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Research Paper

Properties and Characterization of HDTMA- Cl Modified Jordanian Kaolinite and Its Use in Removal of Aniline from Aqueous Solution

Chemistry

KEYWORDS : Modification, Jordanian Kaolinite, Characterization, Aniline, Surfactant.

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ABSTRACT

Cretaceous Jordanian kaolinite from Batn Al-Ghul was modified by cationic surfactant hexadecyltrimethylammomium chloride(HDTMA-Cl). The raw and the resultant organo clay samples were characterized using Total Organic Carbon (TOC), Fourier Transformed (FTIR), X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Thermogravimetry(TG/DTA) and UV/VIS Spectrometry.

The FTIR spectra reveal vibration frequencies shift in bands at 2816 and 2820 cm^{-1} for original kaolinite to 2849 and 2870 cm^{-1} for organo kaolinite. The XRF results show change in the chemical composition between the raw and the modified sample mainly in loss on ignition, which increase to 21.25% in the organo kaolinite due to the loading of the surfactant. XRD results shows contraction in d(001) from 7.01807A° to 6.9795A° indicate change in the interlayer spacing due to the adsorption of HDTMA-Cl on the external of the surface of kaolinite. The DTA shows peaks at 374 C° indicate intercalation of surfactant on the kaolinite, and at 840 C° is the formation of amorphous SiO_2 .The raw and modified kaolinite was investigated to check their ability in removing aniline from aqueous solution. It found that surfactant modified kaolinite increase adsorption of aniline by 11.5% more than the raw kaolinite in the range of 30 -150 ppm concentrations.

1. Introduction:

Kaolin clay is a soft, white mineral mainly composed of fine-grained plates hydrous aluminum silicate particles, formed by hydrothermal alteration. The structure consists of single alumina octahedral sheets combined in a unit. The di octahedral 1:1 layered clay mineral of structural formula $Al_2Si_2O_5(OH)_4$ formed by hydrothermal alteration or weathering of feldspars, feldspathoids and other silicates(Deer et al.,1992) . The structure consists of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit, so that the tips of the silica tetrahedral and one of the octahedral surface are in a common plane.

The ions are arranged in parallel sheets with oxygen and hydroxyl coordinated around the Si and Al cations(Davies,1996) .The silica ions are surrounded by four oxide ions and the alumina ions by octahedral group of six oxides are the hydroxide ions. Hydrogen bonding between these two surfaces imparts a significant cohesive energy between the layers which makes intercalation into kaolinite difficult (Christopher et al, 2002).

Kaolinite has a composition of $Al_4(Si_4O_{10})$ (OH)8 occurs as a clay like mass with monoclinic crystal with a specific gravity of about 2.6 and it has a dull luster. The refractive index is 1.56 and a melting point of (1760 C°). The color of all varieties of koalinite is white, but inferior grades burns to a yellow or brownish color. The exchangeable cations are Na^+, K^+ , Ca^{2+} and Al_{+3} (Thery, 1991). Kaolin is used in many applications, as a unique industrial mineral which remain chemically inert over a relatively wide PH range and it offers excellent covering when used as pigment or extender in coated films and filling applications technologies (Zhang et al., 1993).

Surfactants have amphiphilic nature as their molecular structure contains parts with different polarity and no polar part. The hydrophobic part is commonly hydrocarbons (branched or linear) containing 10-18 carbon atoms which may contain aromatic structure. The hydrophilic functional groups may vary, which may be ionic SO_3^{-2} cationic –N $(CH_3)^+_3$ or(C_5H_5N+) or non ionic $(-OH_2CH_2)$-OH (Speight, 2002, Kaluza et al.,1996) .Surfactants modified clay has attracted considerable attention for their use in removal of contaminations from aqueous solutions (Sharma sarkar et al., 2000).

