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Thermodynamic and Kinetic Behaviors of Copper (II) and Methyl Orange (MO) Adsorption on Unmodified and Modified Kaolinite Clay

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Abstract

In this study, the adsorption of Copper Cu (II) and methyl Orange (MO) from aqueous solution, on Tamanrasset's unmodified and modified Kaolinite clay which as low cost adsorbents, was studied using batch experiments. The adsorption study includes both equilibrium adsorption isotherms, kinetics and thermodynamics study. For the characterization of the adsorbent several properties are determined such as pH, the Specific Surface Area, the Point of Zero Charge and the Cation Exchange Capacity. Indeed, various parameters were investigated such as contact time, initial metal and dye concentration, mass of solid, pH of the solution and temperature. The adsorption process as batch study was investigated under the previews experimental parameters.

Keywords: Adsorption, Kaolinite, Copper, Methyl Orange, Kinetic, Isotherms

1. Introduction

The extensive use of chemicals in developing and developed countries over the last century increased the amount of dyes and heavy metals which is released into surface and underground water through discharges of wastewater produced from metallurgical, mining, chemical, research laboratories, printing paper and battery manufacturing industries [1, 2]. Copper (Cu (II)) is extremely toxic, not biodegradable and it accumulated in living organisms, and may thus pose a threat to human beings. In addition, Copper ions is considered as vital transition metal ion because of its necessity in biological activities of living organism, whereas at certain concentration, it causes serious damages to human health and environment [3–5].

Methyl orange (MO) is an azo soluble dye, shows low biodegradability and is soluble in water hence it is difficult to remove from aqueous solutions by common

water purification methods. As other dyes MO is toxic and carcinogenic, posing serious hazards to humans and the environment [6].

Purification of water can be achieved by physicochemical and biological methods. The physicochemical methods include precipitation [7], membrane filtration [8], liquid-liquid extraction [9] reverse osmosis [10], electrolysis or ultrasonic electrolysis [11], electrodialysis [12], electrodeposition [13], ion exchange resins [14], incineration and electrokinetic method [15], flotation [16], flocculation [17], coagulation [18], photocatalysis [19], adsorption and biosorption [20]. Biological process includes biodegradation or bioremediation [21], phycoremediation [22]. Adsorption method is more effective, economic with high potential and low energy consumption specially it has the advantage of the utilization of abundant with low cost adsorbents.

Clay minerals in the soil play the role of a natural scavenger by removing and accumulating pollutants through ion exchange and adsorption process. Generally, these minerals are categorized into Montmorillonite, smectites, Illite and kaolinite [23]. Kaolinite is a harmful charge clay mineral with a soft consistency. It made up of a silicon tetrahedral (T) sheet and an aluminum octahedral (O) sheet which called 1:1 layer clay (2 sheets). Kaolinite has considered as an excellent adsorbent clay because of its high specific surface area, high exchange capacity, large potential for ion exchange, surface charges, charge density, chemical and mechanical stability, a variety of surface and structural properties, hydroxyl groups on the edge, silanol groups of crystalline defects or broken surfaces, and Lewis and Brönsted acidity [24–27]. Kaolinite clay also has been widely accepted as low cost abundant adsorbent for the removal of copper and methyl orange from wastewater due to the surface structure and edges. Recently many studies used natural kaolinite [28], other scientists used purified kaolinite in other wise other researchers used organo kaolinite as adsorbents [29]. However, kaolinite in its different geological origins may have variable chemical compositions and structural deformation. Elements such as Fe, Ti, Mn, Mg, and Cr, and impure phases, such as quartz, and Illite, are normally contained in natural kaolinite. Even, a small amount of these impurities may significantly affect the chemical properties of kaolinite. Those researches were carried out with physical or chemical modification of kaolinite in order to enhance the properties of kaolinite and to increase the adsorption capacity.

The aim of this paper is to access the ability of Tamanrasset's kaolinite clay and its derivatives (purified, activated, pillared and modified) to adsorb Cu(II) and MO from aqueous solution. The effect of the contact time, temperature, mass of solid, solution pH and concentration of the adsorbate was studied. The kinetics and factors controlling the adsorption were also studied. Therefore, the physicochemical characteristics of materials were considered such as pH, the specific surface area, the point of zero charge and the cation exchange capacity.

