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Customization of Indian diatomite and its use for the Removal of Some Organic Pollutants from Water

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Abstract : Indian diatomaceous clay modified by some cationic surfactantsdodecyltrimethylammoniumbromide (DDTMA-Br), tetradecyl trimethyl ammonium bromide (TDTMA-Br),hexadecyltrimethylammonium bromide (HDTMA-Br), hexadecltrimethylammonium chloride HDTMA-Cl and octadecyltrimethylammonium bromide (ODTMA-Br) were prepared. The chemical and structuralproperties 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 infraredspectroscopy (FTIR).The adsorption capacities were estimated by methylene blue method. The useof surfactants does not change the mineral structure of the diatomaceous clay .Experiments weredone 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 ofphenol was up to 75% at PH equal to 10.5, for 4-chlorophenol 95 % at PH equal to 8.0 and 4-nitrophenolis 98 % at PH equal to 6.5.The adsorption isothermsof modified surfactants diatomaceous clay indicatesthat phenol and its derivatives follow type 1, which is the Langmuir isotherms.The results have revealedthat the modified diatomaceous clay improve the adsorption of phenols from aqueous solutions betterthan the raw ones.

(Keywords: Jordanian diatomaceous clay, Surfactants, Adsorption, Phenols).

Introduction

A chalk-like, soft, friable,earthy, very fine grained, siliceous sedimentaryrock[1] is known as diatomite. Diatomaceous silica is regarded as mineralof organic origin. Where the silica of fossilized diatom skeleton resembles hydrous silica in composition: $SiO_2.nH_2O$.

Diatomite could be noticed to have verylow density, fine particles, high absorbance ability, high porous and high surface area properties[2].Thediatom cells contain an internal, elaborate siliceousskeleton consisting of two valves (frustules) that varyin 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 2.5times its weight of wate[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]. Organ clays form important type of modified clay minerals. Their uses are many including some environmental applications[8]. Organ claysareuseful in water purification by removing oil and toxic chemicals from water. Remediation of industrial waste waters is enabled through the use oforgan clays[9].

Surfactants are compounds that have anamphiphilic 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 inoils (non-polar solvents) but is not very soluble inwater and other polar solvents[10]. Diatomite maybe modified chemically in number of ways[11].

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[12].

This paper reports on work on cataionic surfactants treated diamaceous clay and their possible use in removal of phenol, chlorophenol and nitro phenol from water materials and methods of sample preparation.

Experimental

Materials and Methods

Sample Preparation

Diatomite sample was supplied by the Indian Natural Resources Authority (NRA) brought.

The sample was crushed at chemical research laboratory of Magadh University using vibrating sieve shaker to different particle sizes < 0.5, and >1.00mm. The portion <0.5mm was washed with distilled water three times to remove any insoluble contaminants, and dried overnight in an oven at 110 °C, stored in desiccators.

Pretreatment of sample

Pretreatment of sample with NaOH was done according to Khraisheh (13). sample (200g) was immersed in 125 ml of 6 MNaOHat 92^{0}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 125m 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 110^0 C, and cooled

Modification of Diatomite Raw-D by Different Cationic Surfactants

Diatomite samples were independently modified by five cationic surfactants,i.e., dodecyltrimethylammonium bromide (S1), tetradecyltrimethylammonium bromide (S2), hexadecyltrimethylammonium bromide (S3), hexadecyltrimethylammonium chloride (S4), andoctadecyltrimethylammonium bromide (S5) according to a reported procedure[14]. A solution of 66 mL 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 samplesRaw-D in 125 mL-polyethylene bottles then shaked in a thermostatic table shaker for8 hours. Supernatants were discarded and the precipitates were washed twice with 100 mL distilled water, before drying in the oven at 50^{0}C. The dried sample was stored in desiccator for overnight for further experiment 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 Surfactants Custonized Diatomite Samples

The surfactant modified raw diatomitesamples (D-S1, D-S2, D-S3, D-S4, and D-S5) andthe unmodified sample 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, 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. A interval between5° 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 diffractomete requipped with a cobalt anode, energy is emitted as X-ray photons with 1.78897Å. A monochromator removes X-rays of undesired wave lengths so that only Cobalt Kaolinite can be detected which simplifies the evaluation[15].

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 toX-ray radiation. The smooth surface was achieved by taking 0.8 g of each sample and mixing it with7.2 g of lithium tetra borate (Li2B4O7) 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 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} [16].

