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Interaction between Kaolin and Urea in Organoclay and Its Impact on Removing Methylene Blue from Aqueous Solution

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Abstract

Interaction between kaolin (particle size 53 and 106 µm) and urea was studied by infrared spectroscopy and powder X-ray diffraction. Interaction was found to be dependent on the particle size of kaolin raw material. Nature of interaction achieved through the formation of hydrogen bonds between urea and both AlOH and Si-O surface of kaolinite. Effect of temperature on equilibrium adsorption of methylene blue (MB) from aqueous solution using kaolin also studied, the results were analyzed by Langmuir and frendlich isotherms. Thermodynamic parameters such as ΔG, ΔH and ΔS were calculated. Results suggested that the MB adsorption on kaolin was spontaneous and exothermic process.

Keywords

Kaolin, Urea, Intercalation, Thermodynamic, Methylene Blue and Adsorption

1. Introduction

Kaolin is one of the clay materials widely used in a large number of applications such as in ceramics, paper coating, paper filling, paint extender rubber filler, cracking catalyst or cements, oil refinery and water treatment (adsorption of dyes and other pollutant) [1]-[4] with the chemical composition $Al_2Si_2O_5(OH)_4$. For each application the engineering properties of the clays must be carefully designed to obtain the desired result. Clays are

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usually defined as natural materials presenting fine granulometry. Often, these materials exhibit a lamellar structure as a consequence of the crystalline arrangement formed by the silicon and aluminum oxides, which are the main components of clays. These structures are displayed by these materials. Kaolinite is a common 1:1 dioctahedral phyllosilicate (clay) mineral found throughout the world in highly-weathered environments. Being a 1:1 mineral, it has one silica tetrahedral layer and one aluminum octahedral layer combine to form a unique structural arrangement in which sheets of tetrahedral and octahedral overlap each other, leading to structural changes such as 2:1 (one octahedral sheet between two tetrahedral sheets) and 1:1 (one tetrahedral sheet to one octahedral sheet) that characterize the various clay minerals [5] [6].

Kaolinite is a 1:1 tetrahedral aluminosilicate with two distinct basal cleavge faces. One of them consist of tetrahedral siloxane surface formed by very chemically inert Si-O-Si bonds, while the other constituted by an Octahedral sheet $Al(OH)_3$ can be distributed and broken bands have the ability to accommodate OH group. The layers are bonded by hydrogen bonds. Hydrogen bonds occur between oppositely charged ends of a permanent dipole [7] [8].

Interaction between clays and organic compounds have received increase attention due to the wide ranges of applications especially in chromatography separations [9], to remove organic pollutants from air [10], and water [11], and to develop improved formulation for pesticides and as chemical sensor and molecular sieves [12].

This research primarily studies the nature intercalations between kaolinite and urea by using FTIR and XRD. Furthermore, it also studies the impacts to adsorption capacities made by the interaction, the kineticsod adsorption and application to remove dye from aqueous solution.

2. Experimental

Kaolinite used in this study was hydrated aluninum silicate, which was provided from general company for the manufacture of glass and ceramic (ceramic factory) in Ramadi. Chemical analysis of kaolin is shown in **Table 1**. Urea powder with a melting point of 132˚C - 135˚C, and density of 1.33 g/ml was obtained from sigma Aldrich.

2.1. Preparation of Kaolin-Urea Organoclay (Granular Size 53 µm and 106 µm)

1. 70 gm of grinded kaolin of granular size 53 µm was weighed and placed in a Beaker (capacity of 500 ml).
2. 35 gm of Urea was weighed and then added to the clay on the same Beaker.
3. The mixture was mixed by an electrical mixer in its dry form.
4. Suitable amount of water then added to the mixture with keeping continuous stirring, till getting a solution of kaolin-urea.
5. The mixture then placed at a porcelain crucible and heat in an oven at 90˚C till dryness.
6. The products, finally was grinded and became ready to the required tests (FTIR, XRD and Adsorption of methylene blue (MB).
7. Same procedure was used on kaolin (partical size 106 µm).