Due to the isomorphous substitutions the alumina silicate layers in natural clay, mineral usually have negative charge which is balanced by Na^+, K^+ and Ca^{+2} .The hydration of these cations create a hydrophilic environment on these surface of the koalinite .The substitution of these cations by quaternary ammonium cations of the form $\{(CH_3)_3NR\}^+$ at the exchangeable sites of the kaolinite with organophilic properties can act as sorbent contaminant hydrocarbon (Li z et al., 2003).

Many pollutants can be removed by modified clays from aqueous solutions, such as chlorinated phenols and other organic compounds. The role of surfactants in adsorption is to lower the free energy of the phase boundary (Alkaram et al.,2009) . The degree of adsorption depends on the structure of surfactant and the two phases that meet the interface. The successful utilization of technology based on the surfactant modified clay, the chemical stability of the cationic surfactant clay complex and the composition of the aqueous solutions that may influence the degree of retention via the hydrophobic bonding (Jaynes et al.,1990).

Understanding the retention of cationic surfactants by silicate layers of kaolinite is important due to the wide applications in house hold and industrial activities. The sorption of chemicals from aqueous solutions on the solid phase as a result of (sorption-desorption) reactions. The bond structure of natural kaolinite, formation of stable form, elemental analysis and mineralogical composition of the modified clay can be studied (Khalil, 1994).

The purpose of the present work is to investigate the properties and characterize Jordanian kaolinite clay from Btun Al-Ghu, south Jordan, modify it by cationic surfactant which is hexadecyltrimethyl ammoniumcholride(HDTMA-Cl) to improve the surface properties that could enhance their use as agents for aniline removal from aqueous solutions.

Several techniques like X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform spectroscopy (FTIR), total organic carbon (TOC), Thermo gravimetric measurements (TG/DTA), and UV/VIS Spectrometry were used to characterize the raw and the modified samples.

2. Methods and Materials:

2.1. Kaolinite Clay

Jordanian koalinite was brought from Natural Resources Authority, Jordan. Samples from cretaceous kaolin, Jabal Al-Hrad , Batn Al-Ghul, 70 km south Amman. The samples were grinded and sieved and the mass passed through 250 micron is collected. A 250 g of raw kaolinite were immersed in two liters of distilled water and stirred for 8 hours, then left to settle for 24 hours and decanted, the slurry was dried in oven for two days at 115 C°. Finally the clay was grinded and labeled CK.

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2.2. Surfactant
Cationic surfactant with molecular formula $\{C_{19}H_{42}NCl\}$ named as HDTMA-Cl was used in the preparations of the organo-kaolinite .It was imported from Fluka analytical grade 98% purity. The molecular weight is 320.0g/mole soluble in water, and used without further treatment.

2.3. Surfactant-Kaolinite preparation
A solution of 67mM of the surfactant was prepared and added to 25 g of kaolinite sample in 125 ml polyethylene bottle and shake at 150 rpm at 25 C° using table shaker for 24 hours to achieve equilibrium. The aqueous organoclay was centrifuge at 2000 rpm for 20 minutes. The supernatant was washed twice with100 ml of distilled water each time and dried at 60 C° for 30 hours. The modified sample is CMK.

2.4. Total organic carbon (TOC)
To check the amount of cationic surfactant loaded on the surface of kaolinite, TOC analysis technique has been selected. About 0.1 g of sample was combusted in LECO analyzer at furnace temperature of 1450 C°. The CO_2 was detected from the flow of oxygen gas by thermal conductivity cell detector. The percentage of carbon is displaced on direct reading digital display (Natural Resources Authority 2014).

2.5. Fourier Transform Infrared
The mull technique was used, 2-5 mg of kaolinite samples were mixed with 0.5 g dry potassium bromide (K Br) analytical grade. The mixture was grinded and pressed hydraulically at 10 tons to transparent disk. The disk then placed at light chamber of spectrophotometer. The FTIR spectra were scanned with good resolution in the region 400 -4000 cm^{-1}.

2.6. Thermo gravimetric measurement
DTA and TG were measured using NETZSCH STA-409-PG/PC instrument with correction file purging with N_2 gas at heating rate of 20 C° per minute up to 1040 C°.

