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Adsorption analysis of Pb(II) by nanocomposites of chitosan with methyl cellulose and clay

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ABSTRACT

Chitosan is the one of the most abundant natural biopolymers after cellulose. The chitosan was converted into chitosan nanoparticles and to improve the adsorption efficiency, the polymers kaolin clay and methyl cellulose has been mixed separately to form the binary composites NC+MC and NC+KC. The prepared composites were characterized. Batch adsorption process was carried out and the effects of various parameters influencing the Pb(II) adsorption such as initial concentration of the metal solution, pH, contact time and adsorbent concentration have been studied. The data obtained from adsorption process was used to fit in Langmuir and Freundlich isotherms. Adsorption kinetics was applied to evaluate the order followed by the process. The second order kinetic model was found to correlate well with the experimental data. Both the prepared composites follow the second order kinetic model.

Keywords: Nanochitosan, kaolinclay, methylcellulose, adsorption isotherm, adsorption kinetics.

INTRODUCTION

Water is an essential matter to human and other living organism. Water is polluted in many ways like effluent and chemical industries [1]. Due to the industrial activity contamination of the ground water will be increases. The high level of heavy metal ion concentration were detected with antimony up to 0.42mg/L. Mercury to 0.02mg/L, Lead to 1.82mg/L, and cadmium 1.31 mg/L and including microbial contamination[2]. Environmental pollution caused by toxic heavy metal in industrial effluents is one of the most pressing problems in the world.

It is known that heavy metals ions such as Pb^{2+}, Cd^{2+}, Hg^{2+},Ni^{2+} and Cu^{2+}can cause severe problems, particularly in human body[3]. Different types of methods can be used for the removal process of heavy metals present in the environment.

Chitosan, the deacetylated from of the polysaccharide chitin, which is mainly used biopolymer in now a days, due to its wide versatility, non-toxicity and antimicrobial, non-toxicity. Chitosan has been one of the most popular adsorbents for the removal of metal ions from aqueous solution and it is widely used in water treatment application [4]. Effluent came from the industry may cause long-term health effect to the environment. Therefore the levels are mandatory. This research work mainly concentrated in the removal of Lead ion from the synthetic wastewater. Lead is the transition metal and it is used in many industries. In spite of its various applications, Lead is a very toxic and harmful element [5]. Lead may causes many problems in our human body such as mental disturbance, retardation and semi-permanent brain damage. Lead is very toxic even in a small amounts, with a toxicity limit is < 0.005µg mL^{-1}[6].

Lead can be separated by different methods such as solvent extraction, ion chromatography and flow Injection-Flame Atomic Adsorption spectrometer [7]. The objective of the study describes the batch adsorption process of

Pb(II) ions by using the composites of nanochitosan with methyl cellulose and nanochitosan with clay. This information will be useful for further applications for the system design in the treatment of industrial waste water.

MATERIALS AND METHODS

Materials:
Chitosan (deacetylation was 94%) was a gift sample from the central institute of Fisheries technology, Kerala, India. Kaolin clay, Methyl cellulose, Glutaraldehyde and the other chemicals used in these experiments were of analytical grade without further purification.

Preparation of nanochitosan composites:
20mg nanochitosan and 20mg of methyl cellulose (or) 20mg of kaolin clay were mixed thoroughly with 1ml of the cross linking agent glutaraldehyde in the presence of 40ml formic acid. The mixtures were stirred magnetically for 2 hours and dried, then further dried in vacuum for more than 10 hours, the precipitate were stored in desiccators. Prior to use, the precipitate was again dissolved in formic acid and dried in vacuum for 10h to remove the formic acid. Thus the two binary composite of NC+MC(1:1) and NC+KC(1:1) were prepared.