2.2. Preparation of Methylen Blue Solution

1 gm of MB dye was dissolved in one liter of double distilled water to obtain 1000 ppm MB dye solution. UV-Vis spectra of this solution appeared an absorption band at λ_{max} = 660 nm.

Table 1. Chemical analysis of kaolin.

Al_2O_3	>23%
SiO_2	45% - 50%
Fe_2O_3	<3%
CaO	3%
MgO	<2%
L.O.I	12% - 13%

2.3. Steps of Adsorption

- 0.5 gm of the prepared organoclay was weighed, each alone and placed at 25 ml volumetric flask.
- 10 ml of methylen blue solution dye of the required concentration was added and stirred, very well to the clay.
- The flasks were placed at shaker water bath at different temperatures (10˚C, 30˚C, 40˚C and 50˚C) and stirred for 1 hour each.
- The solutions were filtered.
- The absorption was measured for each filtrate at 660 nm.
- The adsorption required calculation according to (Langmuir and Freundlich isotherms), from which the thermodynamic constant can be obtained (ΔG, ΔH and ΔS).

2.4. Preparation of Nano Organoclays

1) Weigh 5 g of prepared organoclay and placed in a glas Baker 250 ml.
2) Added 200 ml of a solution of urea concentration 2 M and shake well.
3) The solution is placed on the ultrasonic (probe ultrasonic) and placed the amount of ice around the beaker for one hour.
4) Separating the precipitate from the filtrate using a centrifuge.
5) Dried the pricipitate and then grinds it and conducted the tests required.
6) Returned the same previous steps for (Thiourea, Acetamide, DMSO and DMF).

3. Results and Discussion

3.1. FTIR Results

Vibrational spectroscopy is a key technique in the study of formation and structural characterization of kaolinite intercalates [13].

FTIR of kaolin, urea and kaolin-urea complex are shown in **Figure 1** and **Figure 2**. From these figures, one could observed that kaolin show two sharp bands at 3694 cm^{-1} and 3625 cm^{-1}. The literature however shows conflicting assignment of these bands [14], band at 3694 cm^{-1} belong to hydroxyl group in specific lattice sites in the layer and resulting from vibrational coupling of three surface of hydroxyl in the primitive cell and the dipole oscillation in perpendicular to the layer, while band at 3625 cm^{-1} in belong to hydroxyl group lie within lamellae