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 1450^0C. 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 abeam of highly energetic electrons to give magnified three dimensional pictures 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.

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(17). 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 50ppm 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 lmax= 664.4nm using the calibrated Beer's law plot.

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 λmax 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 eachphenol (phenol, 4-chlorophenol, and 4-nitrophenol) were added after being adjusted to pH 9.3 using a buffer solution of pH 11 (12 ml Na_2CO_3/12 ml $MNaHCO_3$), diluted acetic acid, or sometimes both of them. All samples were shaken in the table shakerat 25^0C and 150 rpm for 24 hours. The supernatant of each solution was centrifuged and analyzed for their phenols equilibrium concentrations using UV spectrophotometer, according to the stated calibration curves.

The removal of phenol solutions were further investigated at different pH values, i.e., at pH over and lower the pKa for each phenol solutions shown in Table 3.1.

Results and Discussion

Raw diatomite (Raw-D) was modified byfive cationic surfactants i.e., dodecyl-trimethylammonium bromide (S1), tetradecyl-trimethylammonium bromide (S2), hexadecyl-trimethylammonium bromide (S3), hexadecyl-trimethylammonium chloride (S4), andoctadecyl-trimethylammonium bromide (S5).

The raw diatomite (Raw-D), and theirsurfactant 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 samplesX-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 shownin Table 3.2.

As shown in Table 3.1, the major contenting 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 3.1:
Values of pH used for the removal of phenols

Phenol Solution	pH
Phenol	9.3, 10.5
4-cholorphenol	8, 9.3, 10
4-nitrophenol	6.5,9.3

All diatormite samples Raw-D (D-S, D-S2, D-S3, D-S4 and D-S5) were analysed using XRF technique which trend shows the logs on ignition in diatomite sample. This indicates the amounts of surfactants loaded on diatomite sample.

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-S4
*** major	** minor	*trace	-does not exit		

Table 3.3

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 shif
694	694		694		694		694		694		no shif
	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

Raw Diatomite (Raw-D)

The results of infrared study for the Raw-D sample are shown in Table 3.3.

The absorption bands at 3696 cm^{-1} and 3620cm^{-1} are assigned to terminal Si-OH, the bandit 1626cm^{-1} is due to bending vibration of H2O 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-1reflects 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 467cm^{-1} absorption bands are due to bending vibration of (Si-O-Si) of diatomite[18,19].

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-

Table 3.4:
Infrared absorption bands (cm^{-1}) of raw diatomite sample (RawD)

Wave number (cm^{-1})	Shape of the peak	Assignment
467	M	β[Si-O-Si] of diatomite (466)(1)
438	W	β[Si-O-Si] of diatomite (532) (1)kaolinite (539)(2), and muscovite (535)(2)
694	w,br	ν_{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)(1)
1035	s,br	ν_{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)(2)
3696	M	OH-stretching vibration of SiO-H of kaolinite (3695)(2)

H), the band at 1032 reflects the siloxane (Si-O-Si)group stretching, and the bands at 911cm^{-1} and 798cm^{-1} correspond to (Si-O) stretching of silanolgroup, 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 2849cm^{-1} that is assigned to usy(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-3.4.

From Table 3.4, we can conclude that themodification 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.

Scanning electron microscopy (SEM)

SEM is used to obtain structural and analytical information about minerals (20)

It is observed that diatomite pores cover partially, which indicates the loading of cationic surfactants on the surface of the diatomite samples. Sodalite was appeared as revealed by XRD measurement as a major mineral constituent.

Surface Area Estimation

The results of Langmuir adsorption isotherms for methylene blue (MB) absorption on diatomite samples are summarized. The saturation level of MB absorption and its adsorption isotherms for all ciatomite samples are illustrated .

$$S=Xm.N.Am \qquad \ldots (3.2)$$

Where; S: surface area (m^2/g), N Avogadro's number (molecule/mol), Am: molecular cross sectional area (m^2-/molecule) (1.2 m^2/molecule),X_m:monolayer capacity.

Removal of Phenol

The removal of phenol was investigated at pH values 9.3 and 10.5 the former is lower than pK (phenol)= 9.89 and the letter is higher than pK Thus, the effect of pH on the adsorption of phenol was investigated which show the amounts of phenol adsorbed at pH 9.3 and 10.5 on all diatomite samples, respectively.