2. Material and methods

2.1 The adsorbate and solution

The adsorbates in this study were copper and methyl orange prepared by dissolving CuCl_2 , $2\text{H}_2\text{O}$ and MO into 1000 mL of deionized water to stock solution concentration of 1000 mg/L, the adjustment of pH in the solution was achieved by adding NaOH and HCl 0,1 M are from Sigma-Aldrich. The desirable experimental concentrations of solutions were prepared by diluting the stock solution with distilled water when necessary.

2.2 The adsorbents

2.2.1 Raw clay

The natural clay sample was obtained from Tamanrasset south of Algeria. It was prepared before use by sun drying, then ground into fine particles and sieved to a particle size of 300 μm after that, it was stored in a desiccator for later experimental use.

2.2.2 Purified clay

The clay was purified with the purpose of removing all crystalline phases and organic matter according to the procedure described by Robert and Tessier in order to obtain 2 micrometers clay fractions intercalated with sodium ions (Clay-Na) [30].

2.2.3 Activated clay

The chemical activated clay was carried out by adding 50 g of raw clay to 500 ml of sulfuric acid 1.5 M and refluxing at 110°C for 4 h. The resulting clay suspension was then rapidly quenched by adding 500 ml of ice water. After cooling the sample was washed several times with distilled water until neutral pH, then filtered, dried in oven and calcined at 500°C for 4 hours [31, 32].

2.2.4 Pillared clay

The pillaring solution was prepared by the slow addition of NaOH 0.225 M to a 0.5 M solution of AlCl_3 at room temperature, until a molar ratio of $\text{OH}/\text{Al} = 1.8$ was reached. The pillaring of Clay-Na by polycation of aluminum is carried out according to the conventional procedure (cationic exchange with a heat treatment) [33].

2.2.5 Clay-CTAB

In 500 ml Buchner, 10 g of purified clay was added to 250 ml of CTAB solution 0.02 M, the mixture was stirred at room temperature for 24 h. Then, the suspension was filtered and washed several times until the negative test of Br^- . The CTAB-Clay was dried at 105°C for one hour, ground and stored in sterile glass box [34, 35].

2.3 Physicochemical characteristics of adsorbents

2.3.1 The pH of adsorbent

Ten grams of crushed kaolinite was stirred in 75 ml of deionized water in a beaker over the night then it filtered. The pH was measured by a glass electrode (pH METER HI2210) [36].

2.3.2 The specific surface area

Sear's method was chosen to estimate the surface areas of clay adsorbents [37]. 0.5 g of each clay was acidified with 0.1 M HCl to a pH 3–3.5. The volume was made up to 50 ml with distilled water after addition of 10 g of NaCl. The titration was carried out with standard 0.1 M NaOH buffer solution from pH 4 to pH 9. The volume, V, required to raise the pH from 4 to 9 was noted and the surface area was computed from the following equation:

$$S(\text{m}^2/\text{g}) = 32V - 25 \quad (1)$$

2.3.3 The point of zero charge

The point of zero charge or pHPzc is point where the net charge of the material equal to 0. The PZC was determined by the pH drift method [38, 39].

2.3.4 The cation exchange capacity

The CEC of materials was calculated by methylene blue method [40].

2.4 Bath equilibrium studies

Bath experiments were performed in a set of 250 mL Erlenmeyer flasks that contain a volume of 100 mL in each flask of fixed initial concentrations of metal and dye solutions. The flasks were kept in a thermostated water bath (Wise bath® with Back Control Digital Timer Function, Laboratory Instruments) shaker at a constant speed of 150 rpm for 360 min (6 h). The sample solutions were filtered at equilibrium to determine the residual concentrations. The amount of adsorbate adsorbed at the equilibrium condition, q_e (mg/g), was calculated by the following Equations [41]:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

Where C_0 and C_e are the initial and equilibrium metal and dye concentrations (mg/L), respectively. V is the volume of solution (L) and W is the mass of adsorbent used (g).

