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Preparation and use of solvent impregnated clay containing amine for the removal of copper ion

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ABSTRACT

In this study, montmorilloniteK-10 (Mt) clay was used to adsorb a heavy metal ion, copper (Cu^{2+}). This clay was also modified (Mt-TOA) by incorporating amine group of tri-*n*-octylamine (TOA), a tertiary amine. Experiments were performed in batch mode to determine equilibrium and kinetics of copper adsorption. Several parameters like adsorbent dose (0.1–0.6 g), initial copper concentration (20–80 mg/L), temperature (298 Kto 333 K) and time of contact (t, 0 to 120 min) were varied, and their effect on the adsorption capacity of both the adsorbents were determined. Kinetic equilibrium reached after 80 min time of adsorption with 65.73% and 71.96% removal using Mt (0.2 g) and Mt-TOA (0.2 g). The Langmuir and pseudo second order models fitted the equilibrium and kinetic data, respectively. The change in enthalpy and entropy were also estimated (ΔH^o = 16.44 kJ/mol and ΔS^o = –73.23 J/mol/K for Mt; ΔH^o = 9.26 kJ/mol and ΔS^o = –45.92 J/mol/K for Mt-TOA) by using Gibbs' thermodynamic model.

Keywords: Adsorption; Copper; Equilibrium; Kinetics; Montmorillonite; Thermodynamics; Tri-n-octylamine

1. Introduction

Presence of copper (Cu^{2+}) ion in industrial wastewater is an important environmental problem. This metal ion is hazardous and non-biodegradable by its nature. An increase of Cu^{2+} ion concentration in the aqueous media gives harmful effect to human life, plants, animals and aquatic life [1–3]. WHO proposed a limit of this ion in drinking water to be 2 $mg{\cdot}L^{-1}$ [4]. Therefore, improvement of new types of adsorbents is catching attention day by day to treat wastewater containing heavy metals. There were many studies in the literature on the adsorption of Cu^{2+} ion from wastewater with natural or modified or composite adsorbents [5–8].

Montmorillonite clay is widely used. It has larger specific surface area, better swelling capacity, strong adsorption capacities, large cation exchange capacity (CEC), high platelet aspect ratio, and easy surface modification ability. The clay is hydrophilic in nature because of the presence of inorganic cations (Na^+, K^+ or Ca^{+2}) on its basal planar surface which makes this clay inefficient for the adsorption of aliphatic and relatively hydrophobic compounds [9]. However, natural montmorillonite can be impregnated with organic ternary/quaternary amines which replace the exchangeable cation present in it to possess hydrophobic properties. Such modifications provide with the materials having bigger basal spacing of the layers, and lesser surface energy which can be used for the treatment of wastewater containing organic compounds. The modified compound is termed as organo-clay [10]. The incorporation of amine brings changes in the surface properties of the clay which finds its applications in a wider area. The insertion of a molecule (or ion) into montmorillonite provides with layered structures in between the stacks of the organo-clay [11]. It finds application as performance-enhancing agent properties, as a nano-scale additive in plastics to produce polymer

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nanocomposites [11], and also as nano-filler in making eco-friendly polymer clay nanocomposite. Initially, improved version of montmorillonite were studied fundamentally, and applied in the area of organic-inorganic hybrids, composites and nano-scale composites [10]. Now a days, this type of clays are used for the treatment of wastewater containing heavy metals [12–14].

The use of modified clays as low cost adsorbents has the potential to treat industrial wastewater containing heavy metals. The adsorption of heavy metal ionson the surface of modified montmorillonite will be primarily by ion exchange where Cu^{2+} ions will react and gets fixed. There are two types ofcationsreside on the surface of the modified clay which exchange with metal ion: one that is naturally present cation (like Na, K, Mg or Ca), and second is the H^+ ion that is incorporated due to the impregnation of amine (tri-n-octylamine, TOA). Initially, TOA will ionize in the acid medium, and then the cation (K^+ ion) present in montmorillonite (Mt) clay exchanges Cl^- ion to form the modified clay. This may be used to remove heavy metals (Cu^{2+}, Zn^{2+}, Cr^{6+} etc.) as shown in the following equations.

