.47	1.37	1.42	1.34
CaO	0.46	0.27	0.27	0.23	0.38
Na_2O	14.50	13.25	12.2	14.00	13.5
K_2O	1.62	1.98	1.76	1.80	1.86
P_2O_5	0.14	0.14	0.125	0.151	0.143
L.O.I[a]	15.40	12.20	20.9	13.30	20.5

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

Table 2. indicator ratio of elements of modified samples

Ratio	Raw-D	Al-D	Al-D-S1	Al-D-S2	Al-D-S3	Al-D-S4
SiO_2/(Al_2O_3+Fe_2O_3)	2.32	1.65	1.57	1.62	1.65	1.58
(Si+Al) /O	0.93	0.94	0.95	0.95	0.95	0.95
SiO_2/Al_2O_3	3.36	2.19	2.03	2.13	2.15	2.06
(MgO+CaO+K_2O) /Al_2O_3	0.36	0.18	0.18	0.19	0.18	0.22

The SiO_2/(Al_2O_3+Fe_2O_3) ratio of the raw sample is 2.32 while in the Al-D it decreases to 1.65 and from 1.57 to 1.65 in the surfactant modified samples. The (Si+Al)/O ratio is 0.93 in the

raw diatomite increased to 0.95 in all the modified samples. The SiO_2/Al_2O_3 ratio decreases from 3.36 for the raw diatomite to 2.19, 2.03, 2.13, 2.15, and 2.06 for Al-D, Al-D-S1, Al-D-S2, Al-D-S3 and Al-D-S4 respectively. (MgO+CaO+K_2O) /Al_2O_3 ratio decreased from 0.36 in the raw samples to 0.18 - 0.22 in the modified aluminum surfactants samples. It could be noticed that the silica content decreased in modified samples relative to Raw-D. The same observation applies for CaO, MgO, P_2O_5 and Na_2O. The Fe_2O_3 increased in all modified diatomite samples relative to Raw-D. On the other side, silica content increased in modified samples relative to Al-D sample, the same is in Fe_2O_3, Al_2O_3, MgO and K_2O.

X-Ray diffraction (XRD)

The mineral composition of the original diatomite sample (Raw-D) is quartz as major mineral and kaolinite, muscovite, anorthite and halite as minors and accessory mineral. So dalite was detected as major component in the surfactants aluminum treated diatomite. This is most probably due to the aluminum/NaOH treatment. The halite mineral disappeared in the aluminum/NaOH treated samples. The modification of aluminum treated diatomite sample (Al-D) with the four cationic surfactants (S1, S2, S3, and S4) indicated almost no change in the mineral contents.

Fourier transforms 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 (Marel and Beutelspacher, 1976; Zaitoon *et al.*, 2011). The infrared study for the four cationic surfactants used in the modification process of diatomite samples S1, S2, S3 and S4 shows the main absorption bands for the cationic surfactants. 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 (Table 3). The results of infrared study for the Raw-D sample (Figure 3) are 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. 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 (Zaitoon *et al.*, 2011; Caiots, 2000; Haya Kawa and Hench, 2000).

The results of infrared study for the Al-D sample (Figure 3) shows the most important bands for Al-treated diatomite. Since the bands at 3698 cm⁻¹ and 3618 cm⁻¹ are assigned to terminal Si-OH, the band at 1630 cm⁻¹ is due to bending vibration of H_2O found within Al-treated diatomite structure. 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, two new bands which are 735 and 978 cm^{-1} that assigned to stretching vibration of (Si(Al)-O) and υ_{as} [Si-O] of sodalite, respectively (Haya Kawa and Hench, 2000). The sodalite was formed by the pretreatment of Raw-D with AlCl$_3$/NaOH which confirmed by XRD analysis. The results of infrared study for the aluminum treated diatomite sample (Al-D) compared to aluminum treated diatomite samples (Al-D-S1, Al-D-S2, Al-D-S3, and Al-D-S4) are listed in Table 3. It can be concluded that the modification of Al-D with different cationic surfactants did not change the main structure of Al-D, so that the main absorption bands of Al-D which appear at 465, 530, 735, 798, 978, 1032, 1630, 3428, 3618, and 3698 cm^{-1} appeared in both modified and unmodified samples with some shift in some of them due to the loading of surfactant on Al- treated diatomite samples.
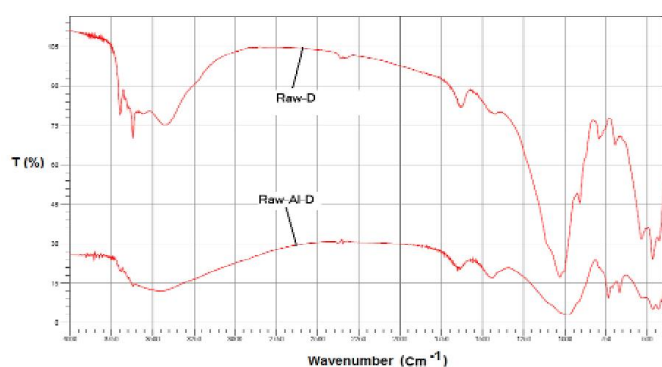