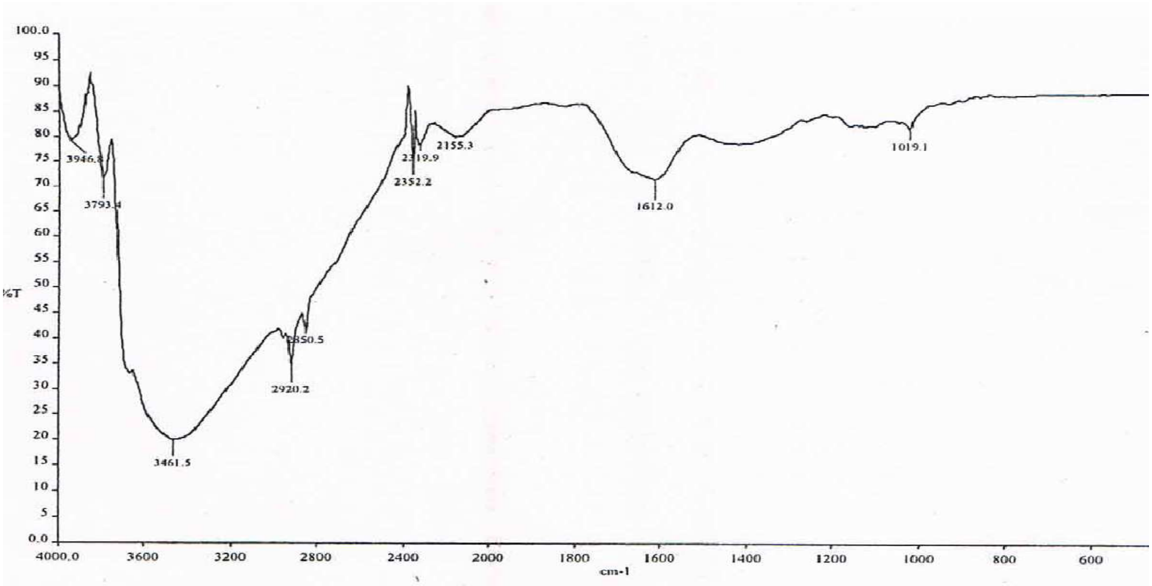
Preparation of stock solution
Synthetic stock solutions of Lead (II) ion were prepared by dissolving required quantity of analar grade $PbNO_3$ is distilled demineralised water. 1:1 Hydrochloric acid and 1% sodium hydroxide solutions were used for pH adjustment. The exact concentration of each metal ion solution was calculated on mass basis and expressed in terms of mg L^{-1}. The required lower concentrations were prepared by dilution of the stock solution.

Experimental process
Batch studies were performed with the lead nitrate solution of specific initial concentration using prepared binary composites with cross linking agent. The metal solution taken in stoppered bottles were agitated at 28°C in orbit shaker at fixed speed of 160rpm. The extent of removal of metals were investigated separately by changing the initial concentration of metal ion, adsorbent does, contact time, the pH of the solution by analysing the Lead(II) ions after each period of remediation by atomic adsorption spectroscopy.