***Modification of clay* [13]**

$$\mathrm{N(C_8}H_{17})_3 + HCl \rightarrow \mathrm{N(C_8}H_{17})_3 \cdot HCl \rightarrow (\mathrm{C_8}H_{17})_3 NH^+Cl^- \quad (1)$$

$$\text{Mt-K}^+ + (\mathrm{C_8H_{17}})_3\mathrm{NH}^+Cl^- \rightarrow \mathrm{Mt} - NH(\mathrm{C_8}H_{17})_3 + \mathrm{KCl} \quad (2)$$

Interaction of Cu^{2+} with Mt-TOA

$$2Mt - NH(C_8H_{17})_3 + Cu^{2+} \rightarrow Mt - N(C_8H_{17})_3 \text{ - } Cu + 2H^+ \quad (3)$$

***Interaction of Cu^{2+} with Mt* [15]**

$$nCu^{2+} + 2K^+ \text{ - } Mt \rightarrow 2K^+ + nCu^{2+} \text{ - } Mt \quad (4)$$

where n: exchangeable cation valence

In the present work, low cost clay, montmorillonite was used to remove Cu^{2+} ion from the wastewater stream generated from industrial effluents. The natural montmorillonite was also modified by using an amine based solvent, tri-*n*-octylamine (TOA). The parameters such as Cu^{2+} ion concentration, amount of montmorillonite, temperature, and contact time that influence the adsorption capacity of the adsorbent are studied. Essential adsorption isotherm models such as Langmuir, Freundlich, Temkin, Sips and Toth were applied to explain the interaction of Cu^{2+} ion with both adsorbents at equilibrium. Also, the experimental kinetic data were validated using pseudo-first order (PFO), pseudo-second order (PSO), and intra-particle diffusion (IPD)models.

2. Materials & procedure

2.1. Materials

Adsorption of Cu^{2+} was studied using Montmorillonite-K10 (a very soft phyllosilicate group of minerals that typically form microscopic crystals) which was obtained from Sigma Aldrich. It has a cation exchange capacity (CEC)of 30–40 meq/100g as provided by the supplier. Tri-n-octylamine (TOA) was the product of Tokyo Chemical Industry Co., Ltd. Japan, which had a purity of about 98% and was procured from Sigma Aldrich. Copper sulphate solution was made by dissolving $CuSO_4{\cdot}5H_2O$ in distilled water. Hexane, hydrochloric acid, methanol, ammonium chloride and ammonia were used from the laboratory. Eriochrome Black T with molecular formula $C_{20}H_{12}N_3NaO_7S$ and hydroxylamine hydrochloride ($HO{\cdot}NH_3Cl$) were used for preparation of EBT indicator. Ethylene diaminetetra-acetic acid (EDTA) was used as received from the laboratory. Deionized water obtained from Millipore Milli-Q water system was used throughout the work.

2.2. Preparation of organoclay

TOA-impregnated clay was prepared by the following procedure. A dispersion of 10 g of clay in 200 mL of distilled water at room temperature was prepared with the help of a magnetic stirrer kept for 7 h. 100 mL of hexane solution containing 5.2 mL TOA, 0.4 mL HCl and 94.4 mL hexane was mixed with the clay solution by using magnetic stirrer for 3 h. The final solution thus obtained had two phases: one is the clear upper organic phase, and second is the turbid bottom mineral phase. After 13 h of sufficient mixing, the bottom phase became translucent, and the organic phase became opaque. This organic phase was collected and kept inside a hot air oven at 70°C to vaporize hexane which turned the organic phase into a sticky solid precipitate. This precipitated organoclay was filtered and dispersed in the warm water maintained at 80°C for 1 h, and then washed three times so that there should not be any presence of chlorides. This is now dried at 80°C for 6 h, and finally grounded manually [10] to get the modified version of the clay.

2.3. Experimental study

In the equilibrium experiments, 20 to 80 ppm of copper solution of 20 mL was placed in 250 mL of conical flask along with 0.4 g of Mt or 0.3 g of Mt-TOA in a shaker incubator at 313 K. The adsorbent dosage study (0.1–0.6 g) was done using 100 ppm Cu^{2+} solution and at 313 K. The samples were equilibriated for 2 h in the shaker incubator. To analyze the effect of temperature, study was performed at 298 K, 313 K, 323 K, and 333 K with 100 ppm Cu^{2+} solution, and 0.4 g of Mt or 0.3 g of Mt-TOA. To determine kinetics of adsorption, 100 ppm Cu^{2+} solution with 0.2 g of Mt or 0.2 g Mt-TOA was taken in 250 mL of conical flasks at 313 K. At regular time interval, sample solution was collected to determine the concentration of Cu^{2+} in the aqueous phase. Cu^{2+} concentration was determined by using a calibration curve obtained by titrating variable concentrations of $CuSO_4$ solutions with 0.1 M EDTA, and EBT buffer solution as an indicator.