Figure 3. IR for Raw-D and Al-D

2920, 2920, 2922 cm^{-1} in Al-D-S1, Al-D-S2, Al-D-S3, and Al-D-S4 samples, respectively. In addition, the band 978 of Al-D has shifted in all modified samples to the value 980 cm^{-1} also confirms the loading of surfactants on Al-treated diatomite samples.

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 coverage on the samples. Figure 7 demonstrates the carbon content in all diatomite samples.TOC percentages of the samples was converted into (mmol carbon/100 g mineral) according to the following equation (Zaitoon *et al.*, 2011; Bazbaz, 2006): [mmol carbon/100g mineral] = [g organic carbon/100g mineral]×[1000/12] As shown in Figure 4, Raw-D sample has a very low amount of organic material equal to 0.6 %, due to the fact that diatomite is a sedimentary rock composed principally of silica microfossils of aquatic unicellular algae (Gao *et al.*, 2005) All modified diatomite samples show higher TOC values relative to the raw samples (Raw-D and Al-D). This trend confirms the loading of surfactants on diatomite samples. The highest TOC content is equal 4.9 % which is found in Al-D-S2. Moreover, the aluminum treated diatomite sample revealed no significant change in carbon content. The difference between TOC contents in all diatomite samples compared to raw diatomite (Raw-D and Al-D) confirm the loading of the cationic surfactants on diatomite samples which is in agreement with
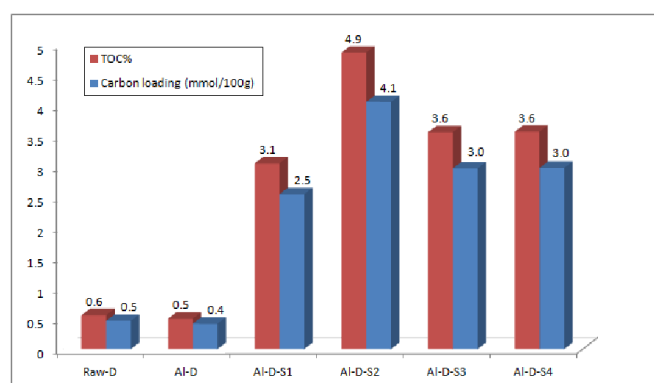
Table 3. Comparison of infrared absorption bands (cm^{-1})

Al-D	Al-D-S1	S1	Al-D-S2	S2	Al-D-S3	S3	Al-D-S4	S4	Assignment
465	465		465		467		465		No shift happened
530	534		534		534		534		Shifted from Al-D band 530
	720	730	720	731	720	729	720	729	Shifted from surfactants band 730
735	735		735		735		735		No shift happened
798	800		800		800		800		Shifted from Al-D band 798
978	980		980		980		981		Shifted from Al-D band 978
	1465	1466	1465	1465	1465	1463	1465	1464	No shift happened
1032	1032		1031		1031		1032		No shift happened
1630	1625		1625		1625		1625		Shifted from Al-D band 1630
	2855	2851	2851	2849	2851	2848	2853	2850	Shifted from surfactants band 2849
	2924	2917	2920	2916	2920	2915	2922	2917	Shifted from surfactants band 2916
3428	3420		3420		3420		3420		Shifted from Al-D band 3428
3618	3618		3619		3619		3618		No shift happened
3698	3698		3694		3694		3694		Shifted from Al-D band 3698