TA correction is 20 to 30000 mg and DSC correction is 20 to 5000uv, using Al2O3 crucible.

2.7. X-ray fluorescence (XRF)
Wave length dispersive spectrometer was used for detection of major elements in raw and modified organoclay. A 0.8 g of sample was mixed with lithium tetra borate ($Li_2B_4O_7$) in platinum crucible, few drops of HBr solution is added to prevent the mixture from sticking to the crucible walls. LECO fluxer-FX 200 is used to melt the mixture to homogeneous solution at 1250 C°. The molten mixture was poured in casting dish to give a glassy disc when cooled to room temperature. The resulting disc is used for XRF analysis.

2.8. Inductive coupled plasma (ICP)
For detection of trace elements in the kaolinite, sample is pretreated with sodium peroxide Na_2O_2, transferred to Zirconium-crucible and heated to 450C° for 45min.After cooling; it was transferred to plastic beaker. A 75ml of de ionized water and 30ml 1:1(V/V) HCl solution were added to the beaker, then filtered, the filtrate was aspirated in ICP instrument at flow rate 3ml/min for 15 min.

2.9. X-ray diffraction (XRD)
Rigaku UY10392 X-ray powder diffract meter fitted with Philips X-ray tube giving Cu Kα (1.5418A°) was used for determination of the mineralogical composition of the samples. The samples were dried, grinded, powder pellets is made, then introduced into the instrument at 40Kv and 40mA operating conditions.

2.10 Analytical measurements
The prepared concentration of organic pollutant ranges between 30-150 ppm solutions. Absorbance measurements were done by UV/VIS spectrophotometer type, the wave length corresponding to maximum absorbance (λmax) was determined by scanning standard known concentration at different wave length. Absorbance values were recorded at maximum absorbance (λmax) equals to 280 nm.

3. Results and discussion
3.1. Total Organic Carbon
The total organic carbon gives accurate results for real $HDTMA^+$ coverage on the samples. Table .1 represents the carbon content of the raw kaolinite and the surfactant modified samples.

Table(1) Total Organic Carbon (TOC).

Sample	TOC%	Carbon loading(m mole/100g)
CK	0.51	0.43
CMK	4.40	3.72

As shown in the Table, the raw kaolinite from Butn Al-Ghul has low amount of organic material due to its origin (Khalil, 1994). The vitrinite reflectance value for raw samples is 0.68 % which agrees with the literature(Khoury, 2002; Ahmad, 2010). In modified samples the TOC is 4.4% confirm the loading of surfactant on the kaolinite sample, which is in agreement of loss on ignition for modified surfactant –kaolinite.

3.2. FTIR Analysis
The overall spectrum of FTIR id divided into two regions,4000-1300cm^{-1} (functional groups region) and 1300-400cm^{-1} (the finger print region) .The frequency assignment approach is used for interpretation of the spectrum. For HDTMA-Cl chain, the most intense absorption band at 2870 and 2849cm^{-1} (Macros A et al., 2004) associated with the ant-symmetric and symmetric stretching vibrations of CH_2 group. The bands at 1430 and 1389cm^{-1} are assigned to CH_3-R (1389cm^{-1}) and CH_3-N (1430cm^{-1}) stretching.

The band at 488cm^{-1} is assigned to the anti symmetric bending mode of the quaternary (alkyl) mode of the head of the methyl group $\{(CH_3)_3N^+\}$ which agrees with the literature. Table 2 shows the vibration frequencies and assignment for HDTMA-Cl (Wong et al., 1997).

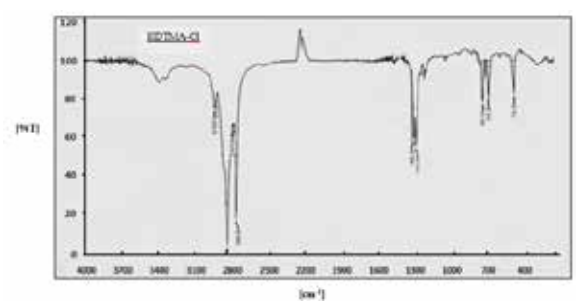

Figure 1. FTIR spectrum of HDTMA-Cl.