The equilibrium and kinetic data were analyzed by calculating adsorption capacity and % removal as given by Eqs. (5) and (6), respectively.

$$q_e = \left(\frac{C_0 - C_e}{w}\right) \times V \quad (5$$

$$\%\text{Removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (6)$$

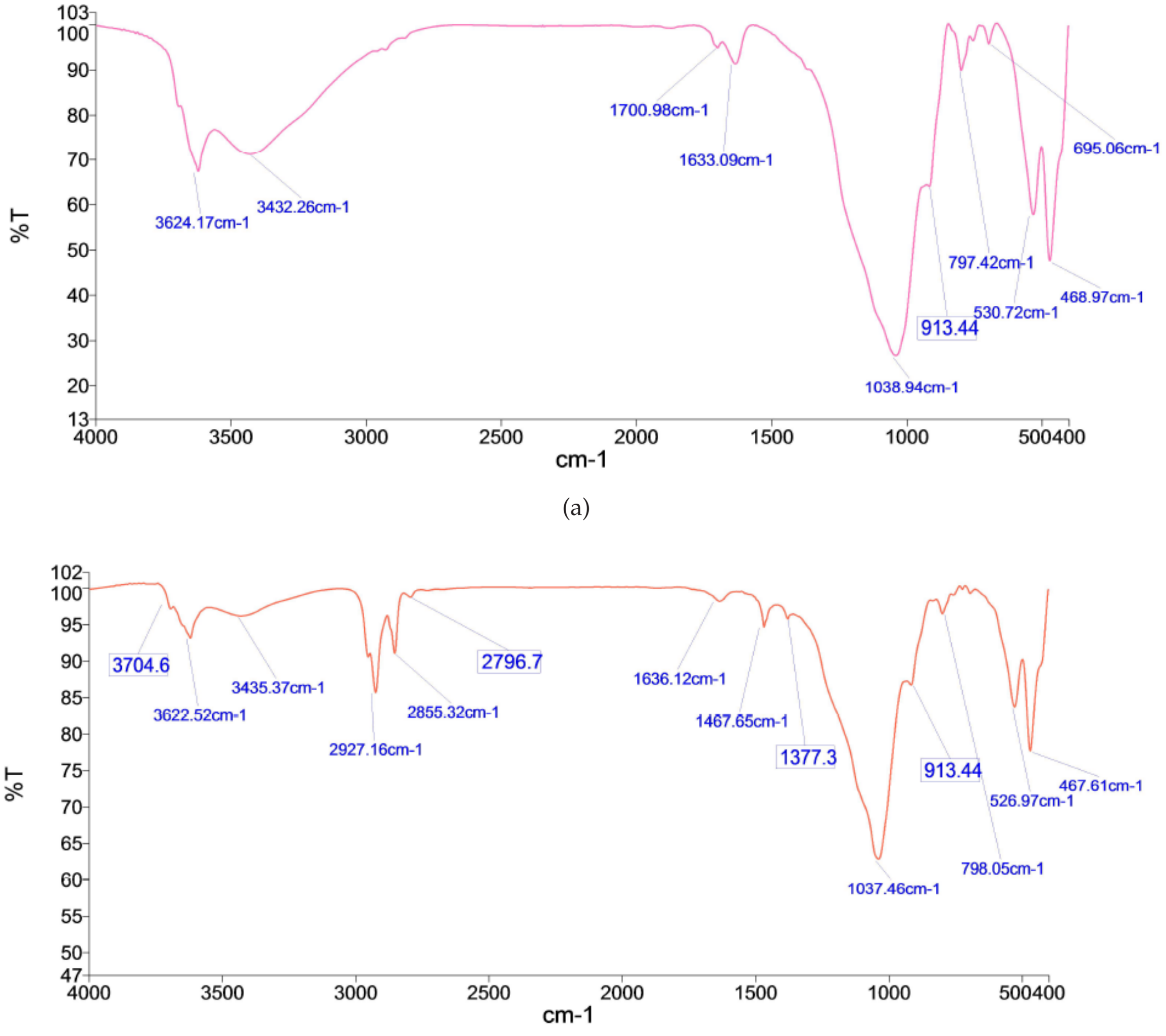
where C_o = initial metal ion concentration (mg/L); C_e = metal ion concentration at equilibrium (mg/L); V = volume of metal ion solution (mL); and w = mass of adsorbent (g).

