Preparation, Characterization and Adsorptive Application of Chemically Modified Chitosan

Samina Begum, Syed Nusrat Shah, Falak Naz, *Khalid Saeed
Department of Chemistry, Bacha Khan University, Charsadda, Khyber Pakhtunkhwa, Pakistan.
khalidkhalil2002@yahoo.com*

Summary: The chitosan was cross linked with ethylene diamine and trepthaldehyde (CM-Chitosan) through Schiff base reaction. The chitosan was successfully cross linked as confirmed by FT-IR spectrometer. The morphological analysis illustrated that CM-Chitosan surface is porous/rough than neat chitosan. The CM-Chitosan and Chitosan were employed as an adsorbent for the elimination of Cu^{+2} and Pb^{+2} ions from aqueous solution. The CM-chitosan adsorbed 8.96 and 2.09 mmol/g while neat chitosan removed 6.71 and 1.58 mmol/g of Cu^{+2} and Pb^{+2} ions, respectively. The adsorption data was also best fitted to Freundlich and Temkin model.

Key words: Cross linked Chitosan, Adsorption, Morphology.

Introduction

Industrial effluents contain toxic heavy metals which are discharge to the environment, cause a serious threat to living resources, human health and ecological systems [1]. The main source of heavy metals are different industrial activities including oil refining, electronic device manufacturing of fertilizers and pesticides, printing, leather, mining, pulp and paper, paint and dyes, petrochemicals chemicals production, metal plating, and textiles industries. Natural weathering processes, waste emissions and atmospheric depositions are also chief sources of heavy metals [2, 3]. The heavy metals from effluents/waste water can be removed by various methods like chemical oxidation/reduction [4], electrochemical treatment [5], and chemical precipitation [6]. Due to some disadvantageous for example, chemical reduction/oxidation requires extra chemicals, precipitation method produces a lot of sludge, and high operating costs on electrochemical process making these methods less technically available for the removal of heavy metals from wastewater treatment [7,8]. Adsorption is one of the most effective methods for waste water treatment. Various types of adsorbents are used for removal of metals ion from aqueous solution/effluent. For example, removal of Pb(II) and Cd(II) by synthetic resin [9], Cd(II) and Zn(II) by low grade phosphate [10], Hg(II) by Nickel ferrite bearing nitrogen-doped mesoporous carbon ($NiFe_2O_4$-NC) [11], Pb(II) and Cu(II) by tree fern [12], removal of Cd(II), Co(II), Cu(II), and Pb(II) metal ions over a composite cation exchanger [13], cadmium(II) and cobalt(II) by chemically treated carob shells [14], Ni(II), Cd(II) [15], Cr(VI) and Pb(II) were removed by bagasse fly ash [16], Cr(VI) by maple sawdust etc [17]. Other adsorbents such as orange peel [18], anaerobic

granular sludge's [19], natural bentonite [2], and chitosan [20, 4] have been used for waste water treatment. Non-conventional materials like chitosan needs to modified chemically in order to improve their performance. Presences of Bronsted and Lewis acidity[6] and high cation exchange capacity have enhanced the adsorptive properties of chitosan.

In present work, the chitosan membrane was prepared by casting method and then cross linked by using cross linking agent. The selection of chitosan is due to easy fabrication without using hazardous solvents, easy availability of free amino group for cross-linking and the cationic nature, which allow ionic cross-linking with multivalent anions. The prepared CM-Chitosan was analyzed using different techniques such as elemental analysis, FT-IR and TGA. The CM-Chitosan was employed for the removal of Pb^{+2} and Cu^{+2} from aqueous solution. The selection of Pb^{+2} and Cu^{+2} is due to the fact that large number of industrial effluents contain both Pb^{+2} and Cu^{+2}. Lead could cause brain damage in children, also affects kidneys, lungs, bones even if present in small concentration [21]. The co-carcinogenic, carcinogenic and allergic effects due to exposure to lead-containing materials have also been well predicted [22]. While the common side effects of copper are irritating respiratory system and gastrointestinal distress is reported. Indian childhood cirrhosis and Wilson's disease are also caused by copper [23]. The effect of various parameters such as amount of adsorbate, pH and initial concentration of sorbent were studied. The adsorption data was also applied to various isotherms like Freundlich, Langmuir and Temkin isotherms.