The concentration of Cu(II) before and after adsorption was determined by a flame atomic absorption spectrometry (Analyst 700 Perkin Elmer Atomic Absorption Spectrometer) and the concentration of MO was determined by UV-Visible spectrometry (M209T Spectronic Camspec).

2.5 Kinetics studies

The kinetic experiments, adsorption capacity of Cu (II) and MO at time t , q_t (mg/g), was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

Where C_t (mg/L) is the concentration of copper/Methyl orange at any time t (min).

3. Results and discussion

3.1 Characterization of adsorbents

3.1.1 pH and the point of zero charge

The surface of kaolinite has a net positive surface charge at $\text{pH} < \text{PZC}$, whereas at $\text{pH} > \text{PZC}$, it has a negative surface charge. The PZC value of natural kaolinite was 8.9. This value indicates that the adsorption of copper and methyl orange by untreated kaolinite will occur at $\text{pH} \geq 8.9$.

3.1.2 Surface area

The specific surface area of 5 to 25 m²/g for the untreated kaolinite clay. The specific surface area of natural, purified, activated, pillared, and CTAB kaolinite are measured as 25.4, 36.7, 30.14, 42.1 and 43.15 m²/g, respectively. The specific surface area increased up to 30.1 for activated clay. Such the high value of specific area is not achieved in the present work by treatment with 1.5 M H₂SO₄ acid. The chemical modification opens up the edge of the platelets and as consequence, the surface area and the pore diameter increase too.

3.1.3 Cation exchange capacity

The kaolinite used in the present work had CEC of 5.92 meq/100 g as measured by methylene blue method. Kaolinite as other clay minerals contain both Brönsted and Lewis acid cites associated respectively with the interlamellar region and the edge sites. The ions exchange capacity of kaolinite is attributed to the structural defects, broken bonds and structural hydroxyl transfers. Chemical modifications increase the total number of exchange sites. The results obtained are summarized in **Table 1**.

3.2 Bath studies

3.2.1 Effect of adsorbent dose

The adsorbent dose is an important parameter too because it determines the capacity of adsorbent for a given initial concentration of metal solution. **Figure 1a** and **b** showed that the amount adsorbed q_e decrease with the increase of adsorbent dosage. This is due to the increase in surface area and hence more available adsorption sites competing for the same number of initial ion concentration [42].

3.2.2 Effect of time contact and initial concentration

Equilibrium time is an important parameter in the studies of wastewater treatment. The adsorption of Cu²⁺ onto clay (0,08 g of raw, purified and pillared clay, 0.1 g of activated clay and 0.06 of modified CTAB clay) at various initial concentrations (5, 25, 50, and 100mg/L), and in the case of methyl orange the dosage of modified and unmodified clay was 0.1 g at various initial concentrations (5, 20, and 35 mg/L) was studied as a function of contact time in order to determine the necessary adsorption equilibrium time.

Figure 2a and **b** shows the effects of contact time and initial concentration on the adsorption of copper and methyl orange into raw clay. We notice that the adsorption is rapid at the initial stages during 10–50 minutes. This is due to the fast

Properties	pH	Point of Zero Charge	Specific Surface Area (m ² /g)	Cation Exchange Capacity (meq/100 g)
Raw clay	7.44	8.9	25.4	5.95
Purified Clay	9.83	3.5	36.7	11.82
Activated Clay	3.40	7.5	30.14	13.75
Pillared Clay	5.43	5.1	42.1	13.05
Clay-CTAB	1.6	3.25	43.15	12.18

Table 1.
Physicochemical properties of adsorbents.