3. Results and discussions

Treatment of wastewater containing Cu^{2+} ion was carried out by using Montmorillonite K-10 and amine impregnated Montmorillonite K-10. Experiments were carried out by changing parameters like contact time, adsorbent dosage, initial concentration of Cu^{2+}, and experimental temperature, and their effect on the adsorption capacity of both the adsorbents were compared and presented.

3.1. Characterization (FTIR)

In Fig. 1, at a wave number equal to 3624.17 cm^{-1} a wide adsorption band of high intensity was obtained which is a characteristic of O–H bond. Then, a wide adsorption band having a single peak was observed corresponding to a wave number of 3432.26 cm^{-1}, indicating the presence of secondary amine. At a wave number of 1700.98 cm^{-1} a moderately weak intensity peak was observed showing the presence of a carbonyl stretch. Another strong intensity peak observed at a wave number equal to 1038.94 cm^{-1}, indicating the presence of C-F bond. Numerous peaks were observed in the fingerprint region (frequency < 1000 cm^{-1}) at a wave number of 913.44, 797.42, 530.72 cm^{-1}, indicating the presence of bend alkanes bond and a chloride, and bromide bond, respectively. Comparison of the two analysis showed that most of the FTIR spectrum is same for both modified and unmodified montmorillonite K-10 with the major difference lying in the region of wave number equal to 2927.16 cm^{-1} to 2796.7 cm^{-1}. This is due to the attachment of C-H bond of tri-*n*-octyl amine onto the montmorillonite K-10. TOA is adsorbed into the silicate layers of montmorillonite K-10.



(a)

(b)

Fig. 1. FTIR of (a) montmorillonite K-10 clay, (b) modified montmorillonite K-10 with TOA.

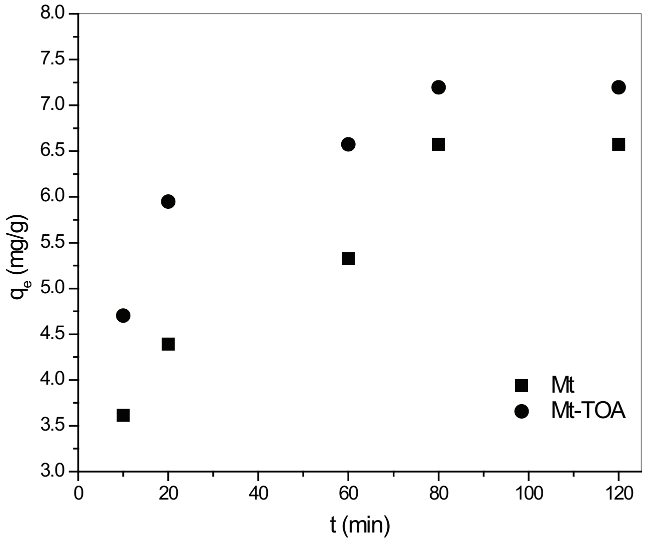


Fig. 2. Kinetic data for the removal of copper ion (100 mg/L) from aqueous solution by using Mt (0.2 g) and Mt-TOA (0.2 g) at 313 K.

3.2. Contact time study

The effect of contact time on the adsorption of Cu^{2+} ion with Mt and Mt-TOA is shown in Fig. 2. At the early stages of adsorption, faster removal of Cu^{2+} ion was observed as large numbers of active sites are available on the surface of adsorbents. As the time passes, unoccupied sites started to fill, and it becomes difficult for the ions to occupy the remaining sites due to force of repulsion by the ions already present on the surface. The % removal of Cu^{2+} became almost constant after 80 min of experimentation, and came out to be 65.73% for Mt and 71.96% for Mt-TOA. Considering a steady state approximation, an equilibrium state was considered after 80 min of time.

3.3. Adsorbent dosage study

The effect of adsorbent dosage on the capacity of Mt and Mt-TOA was analyzed; equilibrium experiment was performed with 100 mg/L of initial Cu^{2+} ion concentration at 313 K. The amount was varied from 0.1 g to 0.6 g for both the adsorbents. The results are shown in the Table 1. The data showed an abrupt decrease in the capacity of adsorption with the increasing amount of adsorbents. The adsorbing capacity decreased from 5.98 mg/g to 2.40 mg/g for Mt, and from 10.34 mg/g to 2.55 mg/g for Mt-TOA. But it was also observed that the amount of Cu^{2+} removed increased as the amount of adsorbents was increased.