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*To whom all correspondence should be addressed.

Experimental

Materials

The chitosan, acetic acid, sodium hydroxide, copper nitrate, lead chloride were received from Merck. The hydrochloric acid, treptaldehyde and ethylene diamine were obtained from Sigma Aldrich.

Preparation of chitosan films

2 g solid chitosan was dissolved in 100 mL of 3% (V/V) acetic acid solution where the mixture is continuously stirred for 4 h in order to obtain a homogeneous solution. The chitosan film was prepared by casting method, where 10 mL dissolved solution was cast on a glass plate and its film is obtained by complete evaporation of solvent. The films are washed with deionized water.

Preparation of cross linked chitosan membrane

Complex cross linking agent was prepared by shiff base reaction. 2 mmol of trepthaldehyde was treated with 2 mmol of ethylene diamine in 25 mL absolute alcohol medium at 80 °C for 3 h at 50 rpm. Then the Chitosan film was kept in 20 mL of complex cross linking agent of trepthaldeyde and ethylenediamine solution for 6 h to crosslink the polymer film. The CM-Chitosan was washed with ethanol and distilled water for removal any attached chemicals and then dried the samples.

Adsorption study

18 mg chitosan and CM-Chitosan films were added separately in different vials, which contain cations solution (25 mL) having concentration range 2.0×10^{-2} - 9.0×10^{-4} mol/L and stirring time was 3 h at room temperature (25± 2 °C). Adsorbent was separated via filtration and filtrates were analyzed via atomic absorption spectrophotometer.

Kinetics experiments were performed to find out the saturation isotherm of metal solution, where 5×10^{-3} mol/L of cations solutions were stirred for 6 h in beaker at T_{room}. The chitosan and CM-Chitosan was removed from the solution and the remaining amount of cations in filtrate was found by atomic absorption method.

The quantity of adsorbates in mmolg^{-1} was determined via Equation (1).

$$N_f = \frac{ni - ns}{m} \qquad (1)$$

where n_i and N_f are the number of moles in initial solution and sorbed on chitosan membrane, respectively. While m and n_s are the mass of adsorbent and number of moles in the supernatant after equilibrium, respectively.

Instruments

The morphological and elemental percentage of sorbents was studied by SEM SM-6490, Joel and EDX (JSM 5910) INCA 200/Oxford instrument UK. The FT-IR analysis of Chitosan and CM-Chitosan was carried out by FT-IR spectrometer (Schimzue, IR prestige-21, FT-IR-8400). The pHPZC of the carbons was determined according the procedure described by Moreno-Castilla *et al*. The TG analysis was performed via Perkin Elimer USA in inert atmosphere. The adsorption study was carried out by atomic absorption spectrophotometer (Analyst 700 Perkin Elimer USA).

Result and Discussion

Morphological and EDX study

Fig. 1 show the SEM and EDX study of Chitosan and CM-Chitosan sheet. The SEM micrgraph (Fig. 1a) present that the surface of neat Chitosan has regular, smooth, flat and without cracks/pores. The flat and dense surface of neat Chitosan was also reported by Lee *et al*.[25]. The micrograph (figure 1b) illustrate that CM-Chitosan film had irregular surface. The smoothness surface of CM-Chitosan may because of cross-linking of Chitosan with ethylene diamine and trepthaldehyde groups partially attached with Chitosan. The spectra (Fig. 1c,d) presented that the content of C, O and N for the Chitosan composition were 52, 40.41 and 8.30%, respectively, while the CM-Chitosan had 37, 27 and 35%, respectively. The increased amount of nitrogen indicated that the Chitosan was chemical modified.