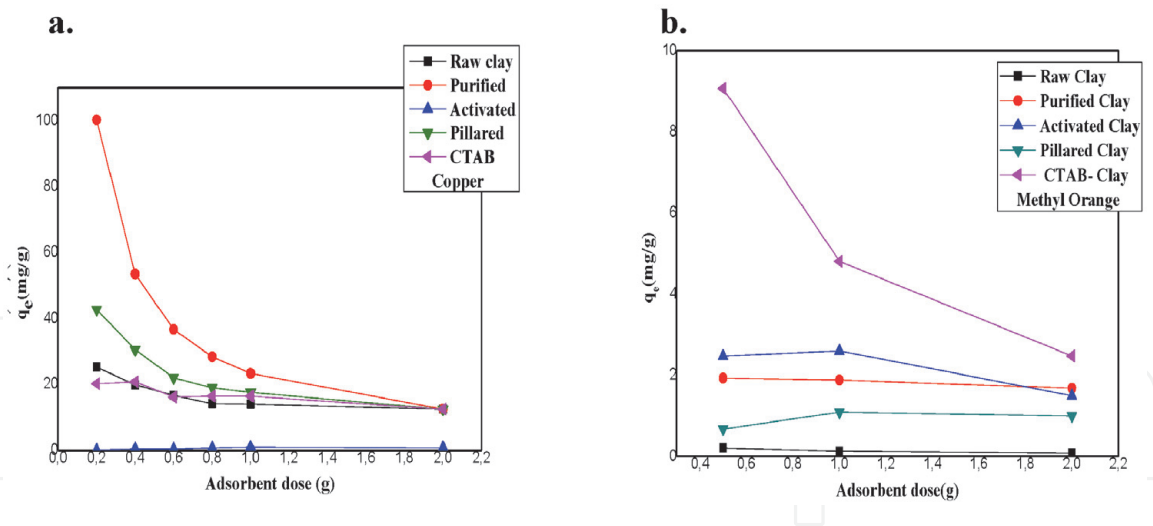


Figure 1.
Effect of adsorbent dose on the amount adsorbed onto copper and methyl orange.

that there were a large number of vacant sites for metal on the external surface of clay particles. Then it's gradually decreases with the progress of adsorption until the equilibrium is reached because of the active sites saturation of the adsorbent [43, 44]. As shown in **Figure 2**, the contact time for the Cu(II) and MO to reach equilibrium was 50 min and 60 min, respectively.

The **Table 2** below shows the adsorption capacity of adsorbed at the equilibrium (q_e) increased with an increase in the initial concentrations.

3.2.3 Effect of pH on the amount adsorbed

pH is the most important environmental factors influencing not only site dissociation, but also the solution chemistry and in the efficiency of adsorption [45], it effects both the dye structure and the surface on the adsorbent. As seen in **Figure 3** the sorption capacity of copper increased whenever pH of the solution increases. While, the adsorption amount of methyl orange onto the clay increases as pH is lowered from 11 to 2, confirmed that the initial solution pH is a key adsorption parameter that strongly affects metal and dye adsorption because of the decreased positive charges on the adsorbent surface with an increased pH. The pH of the solution also affects the solubility and species of adsorbate, the adsorbents, and the degree of ionization of the adsorbate [46–48].

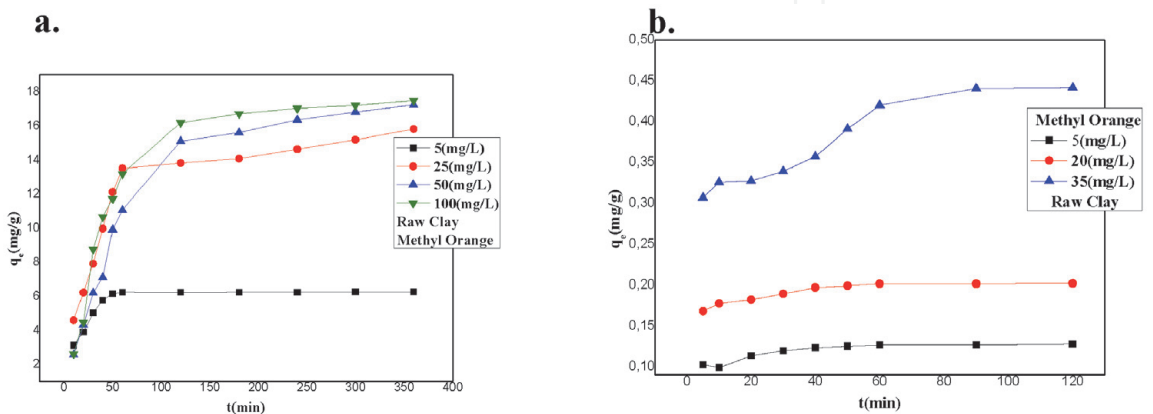


Figure 2.
Effect of initial concentration and contact time.