As observed from Table 1, the adsorption capacity was maximum with 0.1 g of both Mt and Mt-TOA i.e. 5.98 mg/g and 10.34 mg/g, respectively. The adsorption capacity was found to increase by 73.08% (5.98 mg/g to 10.34 mg/g) with modified montmorillonite K-10. The presence of tri-n-octylamine at the adsorption site in modified montmorillonite K-10 had increased the adsorption capacity. Cu^{2+} ions formed complexes of TOA-Cu^{2+}as they got adsorbed in addition to physical adsorption.

Table 1
Effect of dosage of Mt and Mt-TOA on adsorption of Cu^{2+} ion (100 mg/L) and at 313 K

Adsorbent	Amount of adsorbent (g)	C_e (mg/L)	q_e (mg/g)	% Removal
Mt	0.1	70.20	5.97	29.87
	0.3	37.34	4.17	62.60
	0.4	28.05	3.60	71.95
	0.5	28.05	2.88	71.95
	0.6	28.05	2.40	71.95
Mt-TOA	0.1	48.31	10.34	51.69
	0.3	28.05	4.80	71.95
	0.4	26.49	3.68	73.51
	0.5	26.49	2.94	73.51
	0.6	23.37	2.55	76.63

3.4. Study of different initial concentrations of Cu^{2+}

Aqueous solutions of Cu^{2+} were prepared in the concentration range of 20–80 mg/L for carrying out the equilibrium studies, and to check the influence on the equilibrium behavior of Mt and MT-TOA. The results are presented as isotherms between Cu^{2+} concentration adsorbed by adsorbent (solid phase) and concentration of the remaining solution (aqueous phase) in Fig. 3. As seen from the figure, with an increase in the molecules of Cu^{2+} ion, the amount of Cu^{2+} adsorbed by Mt increased from 0.84 to 1.82 mg/g, and for Mt-TOA it increased from 1.23 to 2.95 mg/g. The removal efficiency has decreased from 84.24% to 45.49% for Mt, and from 92.21% to 55.22% for Mt-TOA at 313 K. This may be due to the coverage of possible sites that are available for adsorption on both types of adsorbents.

3.5. Effect of temperature

The analysis was also done to see how variation in solution temperature will affect the removal capacity of the Mt and Mt-TOA. An inverse trend was observed between the temperature and the removal efficiency of the metal (Fig. 4). The study was performed on four different temperatures 298 K, 313 K, 323 K and 333 K. It was seen that as the temperature was increased, the removal efficiency of the adsorbents decreased from 68.85% at 298 K to 53.27% at 333 K for Mt, and from 70.41% at 298 K to 61.06% at 333 K for Mt-TOA.

3.6. Equilibrium and kinetic modeling

The experimental data were validated using five different isotherm (Langmuir, Freundlich, Temkin, Sips, and Toth), and three different kinetic (pseudo-first order = PFO, pseudo-second order = PSO, and intraparticle diffusion = IPD) models.

Langmuir [16]: $$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \qquad (7)$$

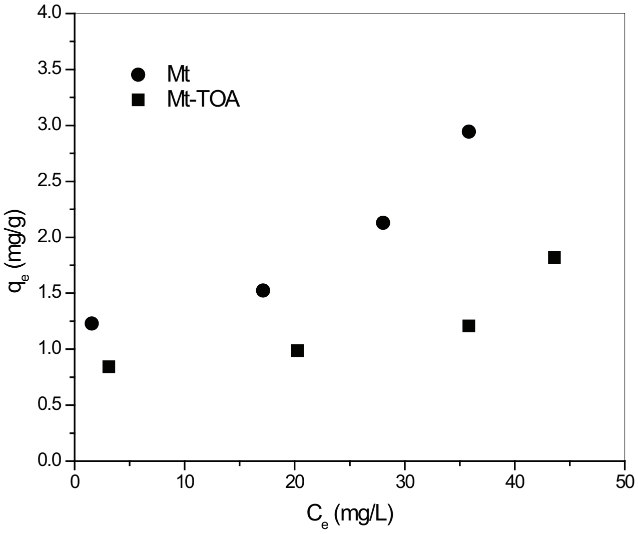


Fig. 3. Equilibrium isotherms for the adsorption of Cu^{2+} ion from water solution by using Mt and Mt-TOA at 313 K.