The band at 3620 is due to the free silanol group (SiO-H), the band at 1032 cm^{-1} reflects the siloxane (Si-O-Si) group The appearance of the band at 1465 cm^{-1} for the modified Al-D 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 Al-D samples. The absorption band appeared at 2849 cm^{-1} that is assigned to υ_{sy} (CH$_2$) group of the tail moiety has shifted to 2855, 2851, 2851, and 2853 cm^{-1} for Al-D-S1, Al-D-S2, Al-D-S3, and Al-D-S4 samples, respectively. Table 5 shows the absorption band appeared at 2916 cm^{-1} that is assigned to υ_{as} (CH$_2$) group of the tail moiety of the pure surfactant has shifted to 2924, 2920,

Figure 4. TOC% and Carbon loading of diatomite samples.

the loss on ignition values determined by XRF analysis in the same samples.

Scanning electron microscopy (SEM)

SEM is usually used to obtain structural build up and textural arrangement inside rocks and minerals. The SEM pictures for Raw-D, Al-D, and Al-D-S1 sample are shown in Figure 5. It is obvious that the unique pores of the diatomite is obscured by the newly formed materials resulted from modification
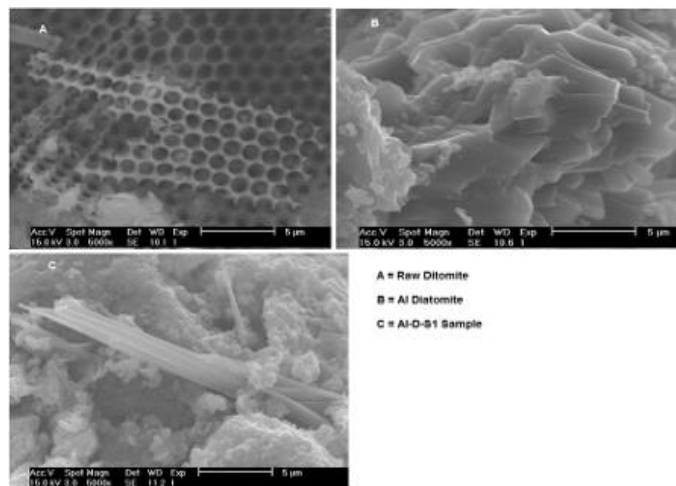

Figure 5. SEM for Raw-D sample (A), Al-D sample (B), and Al-D-S1 sample (C)

Surface area estimation

The results of Langmuir adsorption isotherms for methylene blue (MB) adsorption on diatomite samples are summarized in Table 4. The saturation level of MB adsorption and its adsorption isotherms for all diatomite samples are illustrated in Figures 6 and 7. The surface area (S) in (m²/g) can be calculated according to Langmuir equation as follows: ($S = X_m.N.A_m$), where; N: Avogadro's number (molecule/mol), A_m: molecular cross sectional area (m²/molecule) (1.2 m²/molecule), X_m: monolayer capacity. The results are summarized in Table 4 and Figure 8. It is obvious from Figure 8 that Raw D exhibits surface area equal to 225 m²/g, decrease to 194 m²/g after Al modification, i.e. surface area in Al-D is 86% of the original diatomite. The general trend for the surface areas for aluminum treated diatomite samples is as follows: Al-D>Al-D-S1>Al-D-S4>Al-D-S3>Al-D-S2. Thus raw diatomite samples (Raw-D and Al-D) have higher surface areas compared with their surfactant modified samples. Therefore, modification of Raw-D by Al and modification of Al-D 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 4.

Table 4. Surface areas and the monolayer capacities of the samples

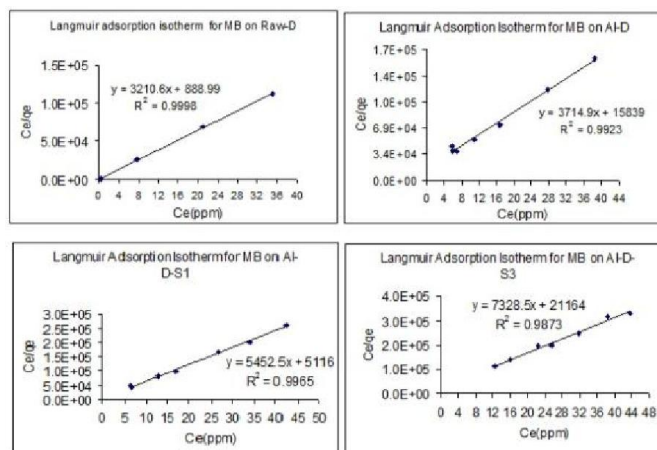| Sample	Slope	Monolayer capacity (mol/g) X_m	Surface area (m²/g) S
RAW-D	3210.6	3.1E-04	225
Al-D	3714.9	2.7E-04	194
Al-D-S1	5452.5	1.8E-04	132
Al-D-S2	13743.0	7.3E-05	53
Al-D-S3	7328.5	1.4E-04	99
Al-D-S4	5724.9	1.7E-04	126