PZC study

Fig. 2 presents the PZC of Chitosan and CM-Chitosan. The PZC was studied by the alike procedure as confer somewhere else [26]. The PZC_{pH} for a definite surface depend upon the relative basic and acidic properties of the solid and allows an evaluation of the net uptake of OH$^-$ and H$^+$ ions. PZC value of the Chitosan (Fig. 2) was found to be 7.3. The similar PZC value was also reported by Hasan *et al*. [27], for Chitosan coated perlite bead. The PZC of CM-Chitosan was found to be 7.6, which represent the neutral surface.
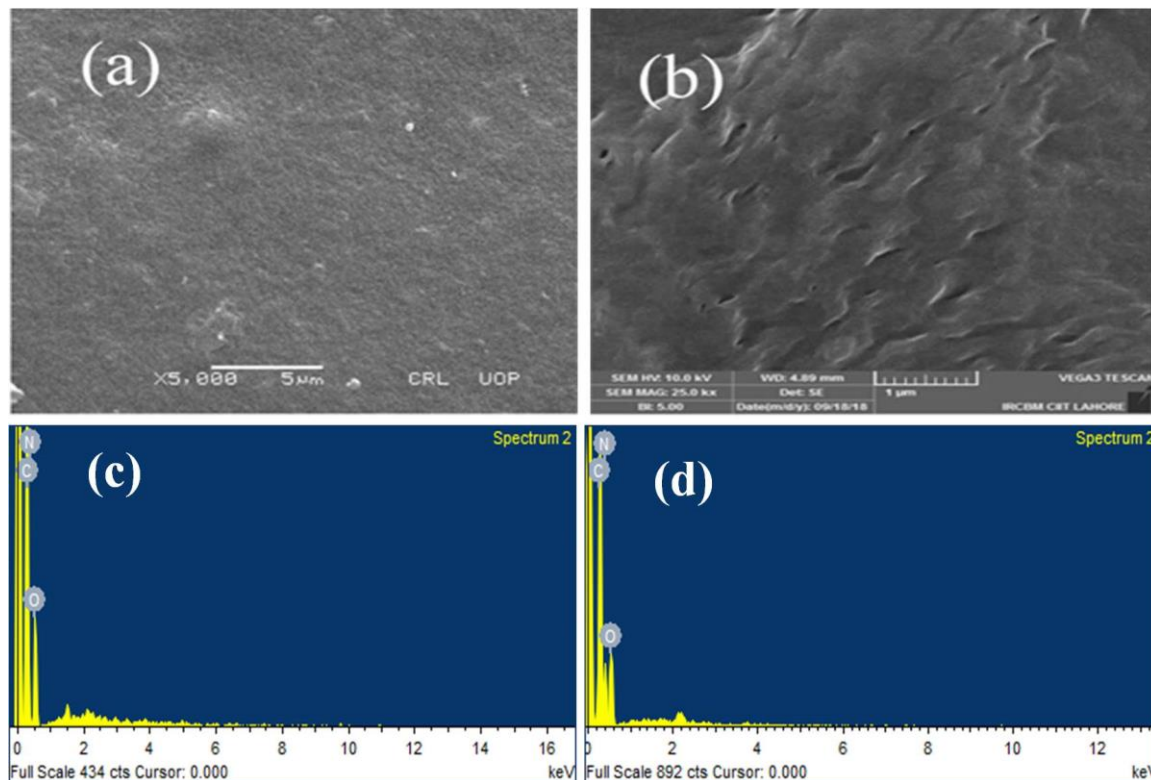
Fig. 1:   SEM images and EDX spectra of chitosan (a), (c) and CM-chitosan (b), (d), respectively.
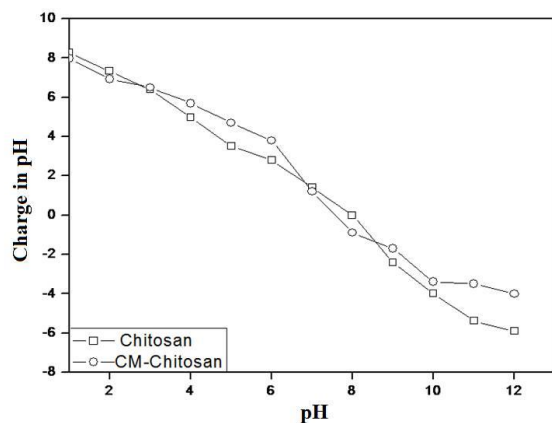

Fig. 2: pHpzc of Chitosan and CM-Chitosan membrane.