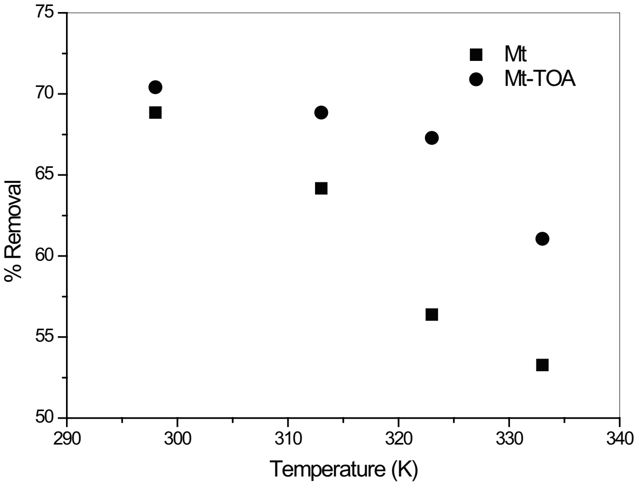


Fig. 4. Effect of solution temperature on the percentage removal of Cu^{2+} using Mt and Mt-TOA.

Freundlich [17]: $$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{8}$$

Temkin [18]: $$q_e = q_m \ln(K_T) + q_m \ln(C_e) \tag{9}$$

Sips [19]: $$q_e = \frac{q_m . K_S . C_e^{m_s}}{(1 + K_S . C_e^{m_s})} \tag{10}$$

Toth [20]: $$q_e = \frac{q_m . C_e}{\left(\frac{1}{K_{To}} + C_e^{m_{To}}\right)^{\frac{1}{m_{To}}}} \tag{11}$$

Pseudo-first order (PFO) [21]: $$\ln(1 - \frac{q_t}{q_m}) = -k_1 t \tag{12}$$

Pseudo-second order (PSO) [22]: $$\frac{t}{q_t} = \frac{1}{k_2 q_m^2} + \frac{1}{q_m} t \tag{13}$$

Intra-particle diffusion (IPD) [23]: $$q_t = k_{in} t^{0.5} + c \tag{14}$$

The linear plots of different models are shown in Figs. 5a–5f. The values of constants for equilibrium and kinetic models for the adsorption of Cu^{2+} are presented in Tables 2 and 3, respectively.

3.7. Comparison of models

The equilibrium data on the adsorption of Cu^{2+} ions using Mt and Mt-TOA as adsorbents were fitted with the Langmuir, Freundlich, Temkin, Sips, and Toth equations. The values of model parameters with statistical analyses are presented in Table 2. It can be seen that comparatively a better fit of equilibrium data were found with the Sips and Toth. Also, the equilibrium parameter, $R_L = \left(\frac{1}{1 + C_0 K_L}\right)$ is also determined to know the feasibility of the isotherm. The removal of Cu^{2+} ion on these adsorbents was found to be favourable (R_L = 0.105 to 0.319 for Mt, and 0.091 to 0.286 for Mt-TOA as per the Langmuir equation). For the kinetic models, the values of rate constants along with other parameters obtained from fitting are listed in Table 3. The pseudo second order yielded a close fit to the kinetics with both the adsorbents. Also, the initial rates of adsorption by the PSO model ($r_0 = k_2 q_m^{\ 2}$) were calculated to be 0.56 $mg \cdot g^{-1} \cdot min^{-1}$ with Mt, and 1.21 $mg \cdot g^{-1} \cdot min^{-1}$ with Mt-TOA. This initial rate of adsorption was improved by a factor of almost 2 when montmorillonite clay was treated with tri-n-octylamine. Therefore, modified form of montmorillonite clay has the potential to remove heavy metals like Cu^{2+} ion from the effluents of wastewater streams. A comparison of prepared montmorillonite modified with tri-n-octylamine is done in terms of the maximum adsorption capacity of different adsorbents as listed in Table 4.