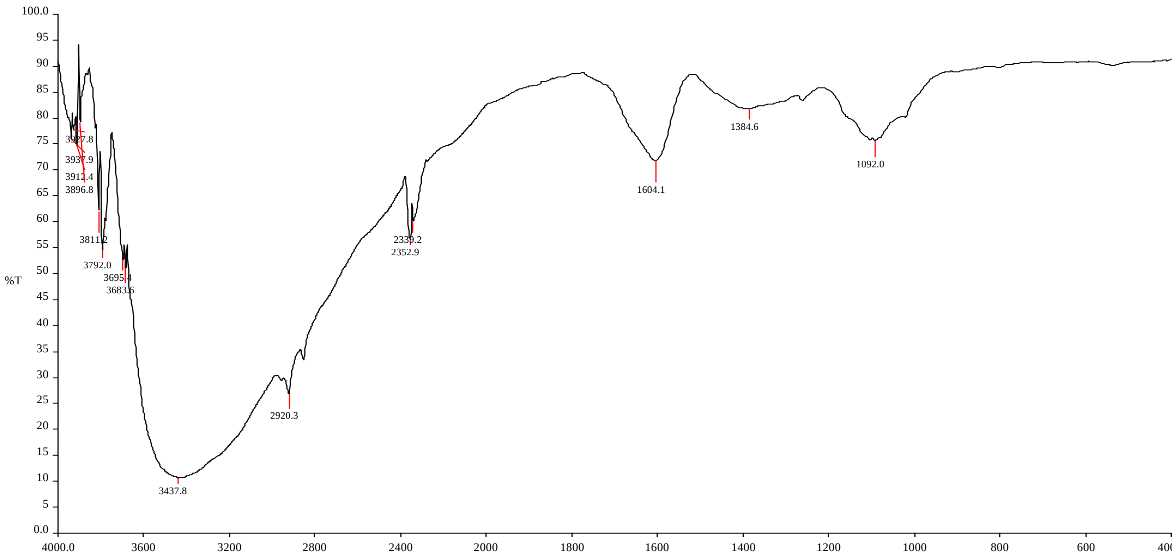
RESULT AND DISCUSSION

Characterisation of the Nanopolymer Composites
FTIR
Nanopolymer composites of chitosan with methyl and kaolin clay were characterized by FTIR spectroscopy. Figure 1(a) shows the FTIR spectrum of nanochitosan with methyl cellulose (1:1).The peak at 3808cm^{-1} and 3772cm^{-1} for free O-H group. Peak observed at 3444cm $^{-1}$ for intermolecular hydrogen bonding, polymeric association and N-H stretching. 2916cm^{-1} and 2760 cm^{-1} for the presence of methyl cellulose aldehydic C-H stretching showing methyl cellulose as participated in the composite formation. Figure 1(b) the peak around 3811.2 cm^{-1}stretching free OH group, and 3695 cm^{-1} due to the Al-O-H stretching. The bands between 3450 and 3670 cm^{-1} are attributed to the OH stretching mode. In the carbonate and C-H bending vibration region the kaolin sample exhibit some weak peaks. The band found at 1348cm^{-1} arises due to the Al-O as Si cage (TO_4) [8].From the FTIR studies confirms the formation of the composites.

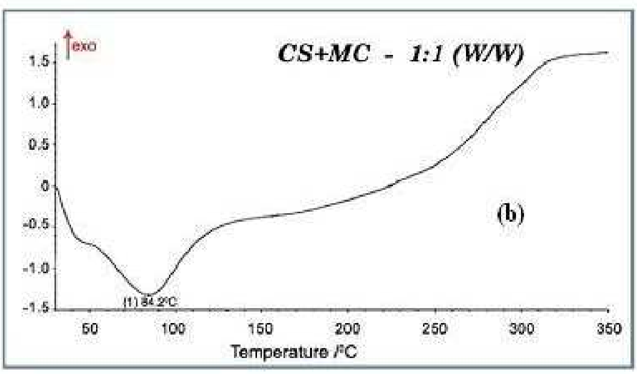
DSC
DSC is an analytical tool which helps to understand the thermal behaviors of polymer and polymer composites. Figure 2(a) and figure 2(b) shows that DSC curves for Nanochitosan+ Methyl Cellulose and Nanochitosan + Kaolinclay respectively. The glass transition temperature for the methyl cellulose composite is at (Tg = 224°C) and Kaolin clay composite is at (Tg=226°C). Appearance of single glass transition temperature indicative of attractive molecular interaction and high degree of compatibility of both the materials [9, 10]. Prepared composite was highly stable than pure Nanochitosan. The exothermic peak is not observed below 250°C for both composites. It shows composite is not decomposed below 250°C, proving that the thermal stability increases during the modification.



FTIR spectra of 1(a) Nanochitosan+ Methylcellulose



FTIR spectra of 1(b) Nanochitosan+ Kaolinclay



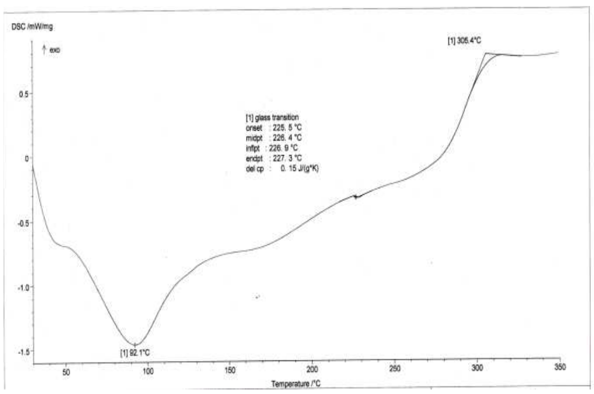
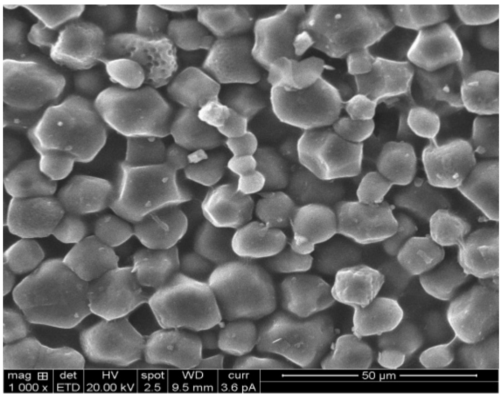