Clay		Natural	Modified			
			Purified	Activated	Pillared	Clay-CTAB
Cu(II)	$q_e(\text{mg/g})$	6.25–20.91	6.25–27.65	0.39–1.17	6.25–24.47	8.33–30.31
MO		0.126–0.423	1.879–2.835	2.599–5.672	1.083–3.591	4.804–10.447

Table 2.
The amount adsorbed.

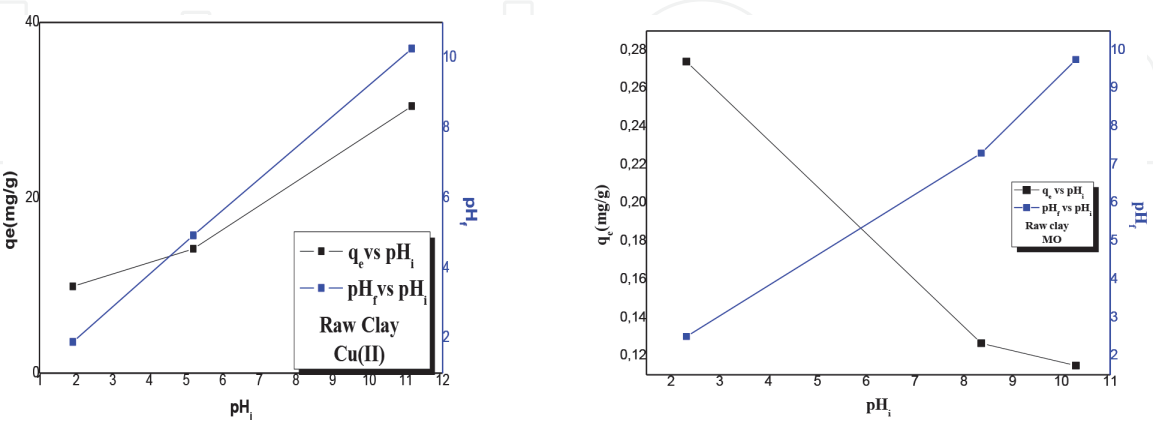


Figure 3.
Effect of pH.

3.2.4 Effect of temperature on the amount of adsorption

Because temperature is an important parameter for adsorption process and bath adsorption studies were carried out at different temperatures and concentrations of Cu(II) ions and MO dye. The amount of sorption increasing with increasing temperature witch indicates that the nature of this adsorption is a chemical sorption [42]. Whereas, the adsorption capacity of MO onto raw and activated kaolinite decrease whenever temperature increase, as shown if **Figure 4**, indicating possibilities of reversible adsorption process [49].

3.3 Kinetic studies

Two kinetic models fitted this adsorption process very well as explained below [50, 51].

3.3.1 Pseudo-first order kinetic model

The pseudo first-order kinetic model is expressed as:

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \tag{4}$$

Where q_t is the amount adsorbed (mg/g) at time t (sec) and k_1 is the pseudo-first order constant (s^{-1}) and calculated by linear regression of $\log(q_e - q_t)$ versus t plot.