Table (2) Stretching frequencies of surfactant

Band(cm^{-1})	Assignment
3016	CH_3-R asymmetric stretching
2870	CH_2 asymmetric stretching
2849	CH_3-R symmetric stretching
1489	CH_3 of $(NCH_3)_3$ asymmetric bending
1417	CH_3 of $N(CH_3)$ symmetric bending
961	C-N stretching
719	CH_2 rocking

For the koalinite samples, the FTIR spectrum shows bands between 3691 and 3672 cm^{-1} indicates the OH stretching (hydroxyl) sheets. Bands at 2622 cm^{-1} is the inner layer OH(Al-O-H) bands at 3448 cm^{-1} is assigned to H-O-H stretching (frequency) bands at 1662-1432cm^{-1} are assigned to H-O-H bending(Olejnik et al.,1971 ;Wilson, 1994; Aroke et al., 2014). This agrees with the literature and difference in band may be due to some impurities in the clay (Davarcioglu B, 2009).

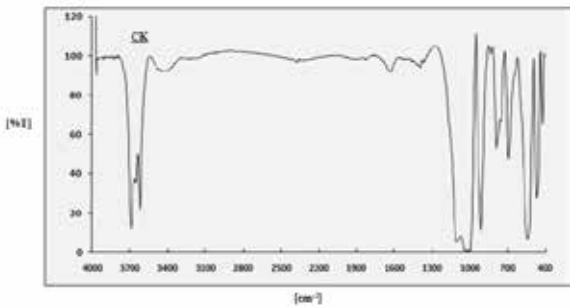

Figure 2. FTIR spectrum of Jordanian kaolinite

Bands at 1119 cm^{-1} is assigned to Si-O normal to plane stretching at 1053 and 1041 cm^{-1} corresponds to Si-O planer stretching which the peak at 918 cm^{-1} corresponds to Al-OH deformation. Bond at 840 cm^{-1} is assigned to OH deformation linked to Al^{3+} and Fe^{2+}, the substation of Fe in the structure of the octahedral sheet in these samples is indicated by the stretching at 794 cm^{-1} based on Fe^{2+}-OH and Fe^{3+}-OH stretching which is indication of impurity in the koalinite.

Table (3) Vibration frequency of Kaolinite clay

Band(cm^{-1})	Assignment
3691	Free OH-stretching
3622	Inner layer OH(Al-O-H) stretching
3448	H-O-H stretching
1432	H-O-H bending
1119	Si-O normal to the plane stretching
1053	Si-O Planner stretching
918	Inner surface Al-OH deformation
794	Deformation of OH linked to Fe+3 and Al+3
698	Si-O deformation

The difference in some vibration compared to literature maybe due to the impurities in the kaolinite samples for surfaces HDTMA-Cl modified kaolinite the spectra shows that the surfactant is intercalated on the surfaces of the clay bands at 3691 and 3448cm^{-1} for OH groups became smaller and appeared at 3742 and 3497 cm^{-1} smaller absorption bands occur 1130 and 968 cm^{-1} shows exchangeable Si with $HDTMA^+$ on the koalinite clay.Some additional band at 2816 and 2820 cm^{-1} as intense peaks observed as 2870 and 2849 cm^{-1} in pure $HDTMA^+Cl^-$ spectra confirm the presence of $HDTMA^+$ in the modified koalinite.

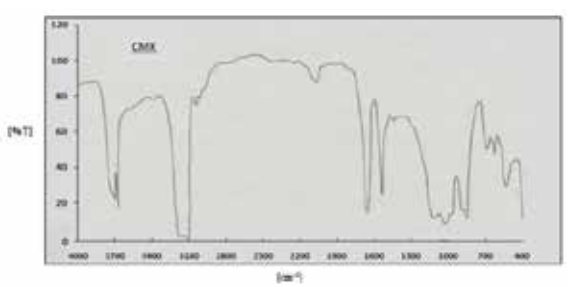

Figure 3. FTIR spectrum of modified Jordanian kaolinite

3.3 X-Ray Fluorescence analysis

The composition of the minerals that are present in the modified and unmodified koalinite as presented in table (4).