The adsorption of phenol at pH 10.5 is greater than that at pH 9.3 for all diatomite samples. The surfactant diatomite samples showed higher adsorption capacities than samples. 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 sampels decreases in the order.D-S2>D-S4-D-S3>D-S1>Raw-D.

Removal of 4-chlorophenol

The removal of 4-chlorophenol on diatomite samples was investigation at pH 8.0, 9.3, and 10.0. show the amount of 4+-chlorophenol adsorbed at pH 8.0, 9.3, and 10.0, respectively.

The adsorption of 4-chlorophenol at pH 8.0 is greater than that at pH 9.3 and 10.0. The surfactant customized diatomite samples showed higher adsorption capacities than unmodified samples.

For customized diatomite samples. the adsorption capacity at pH 8.0 decreases in the order D-S2>D-S5>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-S3Raw-D

At pH 10.0 diatomite samples have an adsorption capacity decreases in the order.
D-S2>D-S5>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 show the amount 4-nitropheol adsorbed at pH 6.5 and 9.3, respectively.

The adsorption of 4-nitrophenol at pH 6.5 is greater than at pH 9.3 for all diatomite samples. The adsorption of 4-nitrophenol on customized treated samples were found to be higher surfactant. customized diatomite samples showed higher adsorption capacities than customized samples in all pH ranges.

For customized diatomite samples, the adsorption capacity at pH 6.5 decreases in the order D-S4>D-S2>D-S5>D-S1S3>>Raw-D.

At pH 9.3 diatomite samples have an adsorption capacity that decreases in the order.D-S4>D-S2>D-S5>D-S1S3>>Raw-D.

Comparing the adsorption capacities for phenol, 4-chlorophenol, and 4-nitrophenol at the same pH value (9.3) are shown which indicates that the adsorption amount of 4-clorophenol on both raw and customized 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 customized diatomite samples have better adsorption capacities for phenol. 4-chlorophnol, and 4-nitrophenol than raw diatomite samples. customized samples absorb phenol better than 4-nitrophenol.

References

1. J. Kadey, *Diatomite Industrial minerals and rocks*, **267**: 677-707. (1973).
2. J. Al ali, and M. Qaqr'a *Diatomite in Jordan. Arabic Edition* (1995)
3. P. Dolley, and R. Moyle, *Geological Survey Bulletin*, pp 2209. Et- E8(2003)
4. C. Baird, *Environmental Chemistry*, 215 (2001)
5. Al-Rashudan, Z.Investigation of Natural Zeolite Tuffs on Their Ability for Sewage Cleaning purposes. PhD thesis, Oldenburg University, Germany (2001).
6. Y. Al-Degs, M. Tutunju, R. Shawabkeh *Separation science and Technology* **35**(14): 2299 (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. Noemie Van Garderen, J. Frank, *Applied, Clay Science*, **52** (1-2): 115-121 (2011)
9. Nezathat EdizismailBentili, Liknur Tatar, I*nternational Journal of Menar Processing* **94**(28): 129 (2010)
10. Reckweg Anders, BASF- personal communication 21st Januray (2000)
11. Y. Al-Degs, M. Tutunju, R. Shawakeh, *Science and Technology* **35**(14), pp. 2299-2310(2000).
12. R. Lide, CRC Handbook of Chemistry and Physics, 73rd edition, CRC Press (1993)
13. M. Khraisheh, Y. Al-Degs, W. Mcminn, *Chemical Engieering Journal*. **99**: 177 (2005)
14. Z. Li, D. Alessi, L. Allen, *Journal of Environmental Quality*, **31**: 1106 (2002).
15. M. He, C. Wu, J. Zhang, Y. Ran, *Journal of Environmental Management* (2005).
16. B. Gao, P. Jiang, F. An, S. Zhao, and Z Ge, *Applied Surface Scinece*, **250**(1-4), 273 (2005)
17. R. Porter, *The Handbook of Surfactants*; **2**. Edition, Chapman & Hall (1994)
18. Reckweg Anders, BASF- personal communication, Presentation at the Danish Varnish and Paint Chemist Association (DLFF) (1999).
19. M. Hellstn, *Special publication* no. **39**: 179 (1987)
20. F. Schuler, and M. Ghosh, *Journal of AWWA*, **82**:67-75(1990)