3.3.2 Pseudo-second order kinetic model

The pseudo second-order kinetic model is given as:

$$\left(\frac{t}{q_t} \right) = \left(\frac{t}{q_e} \right) + \left(\frac{1}{k_2 q_e^2} \right) \tag{5}$$

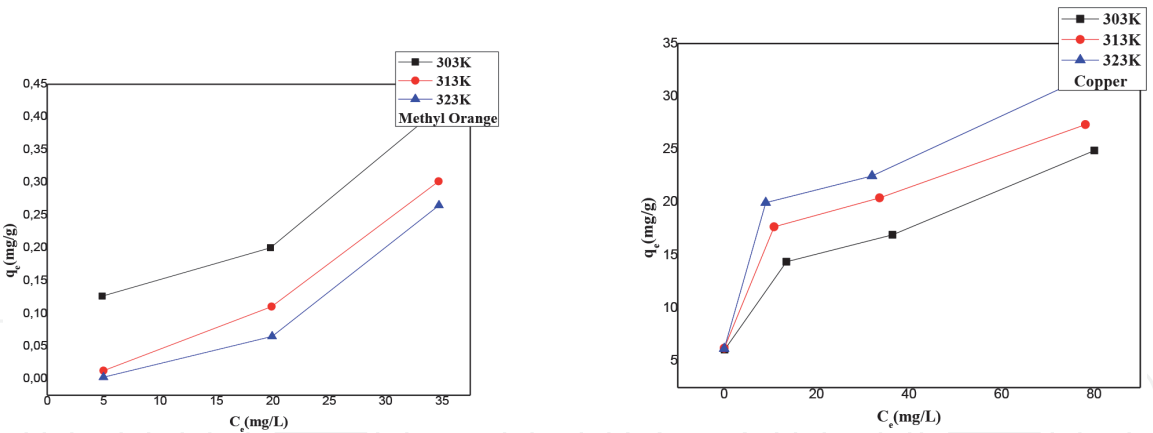


Figure 4.
Effect of varying temperatures on the amount adsorbed.

Where, k_2 is the pseudo second order rate constant ($\text{g.mg}^{-1}.\text{s}^{-1}$) and can be calculated by linear regression of $\frac{t}{q_t}$ versus t plot. The adsorption kinetics constants and the correlation coefficient values R^2 are summarized in **Tables 3** and **4**: The values of the correlation coefficient R^2 of the pseudo-second order model are significantly higher than those of the pseudo-first model.

3.4 Adsorption isotherms

The adsorption isotherm of Cu^{2+} and MO was checked whether it fits the Langmuir and Freundlich isotherms (**Table 5**).

Adsorbent	C_0 (mg/L)	$q_{e,\text{exp}}$ (mg/g)	Pseudo-first order			Pseudo-second order		
			k_1 (min^{-1})	$q_{e,\text{cal}}$ (mg/g)	R^2	k_2 (g/mg. min)	$q_{e,\text{cal}}$ (mg/g)	R^2
Raw Clay	5	6.25	0.032	1.199	0.7	0.0248	6.0402	0.999
	25	16.58	0.006	8.452	0.859	0.0022	16.667	0.996
	50	20.91	0.004	15.066	0.869	0.00074	20.833	0.991
	100	20.12	0.005	12.022	0.797	0.0011	20.06	0.986
Purified Clay	5	6.25	0.044	0.473	0.847	0.0418	6.36	0.999
	25	27.65	0.006	12.82	0.902	0.0017	27.77	0.999
	50	25.98	0.005	11.22	0.709	0.0017	26.31	0.996
	100	21.97	0.006	8.709	0.837	0.0025	22.22	0.998
Activated Clay	5	0.6	0.093	58.88	0.664	0.00141	1.597	−0.039
	25	1.17	0.009	0.807	0.935	0.0192	1.1331	0.985
	50	0.39	0.017	0.364	0.843	0.0291	0.487	0.957
	100	0.4	0.11	0.22	0.734	0.055	0.447	0.991
Pillared Clay	5	6.25	0.221	29.51	0.954	0.1560	6.28	0.999
	25	24.47	0.008	5.49	0.906	0.00578	24.5	0.999
	50	16.45	0.008	6.025	0.863	0.00403	16.66	0.998
	100	23.53	0.006	7.58	0.828	0.00347	23.809	0.997

Adsorbent	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order			Pseudo-second order		
			k ₁ (min ⁻¹)	q _{e,cal} (mg/g)	R ²	k ₂ (g/mg. min)	q _{e,cal} (mg/g)	R ²
Clay-CTAB	5	8.33	0.061	6.29	0.971	0.03868	8.474	0.999
	25	30.31	0.007	7.07	0.797	0.00471	30.303	0.998
	50	22.13	0.007	7.102	0.797	0.0074	16.66	0.997
	100	29.18	0.005	17.37	0.881	0.0013	23.809	0.997

Table 3.
Kinetic parameters for the adsorption of Cu(II) onto adsorbents at different initial concentrations.