Table (4) Major oxides in raw and modified kaolinite.

Chemical Composition (%)	Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	L.O.I	Whiteness %
CK	1.17	0.004	1.41	0.51	1.34	0.08	55.01	29.80	0.41	0.07	10.0	69.90
CMK	1.01	0.003	1.25	0.16	0.32	0.05	47.92	26.41	0.34	0.05	21.25	-

Loss on ignition indicating modification of the koalinte there is a decrease in K_2O and CaO from 1.34 to 0.32% and 0.51 and 0.16% respectively. The indicator ratio of koalinite and modified koalinite samples are shown in table (5).

Table (5) Indicator ratios of oxides.

Indicator ratio	CK	CMK
Al_2O_3/SiO_2	0.541	0.553
Fe_2O_3/SiO_2	0.0213	0.0211
TiO_2/SiO_2	0.0256	0.0261

Since the indicator ratio does not change this proves that the intercalation of $MDTMA^+$ is via hydrophobic interactions among surfactant tail groups.

Trace elements for the raw kaolinite were determined using ICP. The results as part per million (ppm) are shown in Table (6) show high content of chromium and vanadium. This is reflected in whiteness measurements. The Jordanian kaolinite has some radio activity, which agrees with the literature (Ahmad, 2010).

Table(6) Trace elements in Jordanian kaolinite

Element	Ce	Cr	Cu	Mn	Ni	Pb	Sr	Th	U	V
Concentration[ppm]	0.80	106	5.1	11	25	35	17	0.5	0.3	104

3.4 X-Ray diffraction

The mineral composition of the original clay and these surfaces modified samples as shown from the diffraction pattern and measurement of d(001) and d(002) spacing and diffraction peaks intensities give important insight in the effect of the host.

The prominent d(001)basal reflection at about 7.1400 A° and d(002) is at 3.5600A° are usually used for the identification of kaolinite and any changes therein may reflect the occurrence of the intercalation. In the kaolinite sample the d(001) appears at 7.01807A° at angle 2ɵ of 14.645A° with an intensity 369 counts and d(002) appears at 3.54915A° at 29.195 2ɵ with intensity of 384 counts while for the modified surfaces koalinite these values appears at d(001) decrease to 6.9795A at 2ɵ 14.4998 there is slight contraction in the d(001) layer than original clay (Preeti et al.,2007; Yunfei, 2005) . This indicates that the $HDTMA^+Cl^-$ was

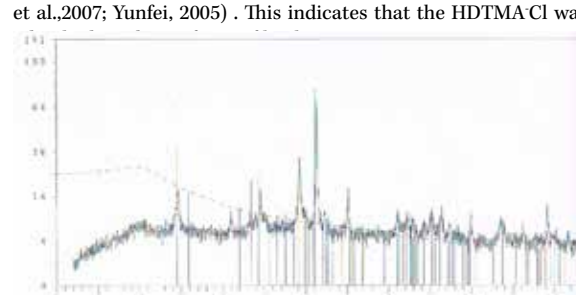

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Table (7) The mineral composition of raw and modified kaolinite.

Sample	CK	CMK
Kaolinite	Major	Major
Quarts	Major	Major
Anorthite	Minor	Minor
muscovite	Trace	Trace

From the table shows that there is no change in mineral composition, this implies that the modification does not affect the internal structure of the clay kaolinite.