Fig. 3 illustrated the FT-IR spectra of Chitosan and CM-Chitosan. The spectrum of neat Chitosan showed peaks at 3050–3650 cm^{-1}, which is due to the stretching vibration of –OH and –NH_2. The spectrum also presented peaks at about 2924 and 2862 cm^{-1} due to the stretching vibration of –CH while the peak about 1080 cm^{-1} represent the stretch vibration of –C–) [28, 29]. The CM-Chitosan spectrum presented new peak at 1700 cm^{-1}, that may be due to the ionic interaction among the +vely charged amino

groups of the modified Chitosan and the negatively charged groups of the ethylene diamine with trepthaldehyde. The addition peaks at 1643, 1400 and 900 cm^{-1} representing C=C stretching,   C–H deformation and C–O stretching, and aromatic ring, respectively [14, 30].
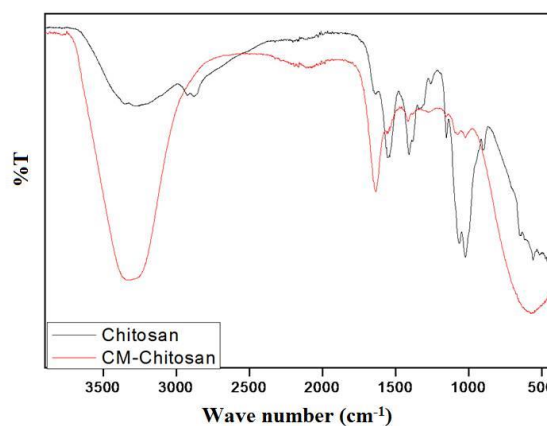

Fig. 3:   FTIR Spectra of Chitosan and CM-Chitosan.

Fig. 4 shows the TG thermograms of neat Chitosan and CM-Chitosan, which presented various stages of degradation. The first degradation stage occurred at about 100-200 °C, which was mainly due

to the loss of water as adsorbed physically on the surface of the materials [11]. While the other the degradation stages were due to the degradation of main organic portion of the Chitosan. The TG thermograms also presented that CM-Chitosan showed more stability as compared to neat Chitosan.
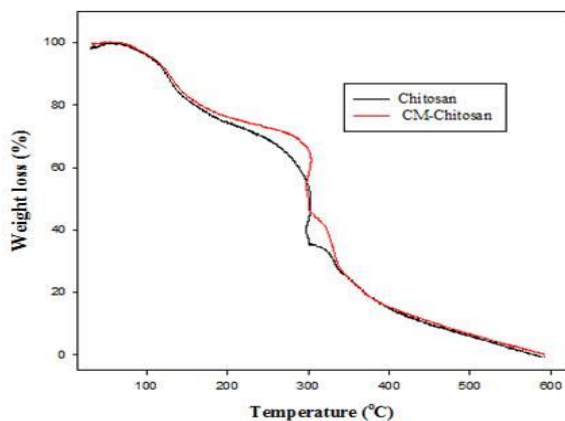

Fig 4:   TGA curve of Chitosan and CM-Chitosan.