Adsorbent	C ₀ (mg/L)	q _{e, exp} (mg/g)	Pseudo-first order			Pseudo-second order		
			k ₁ (min ⁻¹)	q _{e, cal} (mg/g)	R ²	k ₂ (g/mg. min)	q _{e, cal} (mg/g)	R ²
Raw Clay	5	0.128	6.44*10 ⁻⁴	1.048	0.575	3.322	0.130	0.999
	20	0.202	5.25*10 ⁻⁴	1.243	0.575	2.888	0.205	0.999
	35	0.425	2.9*10 ⁻⁴	1.354	0.877	0.354	0.464	0.992
Purified Clay	5	2.003	0.230	10.125	0.641	0.037	2.213	0.996
	20	2.2075	0.027	11.015	0.606	0.041	2.49	0.996
	35	2.921	0.039	36.332	0.613	0.024	3.359	0.992
Activated Clay	5	2.710	0.042	71.186	0.687	0.011	3.745	0.912
	20	2.705	0.045	61.446	0.685	0.014	3.773	0.952
	35	6.1002	0.101	2.741*10 ⁴	0.719	0.004	8.849	0.913
Pillared Clay	5	1.123	0.015	4.027	0.734	0.059	1.307	0.995
	20	2.210	0.033	27.542	0.755	0.018	2.808	0.970
	35	3.825	0.773	2.2*10 ³	0.824	0.004	9.208	0.659
Clay-CTAB	5	5	0.078	2*10 ³	0.787	0.008	6.45	0.996
	20	8.231	0.146	1*10 ⁷	0.926	0.002	15.339	0.982
	35	15.206	0.249	2.5*10 ¹²	0.926	0.001	22.029	0.987

Table 4.
Kinetic parameters for the adsorption of MO onto adsorbents at different initial concentrations.

The Langmuir isotherm theory assumes that the adsorption is single-layer and takes place at homogenous sites specific to the adsorbent. The equation of Langmuir isotherm model is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \tag{6}$$

and the Freundlich isotherm assumes that the adsorption is multi-layer and that the surface of the adsorbent heterogeneous [52]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

Where K_L Langmuir isotherm constant (L/mg), n is the degree of non-linearity and K_F is Freundlich isotherm constant (mg^{1-1/n} L^{1/n}g).

	Temperature (K)	Langmuir			Freundlich		
		q _{max} (mg/g)	K _L (L/mg)	R ²	K _F (mg ^{-11/n} /gL ^{1/n})	1/n	R ²
Copper							
Kaolinite	303	3.099	8.338	0.918	154.88	0.203	0.957
	313	5.366	5.22	0.962	275.42	0.182	0.988
	323	31.86	1.002	0.954	293.764	0.214	0.985
Purified Kaolinite	303	10.64	2.479	0.992	279.25	0.198	0.979
	313	287.35	0.094	0.998	411.14	0.184	0.934
	323	55.55	0.497	0.998	542	0.188	0.872
Activated Kaolinite	303	0.069	18.184	0.984	0.0064	0.53	0.848
	313	0.117	18.512	0.677	0.071	0.406	0.471
	323	0.184	10.725	0.759	0.238	0.284	0.223
Pillared Kaolinite	303	5.714	4.023	0.9124	326.58	0.139	0.776
	313	7.535	3.359	0.937	311.17	0.18	0.704
	323	12.73	2.366	0.979	505.824	0.172	0.922
Kaolinite-CTAB	303	11.83	0.25	0.9725	475.33	0.175	0.83
	313	18.94	1.712	0.987	734.51	0.157	0.885
	323	32.53	1.142	0.996	855.066	0.185	0.899
Methyl Orange							
Kaolinite	303	0.0229	28.411	0.0551	0.049	0.548	0.738
	313	0.0023	44.934	0.821	8.85*10 ⁻⁴	1.633	0.998
	323	0.00051	33.140	0.652	5.80*10 ⁻⁵	2.363	0.999
Purified Kaolinite	303	0.794	5.452	0.943	1.322	0.297	0.965
	313	1.166	5.074	0.993	1.364	0.404	0.912
	323	1.112	5.483	0.957	1.729	0.320	0.987
Activated Kaolinite	303	2.293	2.760	0.988	2.013	0.336	0.841
	313	1.007	6.129	0.948	1.116	0.478	0.818
	323	0.364	21.803	0.986	0.477	0.680	0.973
Pillared Kaolinite	303	0.264	20.148	0.440	0.496	0.538	0.874
	313	0.550	6.993	0.652	1.485	0.194	0.101
	323	2.364	1.726	0.970	2.773	0.084	0.584
Kaolinite-CTAB	303	3.144	3.495	0.720	5.636	0.125	0.297
	313	4.016	3.188	0.773	6.295	0.140	0.48
	323	6.756	2.766	0.697	10.280	0.083	0.535

