

ADSORPTION KINETIC STUDY OF CUPRIC ION ON ORGANO MONTMORILLONITE

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Abstract: Commercially available montmorillonite K10 (Mt) was organically modified by grafting with tetramethylammonium (TMA) and tetrapropylammonium (TPA) cations to obtain potential adsorbents for adsorption metal cations. TMA-Mt and TPA-Mt showed FT-IR bands at 1489 cm^{-1} and 1389 cm^{-1} attributed to C–N vibrations in tertiary amines and σ_{as} (C–H) bending vibrations due to CH_3 groups of the $(\text{CH}_3)_4\text{N}^+$ cation, indicating intercalation of Mt with TMA and TPA. The kinetics of Cu(II) adsorption on these clay hybrids could be appropriately described by second order kinetics with the second order rate coefficients found to be 1.06×10^{-2} , 9.00×10^{-3} and $1.31 \times 10^{-2}\text{ L mg}^{-1}\text{ min}^{-1}$ respectively for Mt, TMA-Mt and TPA-Mt. Thus, this work has significantly highlighted the adsorption studies of Cu(II) ions on the montmorillonite and its derivatives.

Keywords: Cu(II) adsorption kinetics; TMA-montmorillonite; TPA-montmorillonite

1. Introduction:

Water pollution due to the presence of toxic heavy metal cations has been a major cause of concern for the environmental chemist. The compounds of heavy metals have considerable solubility in an aquatic environment and they are easily absorbed by living organisms through water consumption. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body and if the concentration of metals crosses the permissible limit, they can cause serious health disorders [1-2]. Copperedus is a condition referring to the consequences of an excess of copper in the body and can occur from eating acid foods cooked in uncoated copper cookware or from exposure to excess copper in drinking water or other environmental sources. Acute symptoms of copper poisoning include vomiting, hematemesis (vomiting of blood), hypotension (low blood pressure), melina (black "tarry" faeces), coma, jaundice (yellowish pigmentation of the skin), and gastrointestinal distress. Chronic exposure to copper can damage the liver and kidneys [3]. Therefore, it is necessary to treat metal contaminated wastewater for removal of Cu(II) and other metal cations before discharging to the environment.

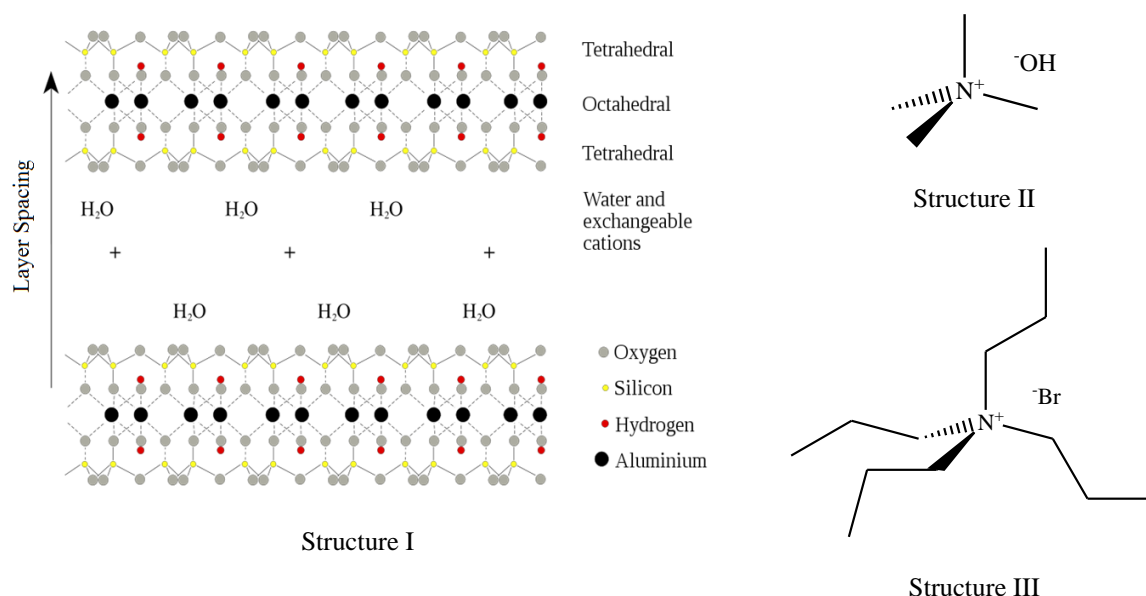
Clays, due to their natural abundance and appropriate physical and chemical properties have found wide use as adsorbents for various pollutants. Presence of inorganic cations in the basal planes of montmorillonite makes it hydrophilic in nature [4]. However, cation-exchange reactions have been traditionally exploited as an effective method to replace these inorganic ions with organic cationic surfactant molecules which intercalate into the clay gallery, resulting in expansion of the interlayer spacing and leading to an increase in the basal spacing. Clays as such and their modified forms have found use as rheological additives, thickeners in coating products, glues, platisols, drilling fluids, cosmetics [5] and in wastewater treatment [6].

