



Sorption Properties of Organo Modified Montmorillonite Clay for the Reclamation of Chromium (VI) from Waste Water

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Abstract

The natural Montmorillonite (Mt) clay was modified with three newly synthesized cationic surfactants such as 2-(dodecanoyloxy)-N,N-bis(2-hydroxyethyl)-N-(oxiran-2-ylmethyl)ethane-1-ammonium chloride, 2-hydroxy-N-(2-hydroxyethyl)-N-(oxiran-2-ylmethyl)-N-(2-(tetradecanoyloxy)ethyl)ethane-1-ammonium chloride and 2-hydroxy-N-(2-hydroxyethyl)-N-(oxiran-2-ylmethyl)-N-palmitoyloxyethyl)ethane-1-ammonium chloride to get organo OMT-I, OMT-II and OMT-III respectively. The three modified clays were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Thermo gravimetric Analysis (TGA), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) techniques. The three modified OMTs were utilized to reclaim Cr (VI) from wastewater and batch adsorption studies were conducted with various operational parameters such as initial Cr (VI) concentration, pH, amount of adsorbent dosage and agitation rate. The effect of pH on the adsorption of Cr (VI) indicates that the adsorption was favorable in the pH range of 6. As the amount of adsorbent dosage increases, the efficiency in the removal of Cr (VI) ions increases. Langmuir and Freundlich adsorption isotherm best fitted with the experimental isotherm data. The results show that the modified Mt has a good affinity toward the reclamation of Cr (VI) ion and the degree of the efficacy was in the order of the surfactant modified OMT III > OMT II > OMT I. This can be attributed to the increasing hydrophobic chain length of cationic surfactants.

Keywords Organo modified montmorillonite · Adsorption isotherm · Reclamation · Heavy metal · Chromium (VI)

Nomenclature

Mt	: Montmorillonite Clay
NaOH	: Sodium Hydroxide
HCl	: Hydrochloric acid
FT-IR	: Fourier Transform Infrared Spectroscopy
SEM	: Scanning Electron Microscope
XRD	: X-ray Diffraction
C _o	: Initial concentration of herbicide (mg/L)
C _e	: Concentration of herbicide at equilibrium (mg/L)
q _e	: Amount of herbicide adsorbed at equilibrium (mg/L)
V	: Volume of aqueous solution in liters (L)
M	: Mass of the adsorbent (g)
q	: Amount of metal ions adsorbed per unit mass of adsorbent (mg/g)

q _{max} (q _m)	: Measure of adsorption capacity of adsorbent (mg/g)
b	: Langmuir Constant which is a measure of energy adsorption
R _L	: Dimensionless Separation Factor
1/n	: Adsorption Intensity
R	: Universal Gas Constant (8.314 J/mol/K)
R ²	: Linear Regression Coefficient

1 Introduction

Due to rapid industrialization, enormous quantum of toxic heavy metals has been discharged across the globe to the ground water ecosystem. This creates many implications to aquatic system by causing health hazards, harming the ecology and interferes with the legitimate use of water [1].

Chromium is a unique metal, which often exist as Cr (III) and Cr (VI) oxidation states in the environment. The hexavalent chromium penetrates easily in soil and aqueous medium due to its water-soluble anionic form [2]. Cr (VI) are released in effluents from metal finishing, paint,

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tannery and textile industries which are toxic and harmful to environment [3]. They are carcinogenic, vulnerable to other diseases like skin, ulcer, allergy, rupture of nasal septum and renal failure.

Scientist has proposed many techniques for the removal of aqueous chromium ion from wastewater. This includes reverse osmosis, ultra filtration, ion exchange, chemical precipitation and electrolytic method which were proven to be uneconomical [4]. Adsorption is another technique by which toxic metals can be effectively eliminated from aqueous systems [5]. Various materials have been used as adsorbents and one among them is the clay [6].

Montmorillonite (Mt) is low cost adsorbent which possesses high surface area, good cationic exchange capacity, high chemical stability, high mechanical stability and high adsorption properties with good chemistry of intercalation [6, 7]. Mt is the naturally occurring clay mineral used for the reclamation of dyes and metals from aqueous wastewater that are outlet from industries [8].