Figure 2(a) shows DSC curves for NC+MC **Figure 2(b) DSC curves for NC+KC**

SEM

The surface morphology of the nanocomposite was examined by scanning electron microscopy. The scanning electron micrograph of crosslinked Nanochitosan/Methyl cellulose composite shows in figure 3(a) and Nanochitosan/Kaolin Clay composite in 3(b) respectively.SEM images of cross linked nanochitosan with methyl cellulose shows roughness in the surface. In the case of images of cross linked Nanochitosan with kaolin clay composites shows large rough surface area for the better adsorption compare to the methyl cellulose composite [11]. All these observation confirm that Nanochitosan with Kaolin clay in the presence of crosslinking agent to allow with greater adsorbing property.



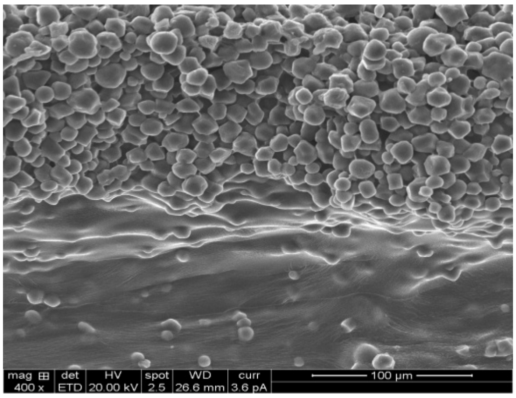


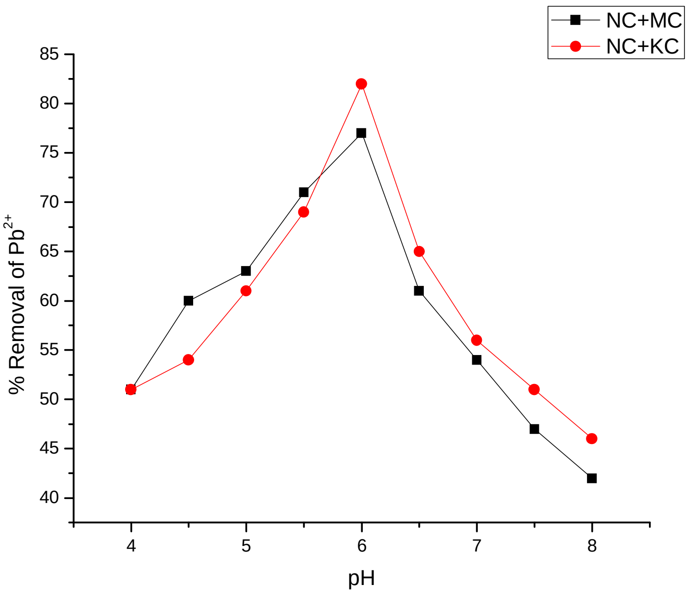
Figure 3(a):CS+MC 1:1 with Cross linking Figure 3(b):CS+KC 1:1 with cross linking

Factors influencing the adsorption of Pb^{2+}ions

Effect of pH

The role of hydrogen ion concentration was examined in solutions at different pH range [12]. The effect of pH on the adsorption of Pb(II) by nanocomposite of chitosan/methyl cellulose and Nanochitosan/clay were shown in the figure-4. The removal of the lead ion was investigated by varying the pH range from 4 to 8. It was observed that initially Pb(II) ion removal increases with increase in the pH of the solution, showing the dependence of adsorption on the solution pH. The increase in the adsorptive capacities of Pb^{2+}ion with increasing the pH value from 4 to 6 was due to the decrease in the hydrogen ion concentration. Maximum lead removal is achieved with both the composite within 70- 80% at pH = 6.The decrease in adsorption was observed at higher pH, probably due to the formation of hydroxide complexes. This is in agreements with the results obtained [12] for the adsorption of lead on rice husk.