The present work focused on the effects of introduction of organic ammonium cations into montmorillonite K10 on the change in adsorption capacity and kinetics of adsorption for removal of Cu(II) from water system.

2. Materials and Method:

Materials :

Montmorillonite K10 (Mt, Structure I), tetramethylammonium hydroxide (TMA-OH, Structure II) and tetrapropylammonium bromide (TPA-Br, Structure III) were obtained from HiMedia Laboratories Pvt, Ltd., Mumbai and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was obtained from Merck Chemicals U.S.



Methods :

Preparation of TMA- and TPA-montmorillonite : K10-montmorillonite (5 g) was first dispersed in 400 mL of distilled water with a magnetic stirrer (~ 600 rpm) for 2 hour at 60 °C in a two-necked round bottom flask fitted with a reflux condenser. 5.0 g of the tetra-alkyl ammonium salt (TMA-OH and TPA-Br) was slowly added to the clay suspension at 60°C with constant stirring. The mixture was stirred for 6 h at 60 °C. The products were thoroughly washed, dried in an air-oven, ground in an agate mortar and stored as adsorbents.

Stock solution of Cupric ion : A stock solution containing 1000 mg Cu(II) /L was prepared by dissolving 3.93 g of CuSO₄.5H₂O in 1 L of deionised water. All other solutions were prepared from this solution by appropriate dilution with de-ionised water.

Characterization techniques : The Fourier Transform Infrared (FT-IR) spectra were recorded with Shimadzu FT-IR 3000 spectrophotometer equipped with DTGS/KBr detector. The KBr pressed disc technique (1.0 mg of sample and 200 mg of KBr) was used. Cu(II) concentration after adsorption was determined with Perkin Elmer AAnalyst 200 Atomic Absorption Spectrometer.

Adsorption Studies : Adsorption of cupric ion was carried out by batch method in 50 mL Erlenmeyer flasks with Mt, TMA-Mt and TPA-Mt loading of 1.5 g/L and 10 mL of Cu(II) solutions (20 mg/L). The Erlenmeyer flasks were subsequently capped and agitated in a thermostatic bath shaker at 200 rpm at 303 K for different time intervals. After adsorption for a fixed time interval, the mixture was centrifuged at 6000 rpm (Remi Research Centrifuge) for 20 min and the supernatant liquid was extracted and kept in an air tight plastic bottle for analysis of Cu(II) by AAS. The amount of Cu(II) adsorbed per unit mass of the adsorbent after time interval, *t*, was obtained from the relation:

$$q_t = (C_0 - C_t) V / W \tag{1}$$

where, *C*₀ and *C*_{*t*} (mg/L) are the concentrations of Cu(II) at *t* = 0 and *t* = *t*, respectively, *V* is the volume of the solution (ml) taken for the batch adsorption and *W* is the dry adsorbent loading (g/L).

3. Results and discussion:

Fourier Transform Infrared spectroscopy

The FT-IR spectra of the synthesized organo-clays, TMA-Mt and TPA-Mt, are shown in figure 1, along with that of the unmodified clay, Mt.

The infrared spectra of montmorillonite showed seven bands. The bands at 2372 cm^{-1} and 3449 cm^{-1} could be attributed to CO_2 stretching vibration and H–O–H stretching vibration [8-9] respectively. Other peaks, characteristics of the clay, appeared at 1057 cm^{-1} (Si-O stretching) [10, 11] and at 1636 cm^{-1} (interlayer water deformation vibrations). The band at 802 cm^{-1} could be assigned to OH deformation frequency of Al-(O-H)-Al structural moiety [12]. Three other bands at 694 cm^{-1} , 525 cm^{-1} and 471 cm^{-1} were due to coupled Al-O and Si-O, out-of-plane, Si–O–Al (octahedral Al) and Si–O–Si bending vibrations respectively [17]. The principal IR bands and their assignments are given in Table 1.