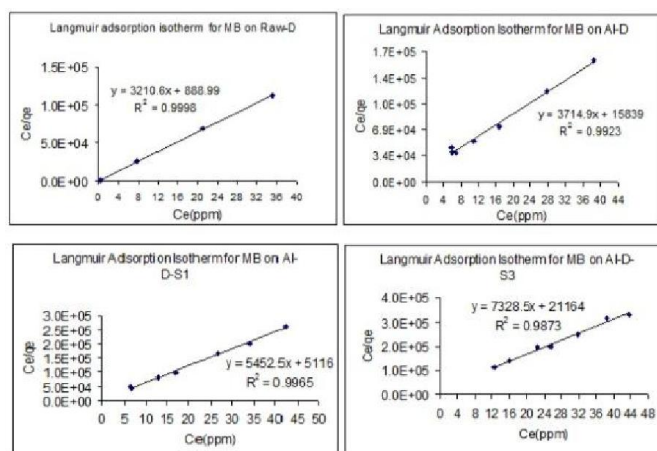**Figure 6. Adsorption of MB on the raw diatomite and the modified samples**

Figure 7. Langmuir adsorption isotherms for the raw diatomite and the modified samples

The largest TOC value exhibits the smallest surface area, and Raw-D, which has the lowest amount of TOC, has the largest surface area. The same idea could be applicable to Al-D samples, since Al-D, which has the lowest amount of TOC, has the largest surface area, and Al-D-S2, which has the largest amount of TOC, has the lowest 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 (phenol) $C_6H_5O^-$ (phenolate ion) $+ H^+$ 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.

Removal of phenol

The removal of phenol was investigated at pH values 9.3 and 10.5 as shown in Figure 9, the former is lower than pK_a (phenol) = 9.89 and the latter is higher than pK_a. The adsorption increases for surfactants modified aluminum diatomite samples as shown in Figure 9. It can be noted that adsorption of phenol at pH 10.5 is grater than that at pH 9.3 for all samples. Thus; the adsorption efficiency of phenol is far more at alkaline medium. The adsorption of phenol on
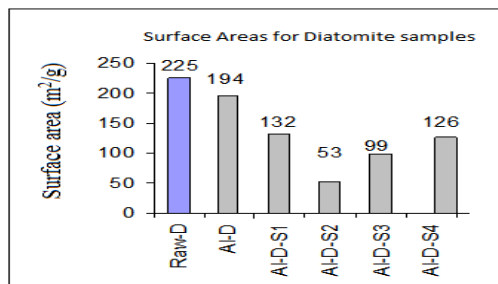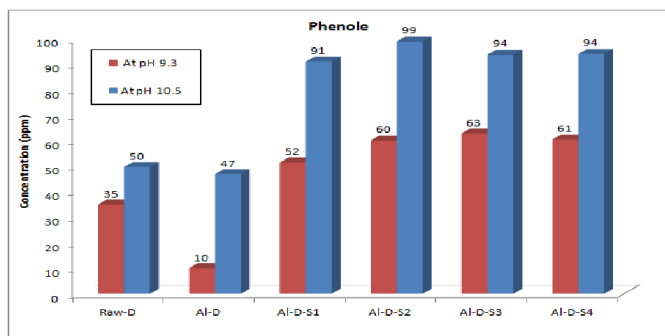
Figure 8. Surface areas for diatomite samples

Figure 9. The amount of phenol adsorbed (ppm) at pH 9.3 and pH 10.5 on diatomite samples

modified aluminum treated samples is found to be higher than modified non-aluminum treated samples at both pH values. This result is in agreement with literature for surfactant modified aluminum treated samples (Gao *et al*., 2005). The adsorption capacity at pH 9.3 decreases in the order: Al-D-S3>Al-D-S>Al-D-S2>Al-D-S1>>Al-D. While at pH 10.5 adsorption capacity of diatomite samples decreases in the order: Al-D-S2> Al-D-S4>Al-D-S3>Al-D-S1>>Al-D. The adsorption of phenol on modified aluminum treated samples were found to be higher than modified non-aluminum treated samples at both pH values, which is in agreement with literature (Wu *et al*., 2013).