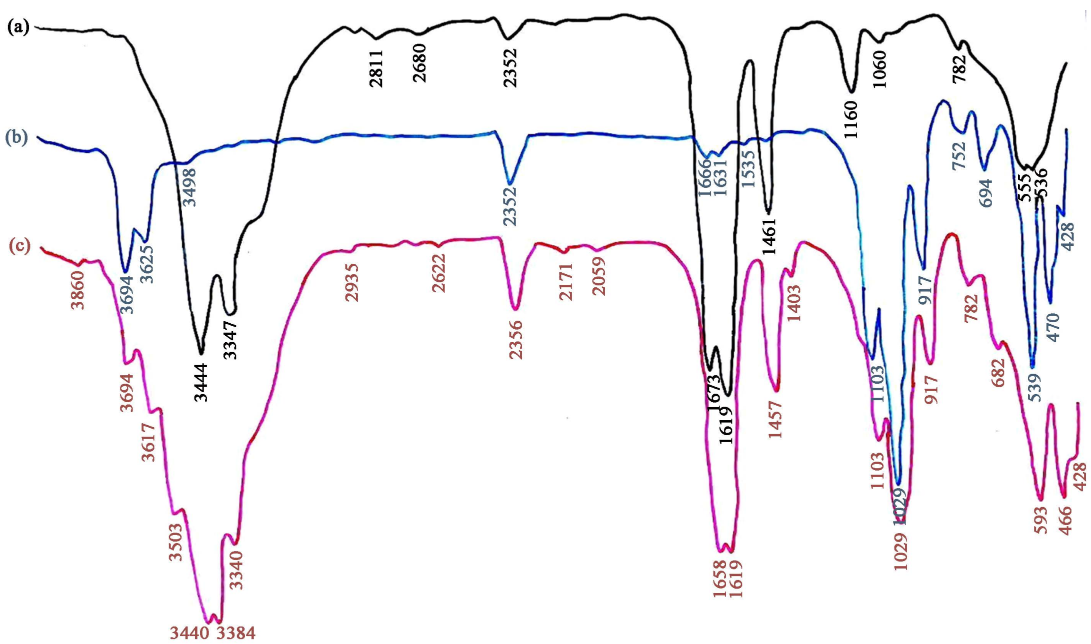

Figure 1. FTIR spectra of (a) urea; (b) kaolin 53 µm and (c) kaolin 53 µm-urea complex.

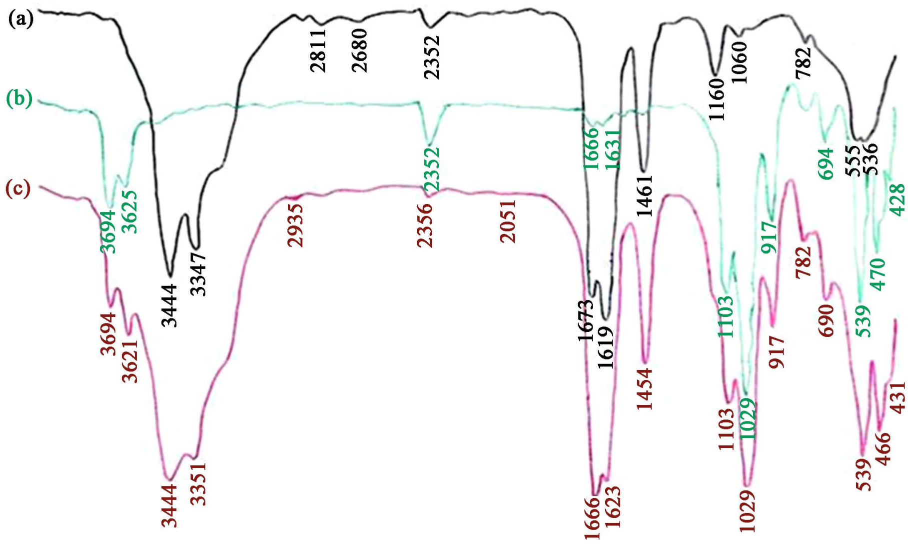

Figure 2. FTIR spectra of (a) kaolin 106 µm; (b) urea and (c) kaolin 106 µm-urea complex.

in plane common to both the tetrahedral and octahedral sheets. Upon intercalation with urea, the intensity of these two bands decrease and shifted to lower frequency, Also a new bands at 3503 cm^{-1} appeared due to the breaking of some hydrogen bonds between the kaolinite layers and formation of new band, which usually involve the inner surface OH group and change are observed in the intensities of bands assigned to vibrations of these groups [13].

Bands at 3440 and 3444 cm^{-1} in the **Figure 1** and **Figure 2** (Chart C) which appear in the results intercalation of kaolinite 53 and 106 µm with urea respectively are attributed to formation H-bond between NH_2 group from urea and Oxygen group of tetrahedral sheet for kaolinite.

The newly formed bands at 3384 and 3503 cm^{-1} in the intercalation of kaolinite 53 µm with urea confirmed the asymmetric and symmetric NH_2 stretching frequencies involved in weak H-bonding with the inner hydroxyls [15]-[18].

Band at 2352 cm^{-1} in urea chart and kaolinite 53 and 106 µm started disappear when intercalated urea with kaolinite 106 µm and happened shifted in this band to the 2356 cm^{-1} when intercalate urea with kaolinite 53 µm.

Also same effect appeared for the band at 1673 cm^{-1}, which assigned for the C═O group of urea, upon interaction with kaolin, formation a bond between C═O and OH group in Gibbsite-like layer so it shifted to 1658 and 1666 cm^{-1} whene kaolinite 53 and 106 µm interactions with urea respectinely (Chart C in **Figure 1** and **Figure 2**). CN stretching of free urea appeared at 1461 cm^{-1}, upon interaction with kaolinite shifted to 1457 and 1454 cm^{-1} in the **Figure 1** and **Figure 2** Chart C respectively, and a new band at 1403 cm^{-1} appeared. This suggest urea in this system would then be considered to exist in two forms anionic and complex (ion dipole) as shown in **Figure 3**.