Effect of initial concentration of cations on sorbent

Fig. 5 shows the effect of initial concentration, which presented that CM-Chitosan removed high amount of Cu^{+2} and Pb^{+2} than neat Chitosan, which is due to the porous and rough surface of the adsorbent. The quantity of adsorbed cations was found by plotting the amounts adsorbate (X) verses equilibrium concentrations (Ci). It is observed that the adsorption of pollutants increases by increasing the concentration of Cu^{+2} and Pb^{+2} and then almost level off. It is because, initially the adsorbates uniformly adsorbed upon the active sites of the adsorbent and a later bit saturation occur. By auxiliary cations adding,
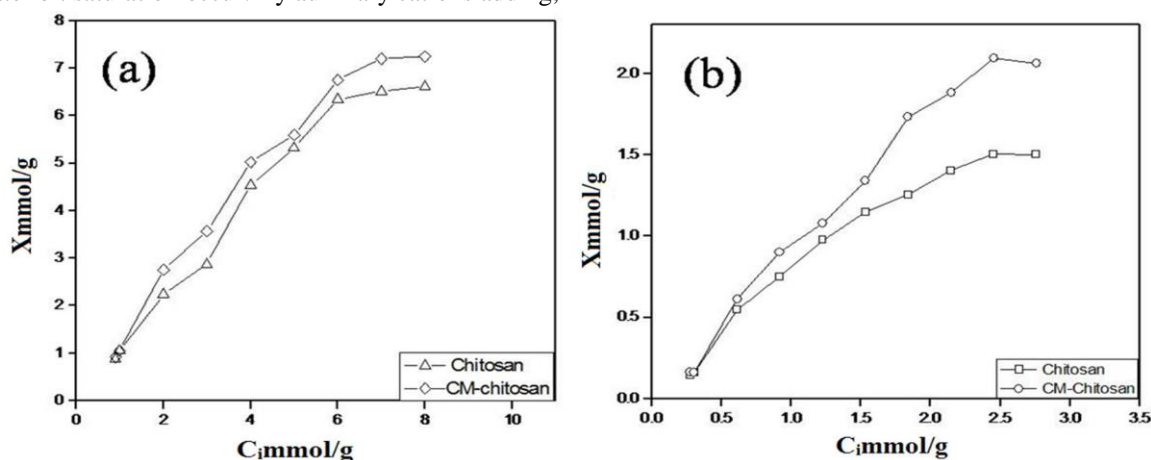
there is no enhancement in adsorption because of unavailability of free active sites metal ions.

pH effect on removal of Pb^{+2} and Cu^{+2} ions

Fig. 6 shows the adsorption of Pb^{+2} and Cu^{+2} ions on Chitosan & CM-Chitosan at different   pH i.e. 2-12, while parameters remain constant. The data illustrated that the removal of metals ion increases as by increasing solution pH. At low pH range, both metal ions and hydrogen are +vely charged, so there is a rivalry between metal ions and hydrogen ions to connect unpaired electrons of adsorbent. The reduction of H^+ ions by increasing pH of solution made it possible to increase the concentration of heavy metal ions to attach with electrons (active sites), which result in higher adsorption of metals ions. Similar observation was also reported by Stafiej and Pyrzynska in the case of Co^{+2} adsorption on the carbon nanotubes [31].

Time study

Fig. 7 shows the adsorption kinetic study of both metal ions onto Chitosan and CM-Chitosan. It was found that both Cu and Pb ions adsorption increases with increasing the contact time and then level off behind 100 minutes. It is because the existing of extra free active sites upon the adsorbents for metal ions adsorption. After 100 min, the adsorption was level off because of unavailability of active sites upon Chitosan and CM-Chitosan. The results too illustrated that CM-Chitosan adsorbed high quantity of copper and Pb lead ions (8.96 mmol/g and 2.09mmol/g) than neat Chitosan (6.71 mmol/g and 1.58mmol/g), respectively.
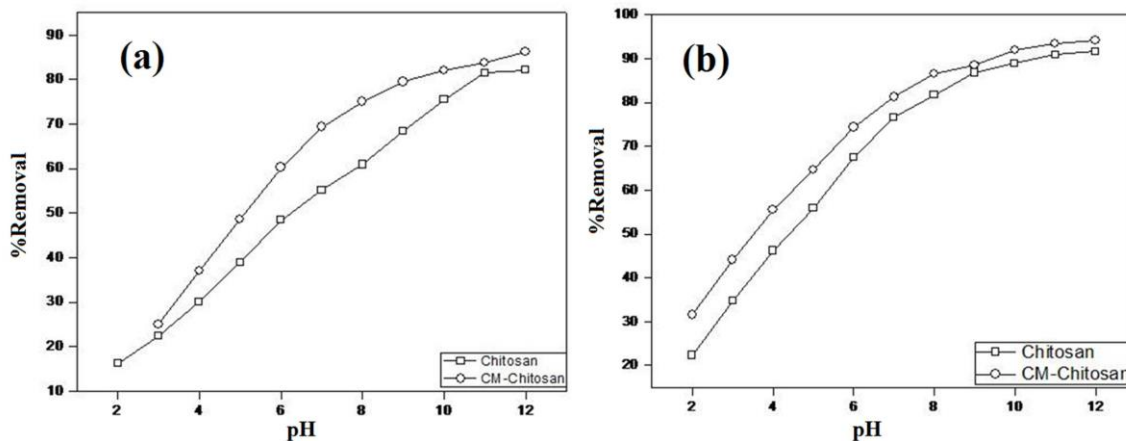

Fig. 5:   Effect of initial concentration of adsorbate on the adsorption of (a) Cu^{+2} and (b) Pb^{+2} by Chitosan and CM-Chitosan.