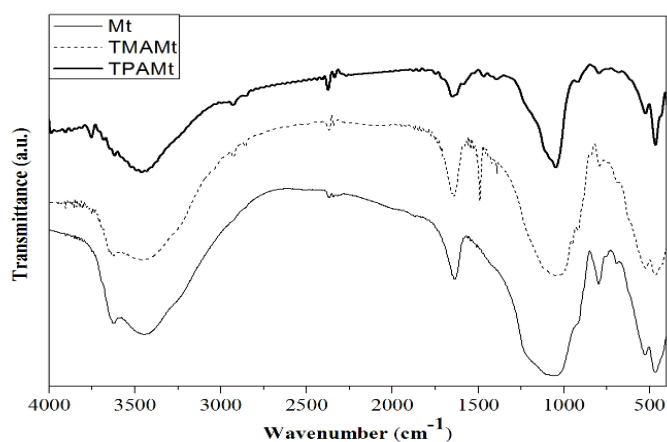


Figure 1: FTIR spectra of Mt, TMA-Mt and TPA-Mt.

The IR spectra of the modified clays, TMA-Mt and TPA-Mt, showed a pattern similar to that of Mt with some modified peaks. TMA-Mt had two additional bands at 1489 cm^{-1} and 1389 cm^{-1} which could be attributed to the C–N vibrations in tertiary amines [9] and σ_{as} (C–H) bending of CH_3 groups of the $(\text{CH}_3)_4\text{N}^+$ cation [13-15]. In case of TPA-Mt, these two bands appeared at 1393 cm^{-1} and at 1470 cm^{-1} . Two other bands appeared at 2855 cm^{-1} and 2924 cm^{-1} in TMA-Mt and these were due to symmetric and anti-symmetric stretching of CH_2 [9, 16-17]. These bands were absent in the parent clay, Mt. TPA-Mt also had the same bands due to symmetric and antisymmetric stretching of CH_2 .

Table 1. FTIR bands and their assignment for Mt, TMA-Mt and TPA-Mt.

Mode of vibration	$1/\lambda$ (cm^{-1})		
	Mt	TMA-Mt	TPA-Mt
Si–O–Si bending vibrations	471	463	467
Si–O–Al (octahedral Al)	525	520	525
Coupled Al-O and Si-O, out-of-plane	694	690	679
Si-O stretching of quartz and silica	799	794	795
Al-Al-OH deformation	914	914	922
Si-O stretching	1057	1045	1045
(C–H) bending of both CH_2 and CH_3 groups	-	1389	1393
Bending vibration of C-N in tertiary amine group	-	1489	1470
Interlayer H_2O deformation vibration of water	1636	1639	1651
CO_2 stretching vibration	2372	2369	2372
Symmetric CH_2 (ν_{as}) stretching	-	2855	2855
Antisymmetric CH_2 (ν_{as}) stretching	-	2924	2924
HOH stretching of water	3449	3449	3460

Adsorption Kinetics study of Cu(II) with Mt, TMA-Mt and TPA-Mt

Equilibrium Adsorption Kinetics

The adsorption kinetics of Cu(II) in aqueous medium was studied at 303 K with the prepared organo-clay using 20 mg L⁻¹ adsorbate solution and 1.5 g L⁻¹ adsorbent loading in 50 ml flasks. The plot of the amount adsorbed per unit mass against time is shown in figure 2.

The organo-clays, particularly, TMA-Mt had better Cu(II) adsorption capacity, q_e (mg/g), in comparison to that of Mt and TPA-Mt. From the experiment it was found that the adsorption equilibrium was attained within about 15 min for each of the cases which reveal the fast interaction of adsorbent (organo-clay) and the adsorbate ions present in aqueous medium. TMA-OH brought from HiMedia, Mumbai, was highly hygroscopic in nature due to which the material prepared TMA-Mt may attain higher hydrophilic nature than to Mt (unmodified clay) and hence showed more q_e value compared to the other two. Again, the modified clay, TPA-Mt showed comparatively good q_e value than to the unmodified one but it showed lower q_e value compared to the modified clay TMA-Mt. Since the organo-clays are known to become more hydrophobic with increase in the length of the alkyl chain [21], and therefore TPA-Mt had a lower adsorption capacity for Cu(II) than TMA-Mt.