3.2. XRD Results

The XRD curves of raw kaolin chart (A), and kaolin-Urea complexes charts (B and C) are shown in **Figure 4**.

From this figure one could observe that the strongest three peaks and their values are recorded in **Table 2**.

From this table:

Peaks at $2\theta = 12.3044$, d(Å) = 7.18765, intensity = 403 and $2\theta = 24.9208$, d(Å) = 3.57009, intensity = 362 are attributed to kaolinite and $2\theta = 26.6345$, d(Å) = 3.34415, intensity = 286 is due to SiO_2.

Peak in Chart B at $2\theta = 22.4669$, d(Å) = 3.95417, intensity = 1019 is attributed to urea, and peaked at $2\theta = 268558$, d(Å) = 3.31709, intensity = 247 is due to SiO_2. Band at 2θ = 25.1508, d(Å) = 3.53796, intensity = 227 is due to kaolinite.

These peaks in Chart C at $2\theta = 22.3047$, d(Å) = 3.98256, intensity = 2249, $2\theta = 29.3554$, d(Å) = 3.04008, intensity = 371 and $2\theta = 24.6676$, d(Å) = 3.60616, intensity = 370 are assigned to urea, SiO_2 and kaolinite respectively.

From the results in **Table 2** and make comparison between these values, on could concluded that strong intercalation between kaolinite layers and urea as a result of appearance high intensity of peaks are due to urea and

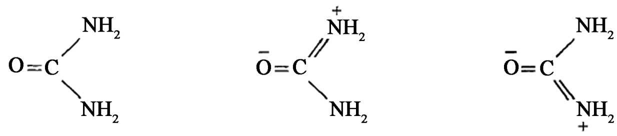

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Figure 3. Anionicformsin ureamolecule.