Montmorillonite (Mt) clay is hydrophilic due to the presence of inorganic cations in the basal planar surface and makes it less effective for the adsorption process. To increase the basal space and replace the inorganic cations, the cationic surfactants have been introduced into the Mt clay [9, 10]. Initially Mt is converted to Na-Mt and then Na⁺ ions are replaced by cationic surfactants through cation exchange process [11]. These cationic surfactant modified clay will adsorb the Cr (VI) ions by Van der Waal's force of attraction. The cationic surfactant drastically increases the organic content and modifies the adsorption of toxic metals. Increase in the tail group of the cationic surfactant, increases the intercalation between the surfactant and Mt clay [12].

Adsorption of cationic surfactant onto the negatively charged clay mineral includes the cation exchange and hydrophobic bonding. In the low amount of loading, cationic surfactants are retained and form a monolayer. As the amount of the surfactant loading increases, the Van der Waals force of interaction play a role between the hydrocarbon tails of the cationic surfactants forming a bilayer. The head groups of the cationic surfactants can adsorb the negatively charged chromate anion [13].

In this present work, Mt clay has been modified by using a homologous series of three surfactants, characterized by the common instrumentation techniques, and availed for the reclamation of Cr (VI) from wastewater.

2 Experimental Method

2.1 Materials

Three surfactants namely 2-(dodecanoyloxy)-N,N-bis(2-hydroxyethyl)-N-(oxiran-2-ylmethyl)ethane-1-ammonium ch-

loride, 2-hydroxy- N- (2-hydroxyethyl) - N (oxiran-2-ylmethyl)-N-(2-(tetradecanoyloxy) ethyl) ethane-1-ammonium chloride and 2-hydroxy- N- (2-hydroxyethyl)-N-(oxiran-2-ylmethyl)-N- palmitoyloxy)ethyl) ethane-1-ammonium chloride were synthesized in the laboratory [14]. Analar grade Sodium Chloride, Potassium dichromate, Hydrochloric acid and Sodium hydroxide were procured from Merck, India. Merck, India supplied Montmorillonite clay with cationic exchange capacity 62 meq / 100g.

2.2 Synthesis of Organic clay

Modification of Mt clay in organo- Mt involves two steps. They are as follows

2.2.1 Preparation of Na-Mt

A known quantity of Mt clay is mixed with 1.0 N NaCl solution and stirred magnetically for 24 hours at 45 °C. Na - Mt so formed by the cationic exchange process is isolated from the suspension by filtrate ion. The isolated Na-Mt is washed many times to eliminate the residual chloride ions and dried overnight in an oven at 60 °C [15, 16].

2.2.2 Preparation of Organo - Mt

A predefined amount of Na- Mt is admixed with 1.0 Liter of distilled water with the help of a magnetic stirrer for 24 hours at 80 °C. A calculated quantity of the synthesized cationic surfactant 2-(dodecanoyloxy)-N,N bis (2-hydroxyethyl)-N (oxiran-2-ylmethyl) ethane-1-ammonium chloride is mixed with distilled water and this solution is slowly added to the Na-Mt suspension with stirring. Further, it is stirred for 10 hours for the completion of cationic exchange reaction. The organo modified Mt (OMt -I) is then separated from the suspension and dried overnight [17, 18]. Similar procedure is adopted for the preparation of OMt -II and OMt -III

2.3 Characterization Techniques

FT-IR spectra were obtained from Perkin-Elmer spectrometer using pellets prepared by blending KBr-Mt, KBr- NaMt, KBr-OMt-I, KBr-OMt-II and KBr-OMt-III. Availing TGA-Perkin Elmer instrument, the thermal behavior was studied for Mt, OMt-I, OMt-II and OMt -III. X-ray diffraction measurements of Mt and OMts were conducted with a Rigaku D/ max -3 c using nickel- filtered CuK α radiation ($\lambda = 1.54 \text{ \AA}$) and between a scan range of 10° - 80° at ambient temperature. Scanning Electron Microscope was carried out by using TESCAN-VEGA 3SBU Scanning Electron Microscope to visualize the surface morphology and texture of Mt, OMt-I, OMt -II, and OMt-III.

2.4 Batch Adsorption Procedure

1000-ppm stock solution of $K_2Cr_2O_7$ was prepared by using Analar grade $K_2Cr_2O_7$ with double distilled water. The adsorption experiment was carried out at ambient temperature. 0.1 g of the sorbent was added to 20 mL of Cr (VI) solution and agitated for 2 hours at 600 rpm. The supernatant was filtered through Whattmann paper 41. Then the residual concentration of metal ion in the filtrate was determined by Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES) Perkin- Elmer technique. Simultaneously blank samples without the adsorbents were performed and monitored the concentration of the Cr (VI). The amount of Cr (VI) ions adsorbed was calculated from the initial concentration and equilibrium concentration differences [19, 20].