Figure -4: Effect of pH

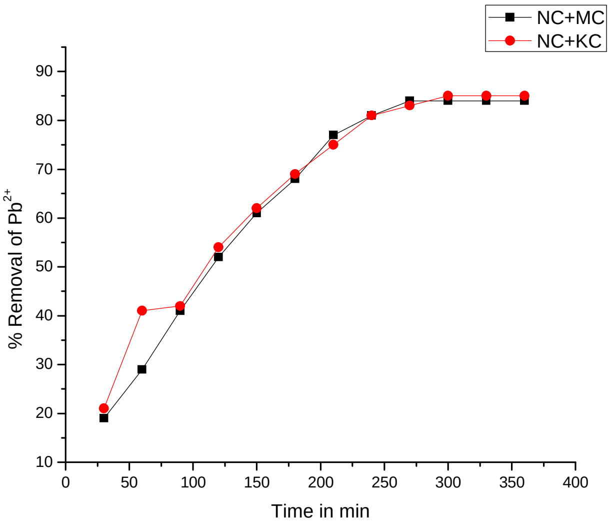


Effect of Contact Time

Effect of contact time on adsorption was studied and the results are shown in figure 5.Batch adsorption studies were carried out to determine the variation in adsorption of Pb(II) ion by the chitosan nanocomposite with a room temperature

(30 ± 10^0C). Figure-5 depict the rate of uptake of Pb(II)ions at various time intervals. It was found that the removal of lead ions increased with increase in the contact time to some extent. But further increase in the contact time did not increase in the uptake of Metal adsorption due to the deposition of metal ions on the available adsorption sites of both the composites(NC+MC) and (NC+KC). Adsorption is rapid at their optimum pH values for both the composites. The initial process of adsorption gives the way to slow approach to attain equilibrium and saturation is reached [13].

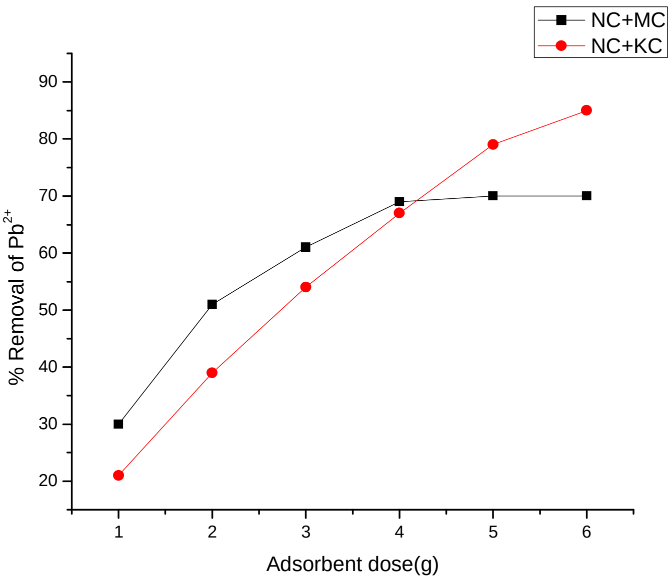
Figure 5:Effect of Contact Time



EFFECT OF ADSORBENT DOSE

The amount of adsorbent employed was found to influence the efficiency of the adsorption process. This parameter was optimized in conjunction with the other optimized parameters (Lead at a pH = 6 and constant contact time of 5 to 6 hrs) by shaking different amount of two composites (NC+MC) and (NC+KC). The effect of the amount of adsorbent on the removal of Lead ions Shows in Figure 6. The percentage of lead removal increases with increases in the amount of adsorbent. The amount of adsorbent dose varied from 1 to 6g [14].This is due to the increase in the active adsorption sites of the adsorbent. Results showed no further increases in adsorption after a certain amount of adsorbent was added (7-8g). The maximum percentage removal of Pb^{2+} was about 85% at the dosage of 6gms of naochitosan with kaolin clay in the presence of cross linking agents. While for nanochitosan with methyl cellulose composites maximum percentage of adsorption is 70% at 6g. Among the two composites, kaolin clay composites get adsorbed at a higher rate than the methyl cellulose composites. Results showed all levels of adsorbent dose is efficient for the removal of lead ions from the synthetic waste water.

Figure 6: Effect of adsorbent dose on the adsorption of lead



ADSORPTION ISOTHERM

Freundlich and Langmuir equations were used to find the patterns of adsorption of pb(II) removal by the adsorbent of nanopolymer composites of chitosan.