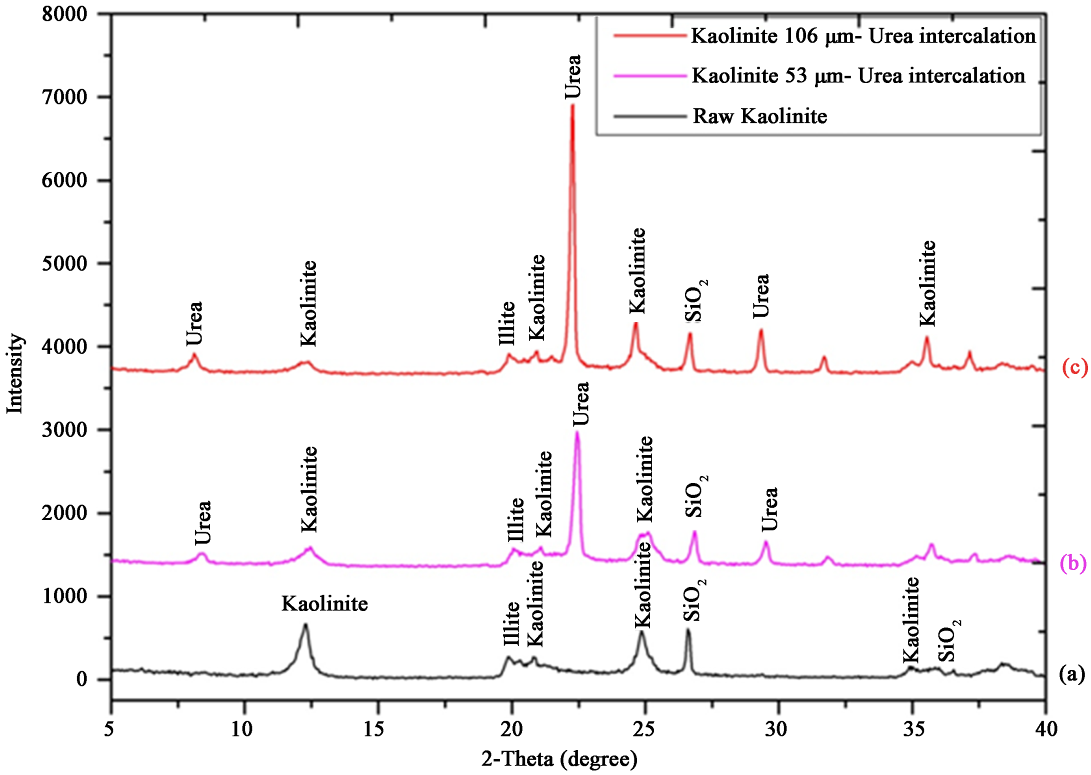

Figure 4. The XRD pattern of raw kaolinite (a); kaolinite 53 μm-urea intercalation (b); and kaolinite 106 μm-urea intercalation (c).

Table 2. Values of XRD for strong peaks in **Figure 4** Chart A.

Assignment	Kaoline	Kaolinite 53 μm-Thiourea Complex	Kaolinite 53 μm-Thiourea Complex
	12.3044	22.4669	22.3047
2θ	24.9208	26.8558	29.3554
	26.6345	25.1508	24.6676
	7.18765	3.95417	3.98256
d-spacing d(Å)	3.57009	3.31709	3.04008
	3.34415	3.53796	3.60616
	403	1019	2249
Intensity (counts)	362	247	371
	286	227	370

in the same time happened shifted and decrease in the intensity of kaolinite and SiO_2 when the intercalation is event. The intercalation caused the destruction of the hydrogen bonding between the kaolinite layers [14]. And from results in this table show decreasing in intensity of peaks when the kaolin 53 µm-urea intercalated with urea compared with other complex this indicates that this kaoline a granular size 53 µm is the best.

3.3. Adsorption Results

Effects of temperature on the equilibrium adsorption of methylene blue from aqueous solution using kaolin (partical size 53 and 106 µm) and kaolin-urea complex were studied.

The equilibrium adsorption data were analyzed using two widely applied isotherms: Langmuir and Freundlich. The results were shown in **Table 3** and **Table 4**. Non-linear method was used for comparing the best fit of the isotherms. Best fit was found to be Langmuir isotherm.

3.3.1. Thermodynamic Parameters

Thermodynamic parameters such as ΔG, ΔH and ΔS were calculated using adsorption equilibrium constant obtained from Langmuir isotherm and shown in **Table 5**.

Results suggested that methylene blue adsorption on kaolin was spontaneous and exothermic process.

Decrease a negative value of ΔG with increase the value of ΔH (-ve) indicate that the adsorption reaction was exothermic.

Percentage of adsorption (Q%) for kaolin and kaolin-urea at conc. 100 ppm of methylen blue are shown in **Table 6**.

3.3.2. Transmission Electron Microscopy (TEM)

TEM is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

Figure 5 and **Figure 6** show the TEM photographs of Kaolin (53 and 106 µm)-urea complexes.