Removal of 4-chlorophenol

The removal of 4-chlorophenol on diatomite samples was investigated at different pH values. Table 5 lists the amount of 4-chlorophenol adsorbed at pH 8.0, 9.3, and 10.0, respectively. General trends could be obtained that adsorption of 4-chlorophenol at pH 8.0 is greater than that at pH 9.3 and 10.0.

Table 5. The amount of 4-chlorophenol adsorbed (ppm) at pH 8.0, 9.3 and 10.5

Sample	At pH 8.0	At pH 9.3	At pH 10.0
Raw-D	41.20	60.40	44.70
Al-D	23.86	20.89	31.96
Al-D-S1	38.92	80.38	25.00
Al-D-S2	98.42	89.05	73.73
Al-D-S3	97.15	88.16	57.91
Al-D-S4	64.24	88.23	22.47

The adsorption of 4-chlorophenol on modified surfactants aluminum treated samples were found to be higher than raw and modified aluminum treated samples at the pH 9.3. The surfactant modified diatomite samples showed higher adsorption capacities than unmodified samples. For treated samples, the adsorption capacity at pH 8.0 decreases in the order: Al-D-S2>Al-D-S3> Al-D-S4>Al-D-S1>>Al-D. At pH 9.3 for the aluminum treated samples, the adsorption capacity

decreases in the order: Al-D-S2>Al-D-S3>Al-D-S4>Al-D-S1. At pH 10.0 adsorption of 4-chlorophenol is the least compared to pH 8.0 and 9.3 respectively. The adsorption capacity decreases in the order-Al-D-S2>Al-D-S4>Al-D-S2>Al-D-S1.

Removal of 4-nitrophenol

The removal of 4-nirophenol was investigated at pH 6.5 and 9.3 by Al-D and surfactants modified aluminum samples as shown Tables 6. It is clear that adsorption of 4-nitrophenol at pH 6.5 is greater than that at pH 9.3 for all diatomite samples. The surfactant modified diatomite samples show higher adsorption capacities than aluminum modified samples. For aluminum treated samples, the adsorption capacity at pH 6.5 decreases in the order: Al-D-S1>Al-D-S4>Al-D-S3>Al-D-S2>Al-D. At pH9, the adsorption capacity decreases in the order: Al-D-S2>Al-D-S3>Al-D-S4>Al-D-S1>Al-D. The experiments indicate that adsorption amount of 4-clorophenol on both aluminum diatomite and surfactants aluminum diatomite samples is the highest when compared with adsorption of phenol and 4-nitrophenol (Figure 10). In general, we can say that surfactant aluminum diatomite samples have better adsorption capacities for phenol, 4-chlorophenol, and 4-nitrophenol than aluminum diatomite and raw samples.

Table 6. The amount of 4-nitrophenol adsorbed (ppm) at pH 6.5 and 9.3

Sample	At pH6.5	At pH 9.3
Raw-D	48.5	4.7
Al-D	47.6	2.3
Al-D-S1	95.3	46.7
Al-D-S2	87.8	87.7
Al-D-S3	89.0	80.4
Al-D-S4	92.3	79.7

Conclusion

Modification and treatment of diatomitaceous clay from Jordan lead to great enhancement of its capacity to remove phenols from water. The modification was done by treatment with aluminum chloride followed by treatment with cationic surfactants. The original sample and the modified derivatives were thoroughly characterized to check for the modification process by X-ray diffraction, X-ray fluorescence, scanning electron microscopy, total organic carbon, and Fourier transform infrared spectroscopy. The surface area by using methylene blue method was estimated and evaluated for all studied samples. Experiments were performed to study the role of modified diatomite and surfactants treated modified diatomite samples in the removal of phenol, 4-chlorophenol, and 4-nitrophenol from their aqueous solutions. The results has revealed, in general, that efficiency of diatomite to remove organic pollutants form aqueous solution is higher than efficiency of the unmodified ones, and the efficiency of the treated modified diatomite samples are higher than the untreated samples.

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