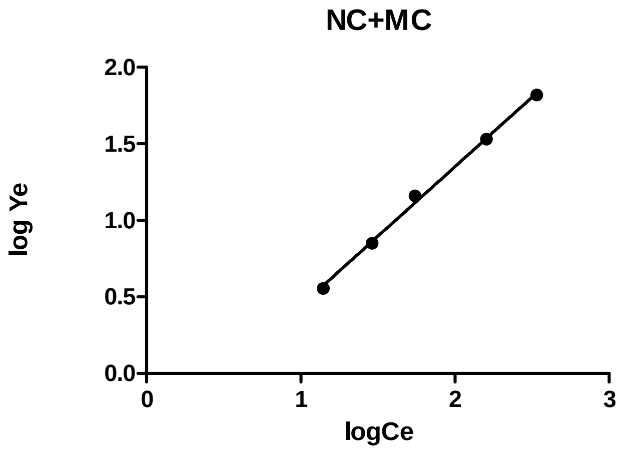
Freundlich Isotherm

Freundlich equation in logarithmic form is as follows.

$$log\left(\frac{X}{M}\right) = \log K + \frac{1}{n}\log Ce$$

where, K and 1/n =Freundlich constant related to adsorption capacity and intensity respectively.

Figure 7.Freundlich Isotherm For Lead(NC+MC)



The plot of log(X/M) with log Ce gives the straight line with slop 1/n (fig.7) and (fig.8), which shows the adsorption of pb(II) with two different composites of NC+MC and NC+KC respectively It follows the freundlich isotherm. The value of 1/n and K_f were calculated from slope and intercept respectively and given in the table 4. The value of 1/n for NC+MC is 0.9 and NC+KC is 0.7. Which indicates favourable adsorption [15]. Table 4 shows the value of the parameters of the two composite. The freundlich model yield a better fit(R^2=0.972) for NC+MC. And (R^2=0.992) for NC+KC rather than the Langmuir model.

Figure 8. Freundlich Isotherm For Lead(NC+KC)

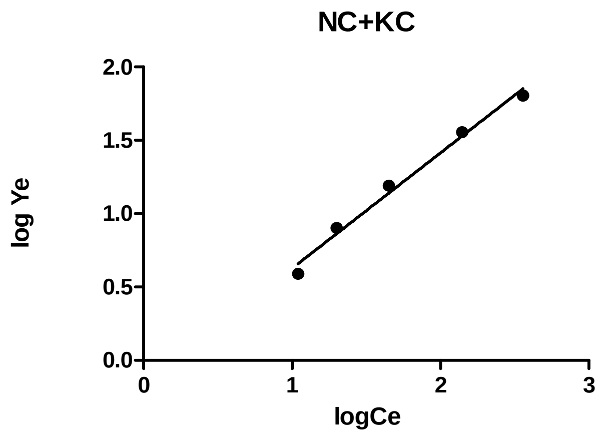


Table – 1:Freundlich Isotherm Parameters

Metal ion	Prepared composites	Freundlich constants		
		K_f	N	R^2
Pb(II)	NC+MC	0.9093	0.9	0.972
	NC+KC	0.7872	0.7	0.998

Langmuir Isotherm
A general form of the Langmuir model equation is

$$q = \frac{q_{max} b C_{eq}}{1 + b C_{eq}}$$

whereq = uptake of species (mg/g), qmax = maximum uptake (mg/g),
Ceq = equilibrium (final) concentration in solution (mg/L),
b = constant related to energy of adsorption.
b is the equilibrium or association constant (L/mg) and is related to the affinity between sorbent and sorbate. It is also represented as K_A. Figure 10 and figure 11 shows the Langmuir isotherm for (NC+MC) and (NC+KC) respectively.

The values of q_{max} and K_A can be found using the linear reciprocal plot of the equilibrium isotherm.

$$\frac{1}{q} = \frac{1}{q_{max} K_A C_{eq}} + \frac{1}{q_{max}}$$

This is a plot of 1/q vs. 1/Ceq, where q_{max} and K_A can be found from the slope and intercept [16, 17]. Table 5 shows the Langmuir parameters for the prepared composites (NC+MC) and(NC+KC).