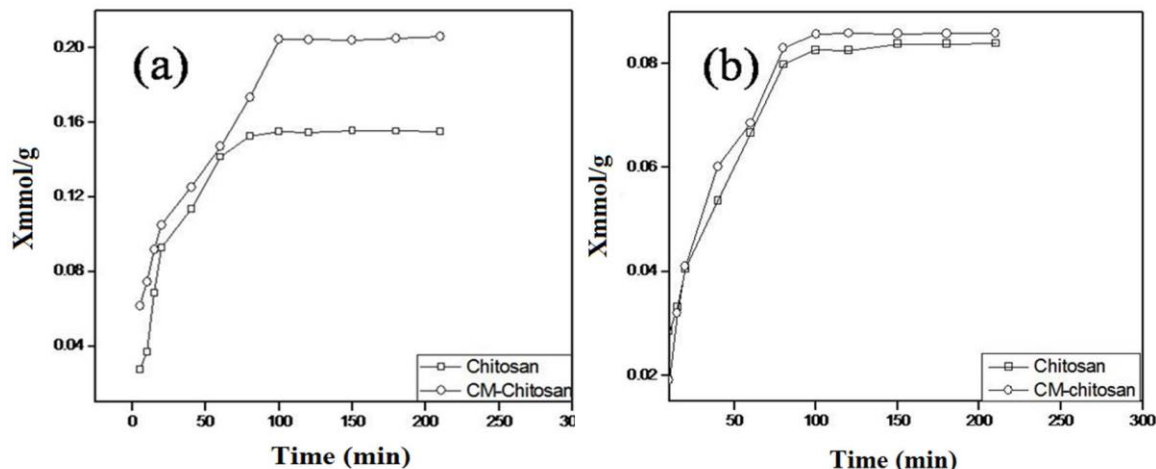Fig. 6: Effect of pH on the adsorption of (a) Cu^{+2} and (b) Pb^{+2} by Chitosan and CM-Chitosan.

Fig. 7: Time study of adsorption of (a) Cu^{+2} and (b) Pb^{+2} by Chitosan and CM-Chitosan.

Table-1: Langmuir parameters, Freundlich parameters and Temkin parameters for cations sorbed onto Chitosan and CM-Chitosan membrane.

		Freundlich parameters			Temkin parameters		
		KF	N	R^2	KT	b(mol/Kg)	R^2
Cu	Chitosan	0.208	0.8006	0.980	1007.43	526.806	0.903
	CM-Chitosan	0.247	0.8190	0.973	981.711	506.040	0.912
Pb	Chitosan	0.674	0.9604	0.953	4.10079	3.911	0.989
	CM-Chitosan	0.784	0.9040	0.956	3.6767	2.8672	0.962

Table-2: Comparison of the adsorption efficiency of present work with the previously reported work.

| Metal ions	Adsorbents	% removal	Contact time (min)	References
Pb(II)	Spent coffee grounds	68	300	34]
	PAN/Sago Lignin-Based Activated Carbon Nanofibers	76	240	[35]
	Rice husk	92	120	[36]
	Chitosan	92	200	Present work
	CM-Chitosan and Chitosan	96	200	Present work
Cu(II)	SA-based attapulgite foams	86	220	[33]
	Spent coffee grounds	68	300	[34]
	Rice husk	75	120	[36]
	Chitosan	88	200	Present work
	CM-Chitosan and Chitosan	90	200	Present work

Pseudo-second order equation

The adsorption kinetic rate pseudo-second order equation is shown as

$$\frac{t}{q_i} = \frac{1}{k_2 q} + \frac{1}{q_e} t \qquad (3)$$

A straight line (Fig. 8) is got via plotting t vs t/q_i where $1/q_e$ shows slope, and $1/k_2 q_e$ shows intercept. By interpreting the experimental data of the pseudo second-order models adsorption kinetics mechanism of metals ions by Chitosan and CM-Chitosan can be find as shown in tables inside the Fig 8. From X_m (theoretically), X_m (experimentally) and R^2 (correlation coefficient) values, it found that pseudo-second order equation is extra applicable.