2.4.1 Impact of pH

The role of pH on Cr (VI) ion adsorption was determined by manipulating the pH variations from pH 2 to pH 11. 0.1 g of the adsorbent was added to 20 mL of 100 mg/L of the stock solution and made to agitate at 600 rpm for 2 hours. The pH of the dispersions was manipulated by the slight addition of 0.1 N NaOH and 0.1 N HCl solutions.

2.4.2 Impact of Adsorbent Dosage

The impact of the amount of adsorbent was examined by varying the amount of sorbent (OMt) from 0.2 to 1.2 g by keeping the other operational parameters such as initial concentration, pH, agitation rate, and temperature independently constant.

2.4.3 Impact of Agitation Rate

The impact of agitation rate were ascertained by varying the agitating speed from 20 to 140 rpm for all the OMT's using 20 mL of Cr (VI) ion solution for 3 hours keeping all other parameters constant.

2.4.4 Theory of Adsorption

Adsorption as a function of Cr (VI) ion concentration (ranging from 10 mg/L to 100 mg/L) was investigated by considering the pH, adsorbent dosage, agitation rate, and temperature constant.

Metal Analysis and Adsorption Efficiency

Concentration of metal (Cr (VI)) was measured using Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The amount of metal adsorbed by the adsorbents was computed by using the following equation, [21].

$$\% \text{ (Efficiency)} = C_o - C_e / C_o \times 100 \quad (1)$$

The amount of metal adsorbed at equilibrium (q_e) is calculated using, [22]

$$q_e = (C_o - C_e) V/m \quad (2)$$

Where C_o - Initial concentration of metal (mg/L), C_e - Concentration of metal at equilibrium, q_e - Amount of metal adsorbed at equilibrium, m - Mass of adsorbent (g) and V - Volume of aqueous solution in liters (L).

Adsorption Isotherm

The isotherm model is an essential tool to design the adsorption systems. The two main adsorption isotherm models are Langmuir and Freundlich isotherm. The Langmuir adsorption isotherm model involves the attachment of only one layer of molecules to the surface (it is a monolayer adsorption) with the adsorption sites having identical energies and without interactions between the adsorbed molecules [23, 24]. Langmuir adsorption isotherm equation can be described as,

$$q_e = q_m \cdot K_L \cdot C_e / 1 + K_L C_e \quad (3)$$

and the linearized form of Langmuir equation is, [25].

$$C_e/q_e = C_e/q_m + 1/K_L \cdot q_m \quad (4)$$

Where, C_e is the concentration of the Cr(VI) metal at equilibrium (mg/L); q_e is the amount of Cr(VI) ions adsorbed at equilibrium (mg/g); K_L is the Langmuir isotherm constant related to free energy of adsorption (mg/L), and q_m is the maximum adsorption capacity (mg/g). q_m and K_L are constants.

According to the Langmuir Equation, a dimensionless separation factor which is constant usually denoted by R_L (R_L is also termed as separation factor) is used to predict the shape of the isotherm and the adsorption system is favorable or unfavorable process using the equation [26].

$$R_L = 1/1 + K_L \cdot C_o \quad (5)$$

Where, R_L is a dimensionless separation factor and C_o is the initial concentration of Cr (VI) ion (mg/L).

The R_L values indicate the isotherm types given below,

Values of R_L	Type of adsorption
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The Freundlich isotherm model is an exponential equation, which assumes a non-uniform adsorption, which is multilayer, heterogeneous in nature [27] and can be expressed by the equation mentioned below,

$$q_e = K_F C_e^n \quad (6)$$

The linearised form of equation is,

$$\log q_e = \log K_F + 1/n \log C_e \quad (7)$$

Where, K_F is the Freundlich Constant of relative adsorption capacity of adsorbent and n is the Freundlich indicative of the intensity of adsorption [28].