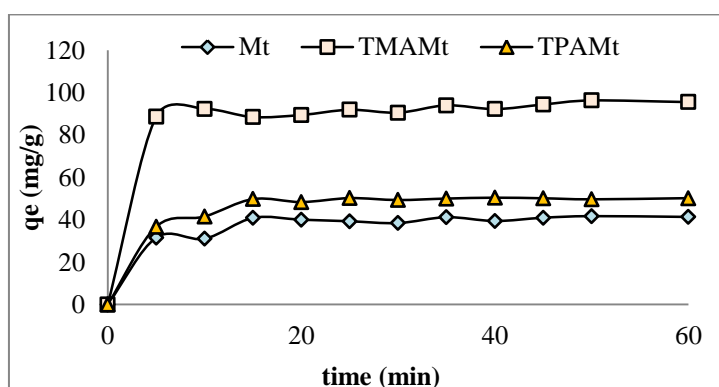


Figure 2: Variation in the amount of Cu(II) adsorbed on unit mass of Mt, TMA-Mt and TPA-Mt with time

Pseudo First Order Kinetics

Lagergren's pseudo first-order equation for adsorption on a solid at the liquid-solid interface [22] is –

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where, q_e and q_t (mg g⁻¹) are the adsorption capacities at equilibrium and at time t (min), respectively. The first order rate coefficient, k_1 (min⁻¹) and q_e were calculated from the slope and the intercept of the plots obtained by plotting $\ln(q_e - q_t)$ versus t (Figure. 3). The validity of the pseudo first order model can be verified by comparing the q_e values obtained from the plots (Figure 3) with the experimental q_e values (Table 2).

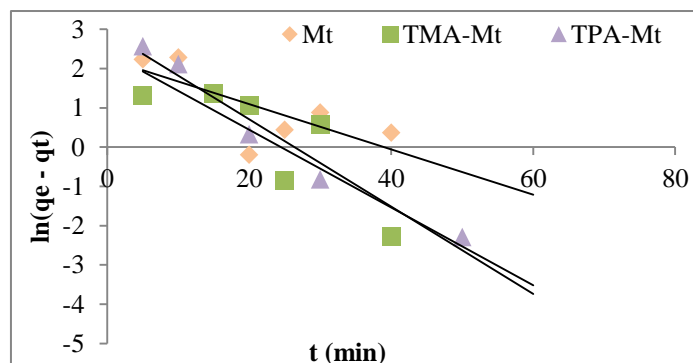


Figure 4: Lagergren's pseudo 1st order kinetic plots for adsorption of Cu(II) on Mt, TMA-Mt and TPA-Mt at 303 K.

Table 3: Values of k_1 and q_e from Lagergren 1st order plots

Clay	k_1 (min ⁻¹)	q_e (plot) (mg/g)	q_e (Expt) (mg/g)	R^2
Mt	5.7×10^{-2}	9.47	40.85	0.52
TMA-Mt	9.9×10^{-2}	11.29	92.34	0.68
TPA-Mt	1.1×10^{-1}	18.76	49.74	0.97

From Table 3, it is observed that the linearity of the pseudo first order plots is not very good (R^2 0.52 to 0.97) and q_e calculated from the plots differ largely from the experimental q_e , suggesting that the first order kinetics is not appropriate to describe adsorption of Cu(II) on montmorillonite or organo-montmorillonite.

Pseudo Second Order Kinetics

The pseudo second-order rate expression, applied for analyzing adsorption kinetics in solutions [23], is based on the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

The second-order adsorption parameters, q_e and k_2 (the rate coefficient) in Eq. (3) could be determined by plotting t/q_t versus t (Fig. 5). The values are shown in Table 4.

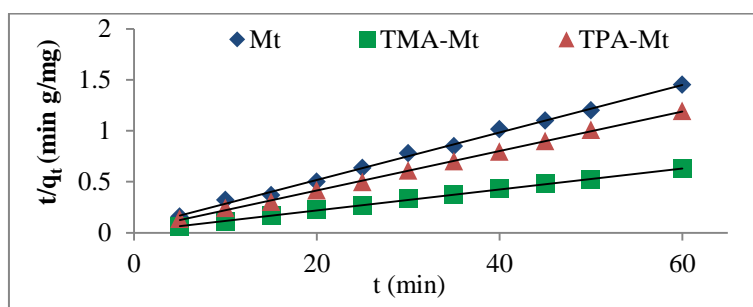


Figure 5: Pseudo second order kinetic plot for adsorption of Cu(II) on Mt, TMA-Mt and TPA-Mt at 303 K