Adsorption isotherms

The data is also fitted to Freundlich and Temkin adsorption isotherms.
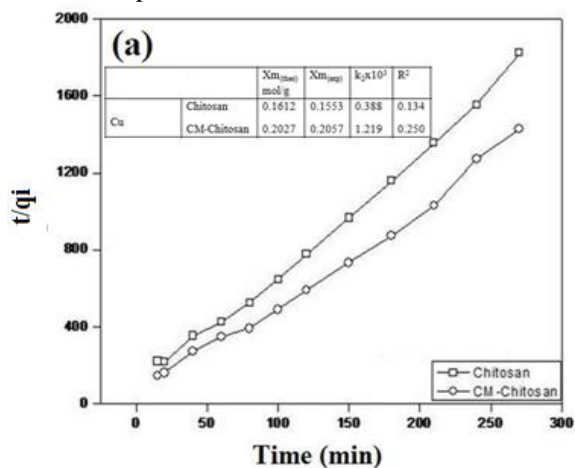
Freundlich adsorption isotherm

Fig. 9 shows the Freundlich adsorption isotherm, which normally showing adsorption in multi-layers. The Freundlich adsorption isotherm model also proposes a monolayer adsorption with a heterogeneous distribution of functionalities [32].

It can be expressed in linear form as:

$$\log X_e = \log K_f + \frac{1}{n} \log C_e \qquad (4)$$

where K_f is the Freundlich constant, C_e is concentration (mg/L), n is adsorption intensity, and X_e is the quantity of cations adsorbed at equilibrium (mg/g).
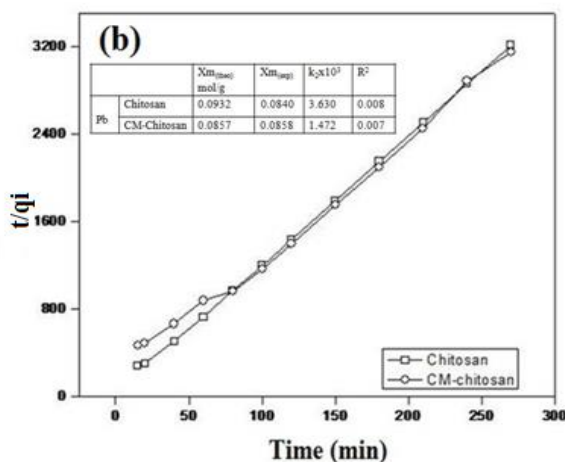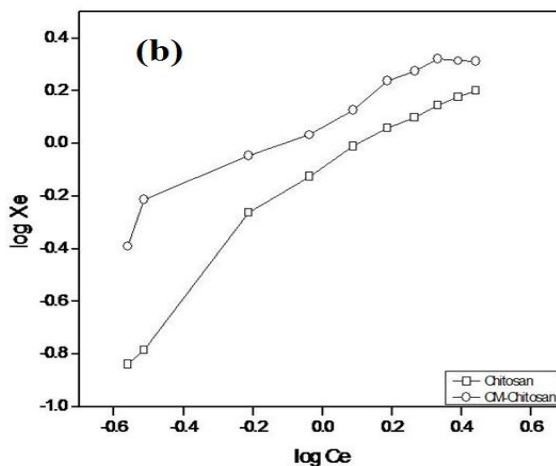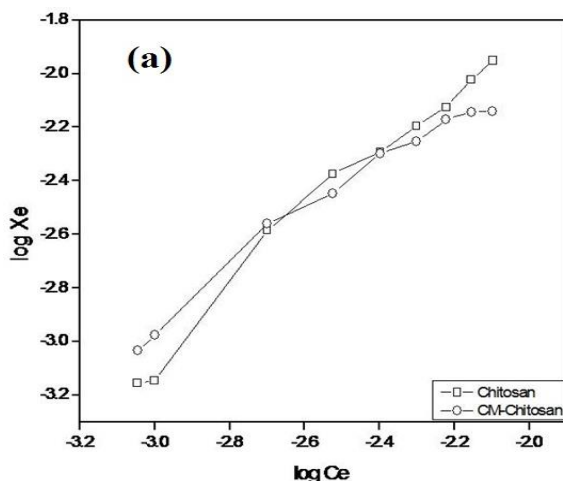