3.5 Thermogravimetry

The mass loss occurring up to 400 C° is mostly attributed to elimination of absorbed water molecules on the external surface of the kaolinite particles. The water release of kaolinite in the temperature range between 450-650 C° and the formation of meta kaolinite is well known. The elimination of water molecules through dehydroxylation is shown (Yunfei et al., 2005; Yariv, 2004).

$$Al_2[Si_2O_5][OH]_4 \rightarrow \quad Al_2O_3 \cdot 2SiO_2 + H_2O$$

This process is observed in the TG/DTA analysis as amass loss beginning after 400 C° and completed around 650 C°. This is explained on the basis of interaction of neighboring OH groups. The OH release from octahedral coordinated Al+3 ions could generate water. Thermal behavior of high temperature region observed at 700 C° in DTA curve as exothermic peak around 870-1000 C°. At temperature around 95^0 C° ,the meta kaolinite is transformed to spinal structure of Si-containing δ-AL_2O_3 and amorphous silica originating by exothermic reaction. The SiO_4 groups combined with AlO_6 group to form [Al-Si] spinal phase appears more than 920 C° and persist until 1100 C°. This can be presented by the reaction

$$2\,(Al_2O_3 \cdot 2SiO_2) \xrightarrow{\textbf{920-1100-C°}} 2\,Al_2O_3 \cdot 3SiO_2 + SiO_2\,(\text{Amorphous})$$

The phase transformation is influenced by the degree of discords of kaolinite structure, formation environment kind and amount of impurities (Alsawalaha et al.,2011; Noumoradi, 2013).

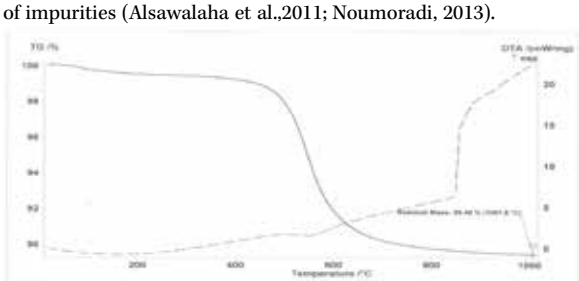

Figure 4. DTA/TG of Jordanian kaolinite

For the organoclay samples DTA loss at 120 C° attributed to desorption of water. The peak at 374 C° indicates bonding of surfactant molecule on kaolinite samples, the temperature of 530C° loss of surfactant while at 840C° is the formation of amorphous SiO2(Valaskova et al.,2007) .The residual mass was 89.46% at temperature of 1007.4 C°.

3.6 Uptake of aniline

To check the effect of initial concentration of aniline uptake by CK and CMK, one gram of each sample K was mixed with 10.0 ml of aniline (with initial concentration 30, 60, 90, 120 and 150 ppm) The samples were shaken at 200 rpm for 30 hours at room temperature in electrostatic shaker, the samples were centrifuged and the clear supernatant are used for analysis.

Table (8) Removal of aniline on raw and modified kaolinite.

Initial contraction of aniline (ppm)	CK		CMK	
	Amount of aniline adsorbed (ppm)	Removal percentage %	Amount of aniline adsorbed (ppm)	Removal percentage %
150	91.3	61.2	113.2	75.5
120	72.7	59.1	95.3	79.6
90	54.6	60.7	68.0	75.6
60	43.8	74.3	46.0	78.3
30	20.1	83.7	26.2	87.2

Data shows that modification of koalinite by surfactant increases the adsorption properties as shown in table.

4. Conclusion

Jordanian koalinite was modified by cationic surfactant HDTMA- Cl .The XRF, XRD, FTIR, TOC and thermoqravimetric measurements were used to characterize the samples.

The XFR reveal a change in the chemical composition which implies a successful intercalation. XRD patterns showed the d (001) is 7.01807A° and for the modified surfactant appears if 6.9795A° This contraction indicates the adsorption on the surface of kaolinite.

Total organic carbon increase from 0.51 to 4.41% for surfactant modified kaolinite. FTIR spectral reveals vibration frequencies shift from 3691cm^{-1} for original koalinite to 3710 cm^{-1} for surfactant modified koalinite.

Thermogravimetry explain the transformation of kaolinite samples. The TG/DTA as a mass loss bearing after 400C° and completed at 650C°, explain the interaction of neighboring OH groups. The removal of aniline using modified surfactant kaolinite increase the adsorption by 11.5% at different concentration ranges.

Acknowledgements

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