3 Result and Discussion

3.1 Infrared Spectra

The IR spectrum of Mt shows the bands at 3421 cm^{-1} and 1656 cm^{-1} denoting the stretching vibration of OH group and deformation of water molecules. The absorption band at 1078 cm^{-1} represents the presence of cristobalite indicating the presences of different phases of SiO_2 . The band appearing at 526 cm^{-1} reveals the deformation of Al-O-Si linkages. The spectrum of Na-Mt shows the peak at 1645 cm^{-1} and this may be due to overtone of bending vibrations of H_2O molecule and a sharp peak at 468 cm^{-1} indicating Si-O-Si bending vibrations [29, 30]. The spectra of OMT-I, OMT-II and OMT-III were observed and there were two peaks at 2855 cm^{-1} and 2926 cm^{-1} that may be due to the aliphatic CH_2 stretching and CH_3 stretching [31]. The bands of silicate moieties appeared at 1043 cm^{-1} , 1050 cm^{-1} and 1048 cm^{-1} for OMT-I, OMT-II and OMT-III respectively. (Figure 1)

3.2 Thermal Analysis

The thermo gravimetric analysis of Mt, Na-Mt and three different organo modified clays such as OMT-I, OMT-II, OMT-III were displayed in Fig. 2. The unmodified Mt

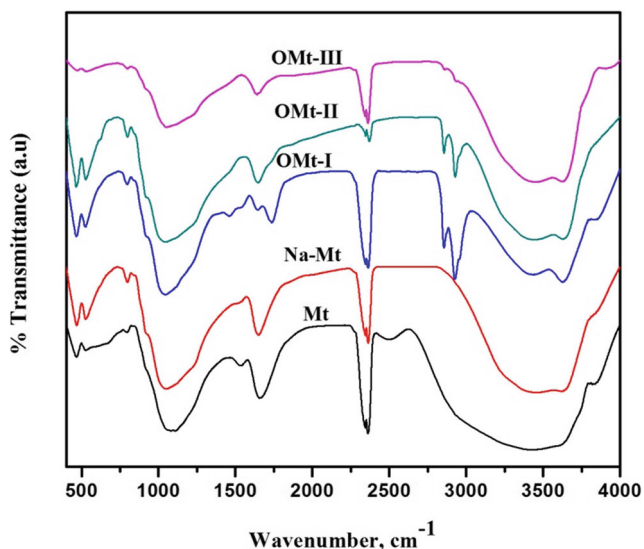


Fig. 1 FT-IR Spectra of Mt, Na-Mt, OMT-I, OMT-II and OMT-III

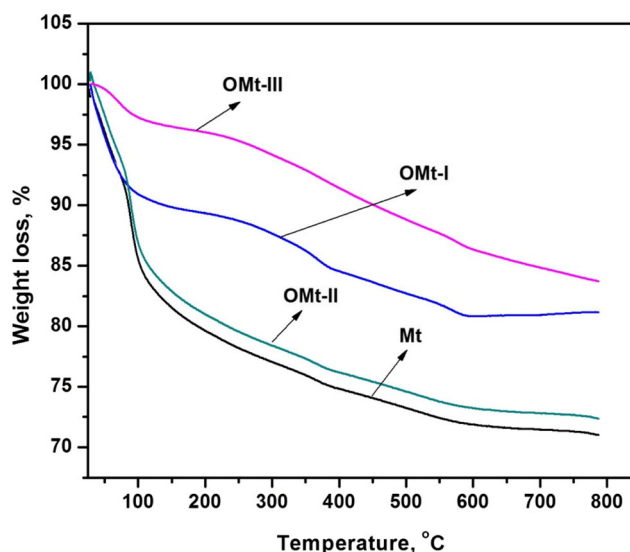


Fig. 2 TGA Curves of Mt, OMT-I, OMT-II and OMT-III

suffered three major weight losses. The first weight loss started from $50\text{--}100 \text{ }^\circ\text{C}$, the second weight loss at $135 \text{ }^\circ\text{C}$ and the third weight loss around $450 \text{ }^\circ\text{C}$. The mass losses can be justified due to the desorption of water molecules, dehydration of the hydrated cations in the interlayer and the dehydroxylation of the Mt clay respectively [32, 33].

Four major weight losses were observed for the OMT-I clay and they are as follows. The first mass loss occurred from $70 \text{ }^\circ\text{C}$, which may be attributed to desorption of water molecule. The second mass loss took place from $150 \text{ }^\circ\text{C}$ to $310 \text{ }^\circ\text{C}$ that may be due to the elimination of water molecules associated with Na^+ ions. The third mass loss found at $410 \text{ }^\circ\text{C}$, which may be due to the removal of surfactant molecule. At $600 \text{ }^\circ\text{C}$, the fourth mass loss was observed and this may be due to the structural hydroxyl group within the clay structure [34]. Similar trend of mass loss were observed for OMT-II and OMT-III.