Fig. 8: Pseudo 2nd order kinetics for (a) Cu^{+2} and (b) Pb$^{+2.}$

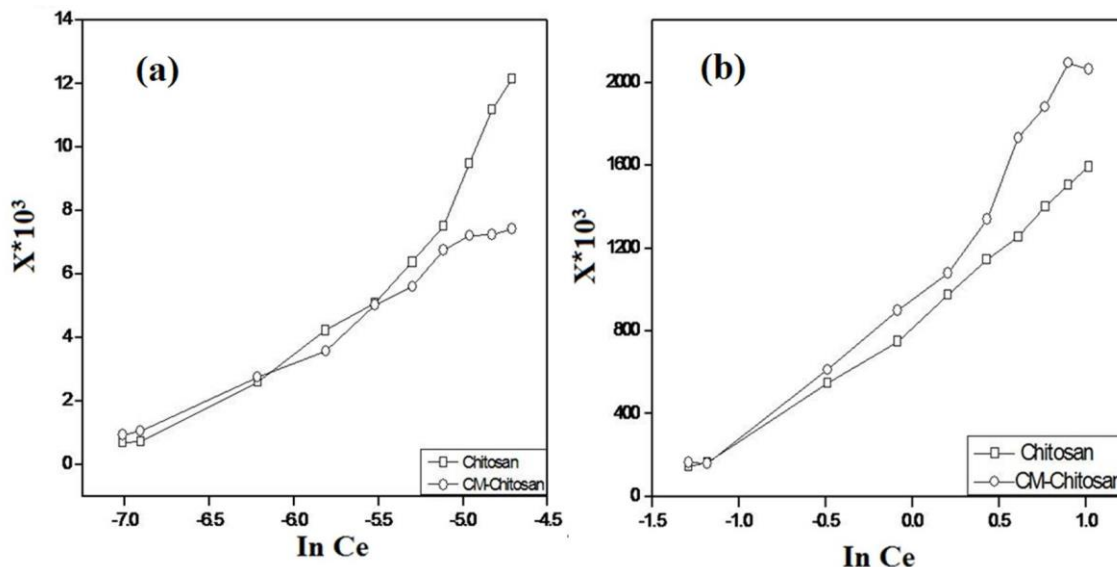Fig. 9: Freundlich isotherm for (a) Cu^{+2} and (b) Pb^{+2}

Fig. 10: Temkin isotherm for adsorption of (a) Cu Cu^{+2} and (b) Pb^{+2}.

Temkin adsorption isotherm

Temkin isotherm is used in order to study the interaction among adsorbent and adsorbate. By coverage of the adsorbate, the heat of adsorption of all the molecules would decrease linearly by adsorbate–adsorbent interactions, showing that the conc. will be neither extremely high nor exceptionally small.

The mathematical expression of Temkin model is:

$$X_e = A - B \ln C_e \qquad (5)$$

$$A = \frac{RT \ln K_t}{b} \qquad (6)$$

where B, A & b slope, intercept, and Temkin constant, respectively. A plot of X_e versus $\ln C_e$ provide "b" and KT values. Where b (constant) is the heat of adsorption. The Table inside Fig. 10 illustrates the high value of b give the heat of adsorption for the Cu and Pb ions upon Chitosan and CM-Chitosan, which present a good interaction between Cu & Pb ions and adsorbent surface, where max. binding energy is illustrated by kT (equilibrium bindingconstant).

Conclusion

SEM study illustrated that the CM-Chitosan surface is rough than neat chitosan. Both CM-Chitosan and Chitosan smaples presented strong affinity towards heavy metals suggesting that this material can be used as adsorbent for adosprtion of heavy metals from industrial effluents. The adsorption capacity of CM-Chitosan was superior to neat Chitosan film. The adsorption process was best fitted to pseudo-second order model and Temkin model.

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