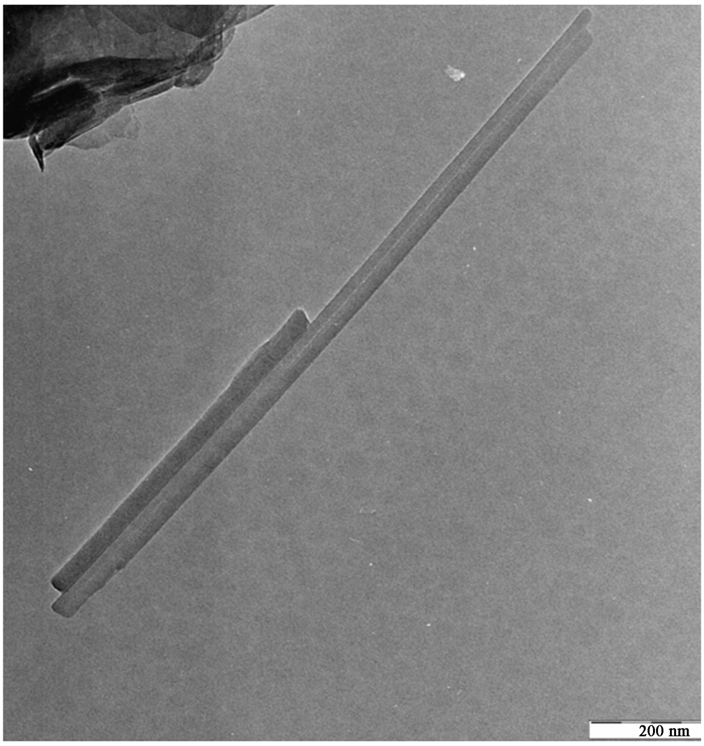

Figure 5. TEM image of kaolinite 53 µm urea complexes.

Figure 6. TEM image of kaolinite 106 µm urea complexes.

Table 3. Langmuir constant for adsorption at conc. 100 ppm of methylene blue.

Sample	Particle Size µm	Langmuir Constant	Temperature K			
			283	303	313	322
Kaolin	53	K_f	1000	1000	1000	500
		a	1	1	1	0.5
		R^2	0.535	0.411	0.504	0.64
Kaolin-Urea	53	K_f	0	0	0	0
		a	0	0	0	0
		R^2	0.758	0.879	0.944	0.957
Kaolin	106	K_f	0	250	142.857	250
		a	0	−1.5	−1.714	−0.5
		R^2	0.817	0.933	0.933	0.345
Kaolin + Urea	106	K_f	1000	1000	500	500
		a	2.0	3.0	1.5	0.5
		R^2	0.65	0.737	0.808	0.640

Table 4. Freundlich constant for adsorption at conc. 100 ppm of methylene blue.

Sample	Particle Size μm	Freundlich Constant	Temperature K			
			283	303	313	322
Kaolin	53	K_f	419.75	404.57	309.2	285.759
		n	1.315	1.207	1.331	1.360
		R^2	0.913	0.938	0.897	0.864
Kaolin-Urea	53	K_f	371.53	297.85	229.08	186.638
		n	1.680	1.980	2.624	2.923
		R^2	0.860	0.876	0.867	0.877
Kaolin	106	K_f	319.15	1127.19	1879.31	434.51
		n	1.751	0.536	0.379	1.360
		R^2	0.880	0.983	0.970	0.864
Kaolin-Urea	106	K_f	263.02	224.38	207.01	202.301
		n	1.633	1.908	1.754	1.481
		$\mathbf{R^2}$	0.885	0.874	0.924	0.920

Table 5. Thermodynamic parameters at conc. 100 ppm Methylen blue.

Sample	Particle Size μm	ΔH KJ/mol	ΔS KJ/mol·k	ΔG KJ/mol			
				283 K	303 K	313 K	322 K
Kaolin	53	−9.877	0.01858	−15.0757	−15.7056	−15.644	−15.8984
Kaolin-Urea	53	−6.59965	0.0325576	−15.661	−16.668	−17.119	−18.742
Kaolin	106	−16.9356	−0.006187	−15.3088	−14.8637	−14.8618	−15.1733
Kaolin-Urea	106	−9.935	0.01738	−14.6689	−15.6398	−15.904	−16.2948

Table 6. Percentage of adsorption (Q%) for kaolin and kaolin-urea at conc. 100 ppm of methylen blue.

Sample	Particle Size μm	Q% at Different Temp.			
		283 K	303 K	313 K	322 K
Kaolin	53	99.853	99.803	99.7521	99.726
Kaolin-Urea	53	99.8714	99.8662	99.861	99.803
Kaolin	106	99.8506	99.726	99.699	99.648
Kaolin-Urea	106	99.8039	99.7987	99.7313	99.6639

From this figures show formation of nanotubeit is also very clearly in the images. The average sizes of particles are in the range of 20.2 - 24.5 nm in **Figure 5** and from 20.8 - 27.7 nm in **Figure 6**.

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