3.3 X-Ray Diffraction Analysis

The X-ray diffraction analysis of Mt and organo modified Mts are revealed in the Fig. 3. The d-spacing of the clays were found from the characteristic peaks using Bragg's equation. The d-spacing of OMT-I, OMT-II, OMT-III were 2.87, 3.11, and 4.06 nm, respectively. The larger value of OMT than Mt may be due to the interaction of surfactant molecules. The increase in d spacing from OMT-I to OMT-III may be due to the ascending order in chain length of the interacting surfactant molecules [35].

3.4 Scanning Electron Microscopy

The surface texture and the modification of the clays were visualized using Scanning Electron Microscope as

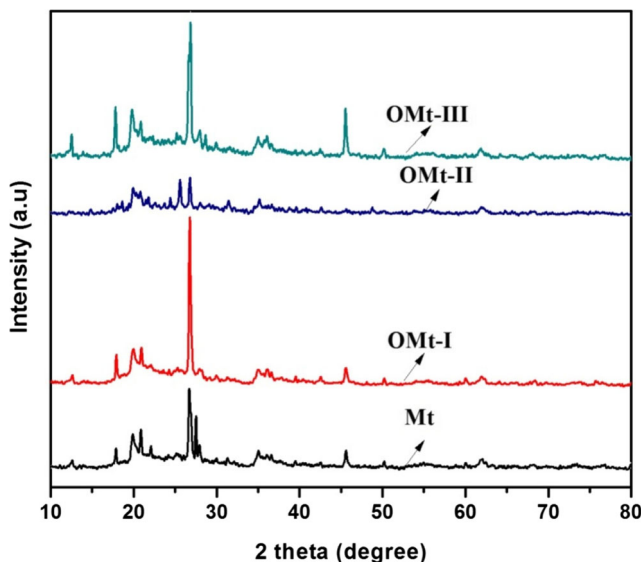


Fig. 3 XRD Spectrum of Mt, OMt-I, OMt-II and OMt-III

shown Fig. 4. Before modification of the clay, the surface is aggregated in the form of plates. Incorporation of the surfactant into the clay changes the surface texture to crown like, which leads to the increase in the specific area and porosity indicating that the surfactant moieties gets intercalated between the layers of the Mt clay. [36].

3.5 Effect of Adsorption Parameters

3.5.1 Influence of initial concentration

0.2 g of dried OMt samples were placed in a series of flasks containing 20 mL of Cr (VI) ions at the desired

Fig. 4 SEM Images of Mt, OMt-I, OMt-II and OMt-III

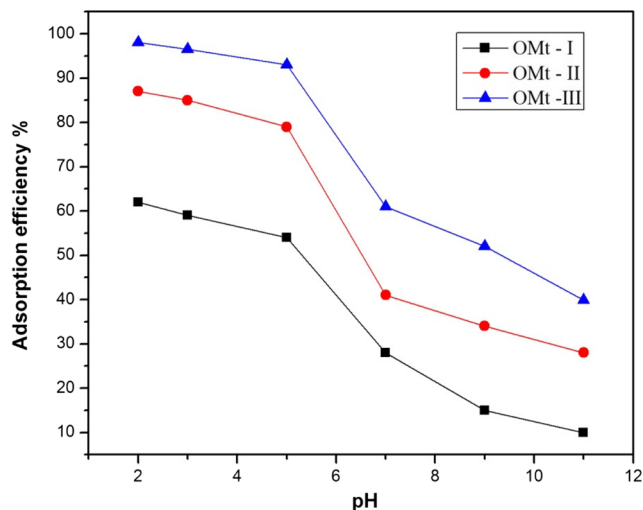
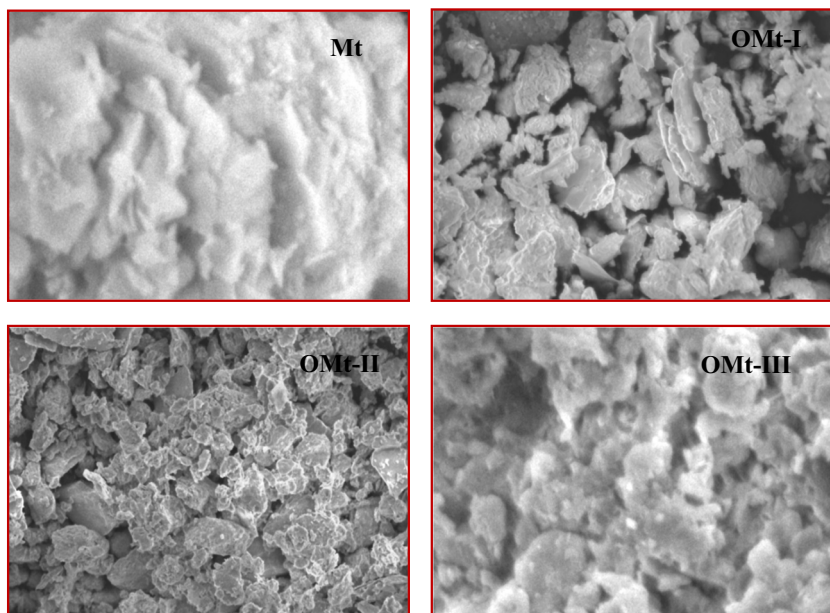