Figure 10. Langmuir isotherm for lead(NC+MC)

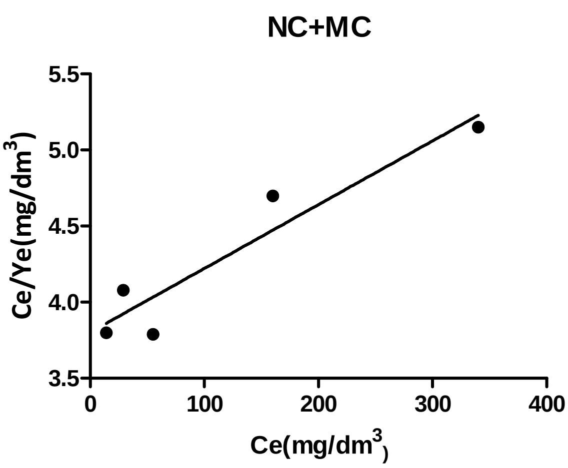


Figure 11. Langmuir isotherm for lead(NC+KC)

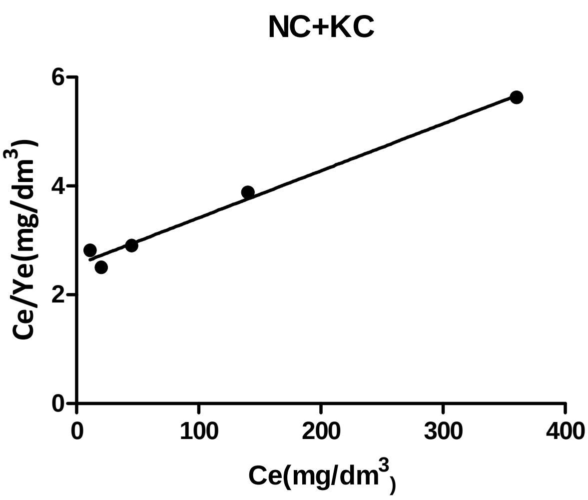


Table 2 Langmuir isotherm parameters when Ceq/Cads were ploted against Ceq gives K_L and b the datas are given in the table.

Prepared composite	Langmuir constants			
	K_L (dm^3/g)	b (dm^3/mg)	Cmax(mg/g)	R^2
NC/MC	3.803	0.0041	907	0.8996
NC/KC	3.89	0.003	976	0.9600

KINETIC STUDY

The kinetics of Pb(II) adsorption onto nanocomposites of chitosan with methyl cellulose and kaolin clay was investigated using different models. Pseudo fist order, pseudo second order kinetics models [18].

The linearized form of first order Lagergren equation is given as Eq. (1).

$$\log(q_e - q_t) = \log q_e - \frac{k1t}{2.303} \qquad (1)$$

The pseudo-second-order rate equation is given as Eq. (2) [19]

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (2)$$

Where
q_e - the amounts of metal adsorbed (mg/g) at equilibrium
q_t - the amount of metal adsorbed at time t(min)
k_1 – rate constant(first order)
k_2 - rate constant(second order)

The linear plots of log (q_e - q_t) versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data. Table 6 shows the comparison of pseudo first order and second order kinetic model.

Table – 3. Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Pb (II) sorption by (NC+MC) and (NC+KC) composites

Metal ion	Prepared composites	Pseudo-first-order kinetic model		Experimental value	Pseudo-second-order kinetic model	
		qe (mg/g)	k_1 (min^{-1})	qe (mg/g)	qe (mg/g)	k_2 (g mg^{-1} min^{-1})
Pb(II)	NC+MC	333	0.007833	144	194	0.0036
	NC+KC	407	0.00594	156	144	0.0040

From the results showed that the second order equation model provided the best correlation with experimental results. This fact clearly explains that the nanocomposite of chitosan with methyl cellulose and nanochitosan with clay follows the second-order kinetics model.

Furthermore, the values of correlation coefficients (R^2) for pseudo – first order kinetic model were slightly lower than the second order kinetic model [20]. So both the composites follows second order kinetic model.

CONCLUSION

From the present study, it is concluded that the nanocomposite of chitosan with methyl cellulose and nanochitosan with kaolin clay in the presence of cross linking agent acts as a good adsorbent to remove the Pb(II) ions from synthetic wastewater. And also from the FTIR, DSC studies conforms the formation of the composites. SEM studies clearly explain the surface morphology of the prepared composites. Percentage removal of Pb(II) ions depends on the initial concentration of the metal solution, pH, contact time and adsorbent dose. Nanochitosan with kaolin clay in the presence of cross linking agent is an effective adsorbent than methyl cellulose composite and also both the composite follows Frendlich isotherm. The result on kinetics data for both the composites follows second order kinetics model. So it can be concluded that cross linked nanopolymer composite of chitosan with kaolin clay can be act as a good adsorbent for the removal of Pb(II) present in the effluent water. It is evident that an adsorbent dose of 6 g/L is enough to treat wastewater with a contact time of 300min in the pH range of 6.

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