3.8. Adsorption thermodynamics: Gibb's free energy model

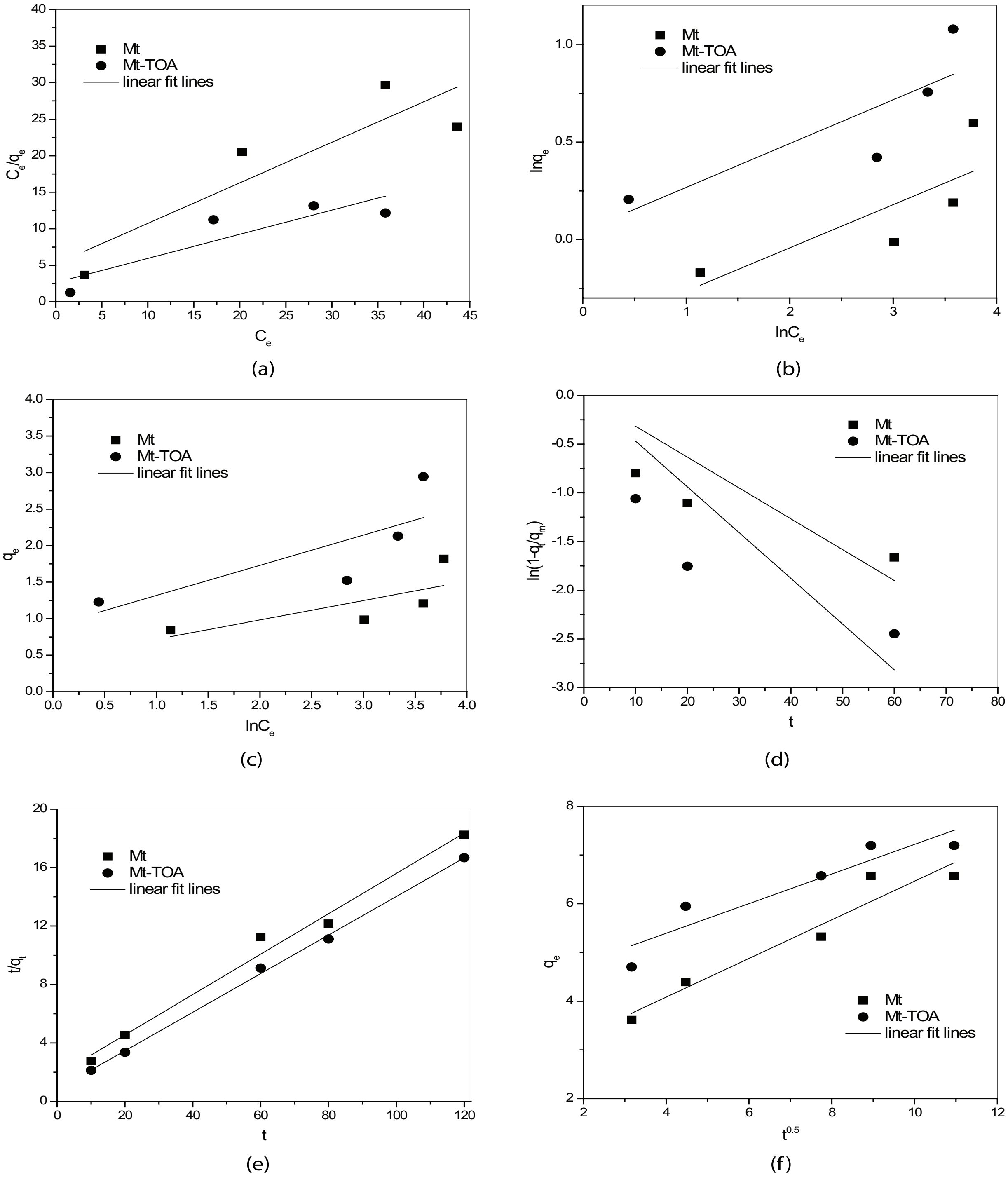
A change in the standard Gibb's free energy (ΔG^o) at different temperatures can be determined by using Eq. (15).

$$\Delta G^o = -RT \ln\left(\frac{q_e}{C_e}\right) \tag{15}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{16}$$

R is the universal gas constant (8.314 J/mol/K), and T is the temperature in K.

To determine the values of standard enthalpy (ΔH°) and entropy (ΔS°), a plot between ΔG° and temperature, T (Fig. 6) was drawn using Eq.(16). Values of ΔH° and ΔS° are shown in Table 5. A positive value of ΔH° indicated that the adsorption process is endothermic in nature, and the positive value of ΔS° showed that there is an increase in the randomness in the adsorption system.



(a) (b)

(c) (d)

(e) (f)

Fig. 5. Linear plot for (a) Langmuir, (b) Freundlich, (c) Temkin, (d) pseudo first order, (e) pseudo second order, and (f) intra particle diffusion models.

4. Conclusion

On the basis of studies performed and the observations made from the results and discussions, the following conclusions are drawn:

- The equilibrium or saturation of adsorbent came around after 80 min for both the adsorbents.
- Percent removal of Cu^{2+} increased with the increase in adsorbent concentration, while removal per unit mass of adsorbent increased with the decrease in adsorbent concentration.
- The maximum removal observed for Mt (0.4 g) and Mt-TOA (0.3 g) are to be 84.42% and 92.21% with 100 mg/L initial concentration of copper solution.