Table 5.
Adsorption isotherms of copper onto kaolinite clay.

The data show that Langmuir model is more suitable to describe the adsorption reaction of copper and methyl orange on modified kaolinite and it is better fitted to Freundlich isotherm model onto natural clay with experimental data with higher R² values. So it's surface mono-layer adsorption and the adsorption sites are homogeneous.

	ΔH° (KJ.mol ⁻¹)	ΔS° (KJ.mol ⁻¹)	ΔG° (KJ.mol ⁻¹)		
			303 K	313 K	323 K
Copper Cu (II)					
Raw Clay	-4.164	0.015	-5.681	-5.695	-8.322
Purified Clay	-0.068	0.0032	-6.942	-8.841	-7.4
Activated Clay	—	—	—	—	—
Pillared Clay	-2.801	0.012	-6.833	-7.901	-8.788
Clay-CTAB	-2.976	0.013	-7.263	-8.399	-9.34
Methyl Orange					
Raw Clay	6454.238	49.531	-8553.66	-9048.97	2769285
Purified Clay	162.425	14.139	-4121.69	-4263.08	1331469
Activated Clay	82099.03	278.510	-2289.5	-5074.6	821607.5
Pillared Clay	-97702.93	-297.451	-7575.28	-4600.77	2349112
Clay-CTAB	-9293.706	-20.406	.31110.69	-2906.63	995458.5

Table 6.
Thermodynamics parameters at different temperatures.

3.5 The thermodynamic studies

The thermodynamic parameters ΔG° , ΔH° and ΔS° are computed from the plots on $\ln K_L$ vs. $1/T$, and are better described by following Equations [53]:

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

Where, **R** is The gas constant 8.314×10^3 (KJ/mol. K), **T** is temperature (K) and **K_L** known as the distribution coefficient of the adsorbate, is equal to C_e/q_e (L/g) (**Table 6**).

4. Conclusion

The thermodynamics and kinetic study of the removal of copper (II) and methyl orange from aqueous solution using natural clay and its composites has been investigated in this work. The adsorption process showed that purified and CTAB clays were effective in the uptake of copper and methyl orange from aqueous solutions until 34.12 mg/g and 15.78 mg/g, respectively. Whereas, activated and pillared kaolinite are not efficient adsorbent for the removal of Cu(II) and methyl orange, respectively; with amount of adsorption less than 2 mg/g. The amounts of Cu²⁺ and MO were found to vary with pH and the dose of adsorbent. The adsorption data conformed to Langmuir model, and its fitted to pseudo first order and pseudo second order. However, pseudo second order best described for the adsorption process. The determined negative free energy changes ΔG° and positive entropy ΔS° indicated the feasibility and spontaneous nature of the adsorption process. The negative value of enthalpy change ΔH° suggests that the adsorption process is exothermic, while, the interactions are entothermic accompanied by increase in entropy and Gibbs energy.

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