Fig. 5 Effect of pH on adsorption of Cr(VI) with OMt Adsorbents (Cr (VI) concentration: 100 mg/ L; adsorbent dosage: 1 g/L; Shaking rate: 120 rpm; temperature: 25 °C)

concentrations. The flask was agitated for 2 hours at ambient temperature. The equilibrium concentration of Cr (VI) ions from each flask was determined for all the three organo-modified Mt. In general, increase in the initial concentration of the metal ion the adsorption capacity increases. As the number of collisions between the adsorbate and adsorbent molecules increases, the Cr (VI) ion concentration increases. The chemically modified Mt clays shows a good increase in the uptake of Cr (VI) ions by increasing the concentration as it forms an interface between the adsorbate and the adsorbent molecules with high specific surface area [18, 37].

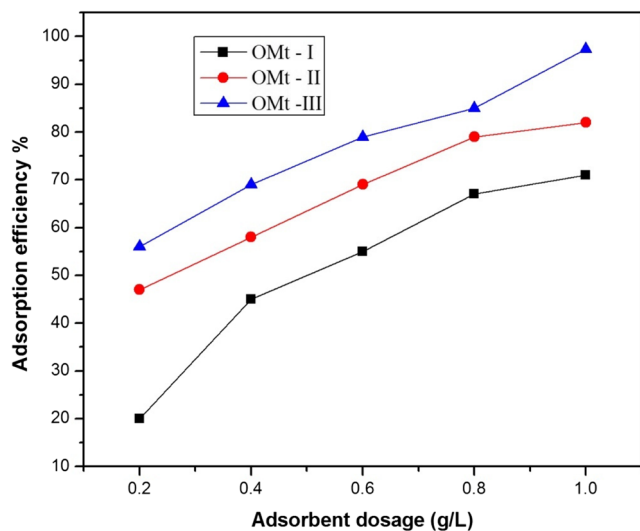


Fig. 6 Effect of OMt adsorbents dose on adsorption of Cr(VI) (Cr (VI) concentration: 100 mg/L; adsorbent dosage: 1 g/L; pH: 6; Shaking rate: 120 rpm; temperature: 25 °C)

3.5.2 pH

The pH of the solution plays a pivotal role in the adsorption process of Cr (VI) metal ions over the surface of the clay. Slight decrease in the adsorption efficiency was seen from pH 2 to 5. Thereafter, there were drastic decrease in the adsorption process from pH 5 to 7 and therefore a moderate decrease were observed upto pH 11. At lower pH, the adsorption of Cr (VI) onto the adsorbent is high and thereafter decreases with increasing the pH range. This is because of the protonation and deprotonation of the functional groups present in the adsorbents. At low pH, protonation reaction of amino group occurs and the

formation of monovalent species HCrO_4^- starts. At pH 7-6 different ionic species of chromium in the aqueous phase co-exists, such as the monovalent HCrO_4^- and divalent species of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ [38] (Fig. 5).

Gradual decrease in the adsorption efficiency of the adsorbents as the pH increases was noticed, which is due to the loss of the positive charge due to the deprotonation and high competition of the OH^- ions for the adsorption sites of the adsorbent surface to take place. At pH 9-10 the CrO_4^{2-} is the dominating chromium species where the amount of Cr (VI) ions adsorbed is less as in the case of $\text{Cr}_2\text{O}_7^{2-}$ [39].