Table 2
Equilibrium isotherms model parameters for the adsorption of Cu^{2+} ion with Mt and Mt-TOA at a temperature of 313 K

Langmuir			Freundlich			Temkin			Sips			Toth		
Parameter	Value		Parameter	Value		Parameter	Value		Parameter	Value		Parameter	Value	
	Mt	Mt-TOA		Mt	Mt-TOA		Mt	Mt-TOA		Mt	Mt-TOA		Mt	Mt-TOA
q_m (mg·g^{-1})	1.8025	3.0281	K_F [(mg·g^{-1}) (L·g^{-1})$^{1/n}$]	0.6145	1.0438	q_m (mg·g^{-1})	0.2655	0.4131	q_m(mg·g^{-1})	91.68	114.60	q_m(mg·g^{-1})	2543.97	6643.9
K_L (L·mg^{-1})	0.1068	0.1250	n	4.5030	4.4460	K_T (L·mg^{-1})	5.4801	8.9289	K_s (L·mg^{-1})	0.0055	0.0074	K_{TO} (–)	2.282	2.198
R^2	0.7931	0.7905	R^2	0.6474	0.7114	R^2	0.5526	0.3521	m_s (–)	0.292	0.306	m_{TO} (–)	0.04262	0.04185
SD	6.2164	3.0915	*SD*	0.2415	0.2521	*SD*	0.3521	0.5768	*R2*	0.967	0.969	*R2*	0.966	0.968

Table 3
Kinetic model parameters for the adsorption of Cu^{2+} ion with Mt and Mt-TOA at 313 K

PFO			PSO			IPD		
Parameter	Value		Parameter	Value		Parameter	Value	
	Mt	Mt-TOA		Mt	Mt-TOA		Mt	Mt-TOA
q_m (mg·g^{-1})	8.57	10.60	q_m (mg·g^{-1})	7.2385	7.5734	k_{in}	0.3967	0.3041
k_1 (min^{-1})	0.0316	0.0469	k_2 (g·g^{-1}·min^{-1})	0.0106	0.0211	c	2.4968	4.1782
R^2	0.8898	0.8871	R^2	0.9870	0.9983	R^2	0.9357	0.8739
SD	0.5044	0.7582	SD	0.8223	0.2767	SD	0.3847	0.4274

Table 4
Adsorption of copper using different adsorbents

Adsorbent	Maximum adsorption capacity (mg·g^{-1})	Ref.
Mt	1.803	Present study
Mt-TOA	3.028	
Activated carbon prepared from grape bagasse	43.47	[24]
Shells of lentil	8.977	[25]
Shells of wheat	9.51	
Shells of rice	9.588	
Garden grass	58.34	[26]
Pristine natural zeolite	14.93	[27]
Polydopamine treated zeolite	28.58	

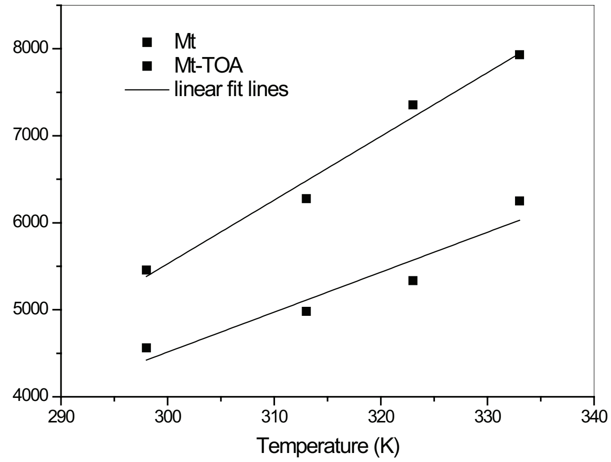


Fig. 6. Plot of ΔG vs. temperature for the adsorption of Cu^{2+} for Mt and Mt-TOA.

- Both the models like Sips and Toth well represented the equilibrium adsorption of Cu^{2+} onto Mt and Mt-TOA.
- The adsorption kinetics of Cu^{2+} onto Mt and Mt-TOAcould be represented by the pseudo second order kinetic model.

Table 5
Thermodynamic parameters for the adsorption of Cu^{2+} for Mt and Mt-TOA

Adsorbent	$-\Delta H^o$ (kJ/mol)	ΔS^o (J/mol/K)
Mt	16.44	–73.23
Mt-TOA	9.26	–45.92

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