Table 4: Second order adsorption parameters (k_2 and q_e)

Clay	$1/(k_2 q_e^2)$	k_2 (L mg ⁻¹ min ⁻¹)	q_e (plot) (mg/g)	q_e (Expt) (mg/g)	R^2
Mt	0.0513	1.06×10^{-2}	42.86	40.85	0.99
TMA-Mt	0.0118	9.00×10^{-3}	96.81	92.34	0.99
TPA-Mt	0.0286	1.31×10^{-2}	51.71	49.74	0.99

The second order plots have perfect linearity with $R^2 \sim 1$. It is also observed that the values of q_e obtained from the plots and the experiments agree very well (Table 4). Thus, it could be confirmed that the adsorption of Cu(II) by the clay (Mt) and organo- clays (TMA-Mt and TPA-Mt) follows pseudo second order kinetics with a rate coefficient of 1.06×10^{-2} , 9.00×10^{-3} and 1.31×10^{-2} L mg⁻¹ min⁻¹ respectively for Mt, TMA-Mt and TPA-Mt.

Intra-particle Diffusion Kinetics

In order to gain insight into the mechanism and the rate controlling steps that influence the kinetics of adsorption, the experimental results were fitted to Weber's intraparticle diffusion model [24] given by the expression:

$$q_t = k_{id} t^{1/2} + C \tag{6}$$

The diffusion rate coefficient, k_{id} (mg g⁻¹ min^{-1/2}) could be evaluated from the slope of the plot of q_t versus $t^{1/2}$ (Fig. 6). Ideally, if the intra-particle diffusion model is the rate-controlling step in the adsorption mechanism, the plots should have zero intercept ($C = 0$). In other cases, the intercept is related to the boundary layer effect and it is shown that a large intercept indicates surface sorption to be the major process with very little diffusion into the interior layers.

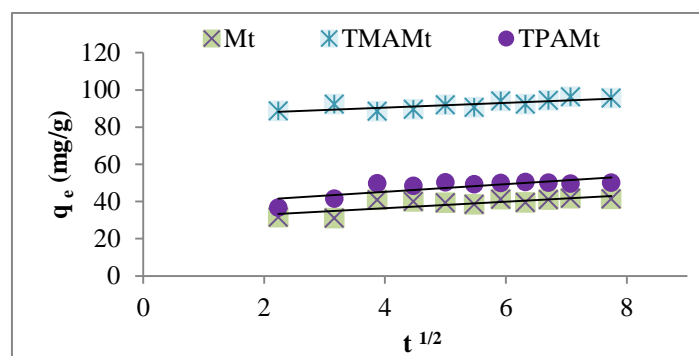


Figure 6: q_t versus $t^{1/2}$ plot for Cu (II) ion on Mt, TMA-Mt and TPA-Mt.

Table 5: Values of intercept and k_{id} calculated from Fig. 6.

Adsorbent	Intercept	k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$)	R^2
Mt	29.51	1.74	0.62
TMA-Mt	85.41	1.28	0.66
TPA-Mt	37.01	2.05	0.61

The calculated intra-particle diffusion coefficient k_{id} values are $1.74 \text{ mg/g min}^{1/2}$, $1.28 \text{ mg/g min}^{1/2}$ and $2.05 \text{ mg/g min}^{1/2}$ for Mt, TMA-Mt and TPA-Mt respectively (table: 5). If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate limiting step. However, the linear plots for each adsorbent did not pass through the origin. This indicates that the intra-particle diffusion was not only the rate controlling step [24] but also there are some other which helps in reaching fast equilibrium kinetics.

4. Conclusions:

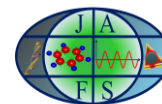
Montmorillonite was successfully modified using TMAH and TPAB cationic surfactants as observed from FTIR characterisation. From the adsorption study of Cu(II) it was found that TMA-Mt have better adsorption capacity than the unmodified montmorillonite, this is may be due to enhanced hydrophilicity with modification as because of hygroscopic nature of TMAH. But TPA-Mt showed lower adsorption capacity towards Cu(II) compared to TMA-Mt, because with the increase of size of the alkyl group in tetraalkylammonium halide, hydrophobicity of the material increases and hence cationic, Cu(II), adsorption on the surfaces of the modified montmorillonite decreases with the increasing size of the alkyl group of tetraalkylammonium halide.

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