3.5.3 Adsorbent Dosage

The effect of the amount of adsorbent was determined by varying the amount of the OMt from 0.2 g to 1.4 g keeping other parameters constant. Adsorption dosage determines the adsorbent capacity of the metal ions. Increase in adsorbent from 0.2 to 1.0 g/L increase the adsorption efficiency for all the three organo modified Mt clays was revealed in Fig. 6. The decrease in the uptake with increasing adsorbent dose was due to the non-availability sites of the chromate ion, which is attributed to overcrowding and agglomeration [15]. The order of adsorption efficiency of the three organo modified clays are as follows OMt III > OMt II > OMt I. The increase in the order from OMt I to OMt III may be due to the increase in chain length of the surfactants.

3.5.4 Agitation Rate

Agitation rate is the time required to attain the equilibrium depending on the pore size of the adsorbent, the type of

Fig. 7 Langmuir plots for the adsorption of Cr(VI) on OMt

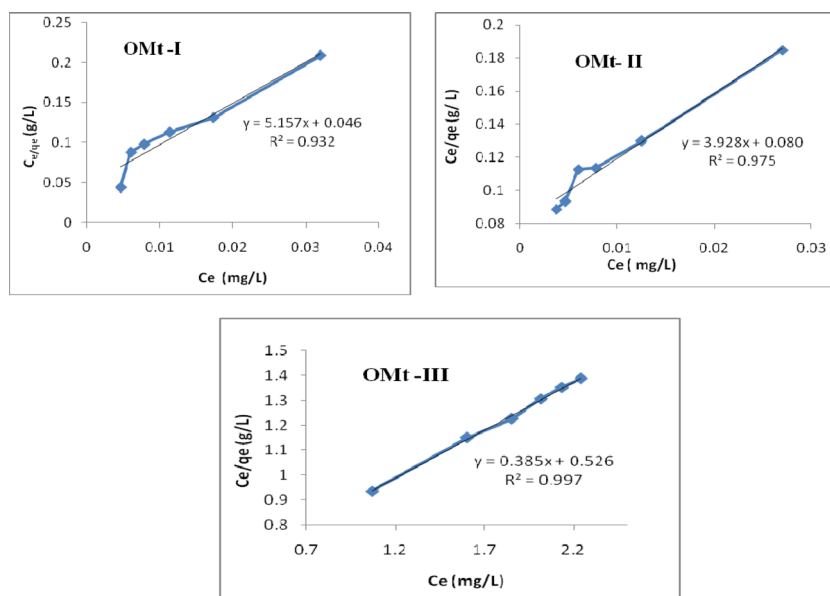
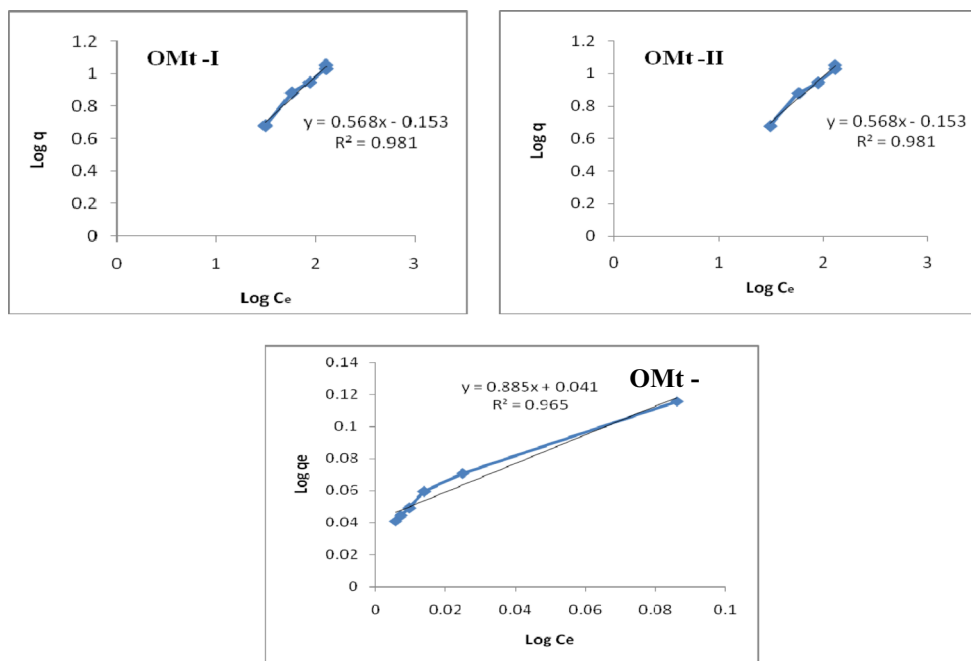


Fig. 8 Freundlich plot for the adsorption of Cr (VI) on OMt



adsorbent and the adsorbate concentration. The effects of agitation rate were ascertained by varying the agitation speed from 20 to 140 rpm for all the three OMt using 20 mL of 100 mg/L of Cr (VI) solution for 3 hour. The interaction between the adsorbent (sorbent) and adsorbate (sorbate) have been magnified by agitation process [15].

3.6 Adsorption Isotherms

The adsorption of hexavalent Chromium was investigated as a function of initial concentration of Cr (VI) ion. Two important adsorption isotherm models such as Langmuir adsorption isotherm and Freundlich adsorption isotherm models were used.

3.6.1 Langmuir Adsorption Isotherm

Adsorption of Cr (VI) ion using the modified OMt's has been found to fit well with the Langmuir model. The plot of C_e/q_e against C_e gives the value of q_m and K_L from the slope of $1/q_m$ and the intercept of $1/K_L \cdot q_m$ with the correlation coefficients (R^2) of 0.932, 0.975 and 0.997 for OMt-I, OMt-II and OMt-III respectively. This is an indicative, that the adsorption process is carried out by formation of monolayer coverage on the surface of adsorbate molecules [24, 40]. Figure 7 show the Langmuir plots of OMt-I, OMt-II and OMt-III respectively.

The R_L (dimensionless separation factor) values were found to be in the range of 0 and 1, which indicates a favorable isotherm shape ($0 < R_L < 1$) for adsorption of Cr (VI) ions onto the organo modified cationic surfactants. The R_L values of OMt-I, OMt-II and OMt-III are 0.147, 0.154,

0.169 respectively. Since the values lie between 0 and 1, Langmuir adsorption process is feasible.

3.6.2 Freundlich Adsorption Isotherm

Adsorption isotherm of Cr (VI) onto OMt has fitted well with the isotherm. The plot of $\log q_e$ against $\log C_e$ gave a slope of $1/n$ and intercept of K_F (Fig. 8). The correlation coefficients (R^2) of OMt-I, OMt-II and OMt-III are 0.981, 0.974, and 0.965 respectively. The n values favor the adsorption of Cr (VI) ions on to the three different organo OMt. The n values of OMt-I, OMt-II and OMt-III are 1.43, 1.54 and 1.71 respectively where n stands for the adsorption intensity in Freundlich Isotherm model. from the plot of $\log q_e$ versus $\log C_e$, a straight line is obtained. the intercept on extrapolation gives the K_F value and the from the slope n value is arrived. [24].

4 Conclusion

Montmorillonite clay (Mt) modified with three different homologous series of cationic surfactants such as 2-(dodecanoyloxy)-N,N-bis(2-hydroxyethyl)-N-(oxiran-2-ylmethyl)ethane-1-ammonium chloride, 2-hydroxy-N-(2-hydroxyethyl)-N-(oxiran-2-ylmethyl)-N-(2-(tetradecanoyloxy)ethyl)ethane-1-ammonium chloride and 2-hydroxy-N-(2-hydroxyethyl)-N-(oxiran-2-ylmethyl)-N-palmitoyloxyethyl)ethane-1-ammonium chloride were found to be an excellent adsorbent in the adsorption of Cr (VI) than the unmodified Mt. The FT-IR, XRD, TGA and SEM techniques explains the intercalation of the cationic surfactants on to the surface of

raw Mt in the adsorption of Cr (VI) ion. Various parameters such initial concentration of metal, pH, adsorbent dosage, and agitation rate were studied. The adsorption of chromium ion may be due to the Van der Waals forces of attraction between the lipophilic ends of the surfactants and the Cr (VI) ions or due to the electrostatic forces of attraction between the polarized group and the positive charges of the cationic surfactants. Langmuir and Freundlich adsorption isotherm models fitted well for all the three OMTs with the correlation factor (R^2) value near to unity. As the chain length of the OMT-I, OMT-II and OMT-III increases, the adsorption capacity also increases and therefore the efficacy order is,

OMT-III > OMT-II > OMT-I

Further, these modified clays can be used as an economical adsorbent for the removal of Cr (VI) ions from the effluents.

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