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Research Article

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Adsorption studies on the removal of Pb(II) ions using carboxymethyl chitosan Schiff base derivatives

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ABSTRACT

Chitosan based Schiff bases have received much attention now-a-days in various fields. Thus the present study deals with the synthesis and the application of carboxymethyl chitosan Schiff base derivatives for the wastewater treatment. Carboxymethyl Chitosan (CMC)/2, 3-Dimethoxy Benzaldehyde Schiff base derivative was synthesized and characterized Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) studies. FTIR analysis indicated that Schiff base reaction take place in between CMC and 2, 3-Dimethoxy Benzaldehyde. The XRD results demonstrated the appearance of a new crystallization peak of Carboxymethyl chitosan Schiff base (CMC-SB). The prepared adsorbent was used to adsorb lead (II) ions in aqueous solution. Various parameters such as adsorbent dose, initial pH, agitation period and different initial concentration of lead (II) ions which influenced the adsorption capacity were investigated. The equilibrium adsorption data were fitted to Langmuir and Freundlich isotherm models. Kinetic data correlated well with the pseudo second-order kinetic model.

Keywords: carboxymethyl chitosan, Schiff base, adsorption, lead (II) ions

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INTRODUCTION

Chitosan is a promising homo-polymer of ß-(1→4)-linked *N*-acetyl-D-glucosamine derived from chitin [1]. Chitin is the second most abundant organic compound in nature after cellulose widely distributed in marine invertebrates, insects, fungi, and yeast [2-3]. Chitosan are biodegradable, high molecular weight cationic polysaccharides degraded by lysozyme a human enzyme. Though chitosan acts as a promising material for wide range of applications, the solubility in low pH and its poor mechanical properties lower its applications. Chemical modification of chitosan changes the properties of chitosan. It includes substitution reactions, chain elongation (cross-linking, graft copolymerization, and polymer networks), and depolymerisation (chemical, physical, and enzymatic) [4].

Compared with other water-soluble chitosan derivatives, carboxymethyl chitosan (CMC) has been widely studied because of its ease of synthesis, ampholytic character and possibilities of ample of applications. Since the CMC is water soluble, it cannot be used water treatment. Thus the CMC was modified as a Schiff base derivative using 2, 3-dimethoxy benzaldehyde. The Schiff bases obtained from chitosan derivatives are of highly remarkable, because of their diverse applications. In addition, the chelating ability of such Schiff bases further enhances their application in removal of toxic heavy metal.

The metal selected for this study is lead. Lead is considered to have a stable oxidation state (Pb^{2+}) that furnishes a divalent ion. Lead pollution primarily came from cars in the past. Today, lead pollution primarily comes from lead smelters, metal processing plants and incinerators. Lead is "absorbed" into the blood plasma, where it rapidly equilibrates with extra cellular fluid. Lead can damage various systems of the body including the nervous and reproductive systems and kidneys, and it can cause high blood pressure and anemia. Thus the removal of lead becomes much essential. Therefore in the present work, carboxymethyl chitosan Schiff base was synthesized, characterized and investigated for its adsorption capacity. The results are discussed.

EXPERIMENTAL SECTION

Materials

Carboxymethyl chitosan were purchased from India Sea Foods, Cochin, Kerala, India. The aldehyde such as 2, 3-Dimethoxy Benzaldehyde was purchased from Sigma Aldrich, India. All the chemicals used were of analytical grade.

Synthesis of Carboxymethyl chitosan Schiff Bases (CMC-SB)

Carboxymethyl chitosan was dissolved in water and stirred at room temperature for 30 min. Then, 2,3-dimetoxybenzaldehyde an aromatic aldehyde was added to the mixture. The mixture was stirred and heated at 60°C for 12 h under water bath heating. After cooling, the crude product was washed with ethanol to the point of colorless filtrate. The product was dried at 60°C in vacuum for 24 h [5].

Characterization

FTIR studies

Fourier transform infrared spectra of chitosan Schiff base derivatives using KBR pellet method were recorded in the frequency range of 400 – 4000 cm^{-1} using Thermo Nicolet AVATAR 330 spectrophotometer.

X – ray diffraction studies

X – ray diffractograms of samples were obtained using an X – ray powder diffractometer (XRD – SHIMADZU XD – D1) with Ni – filter and Cu Kα radiation source. The relative intensity was recorded in the scattering range 2θ, varying from 10^o to 90^o.

Heavy metal removal by batch adsorption studies

Synthetic solutions of Pb (II) ions were taken in stopper bottles and agitated with schiff base at 30^oC in orbit shaker at fixed speed of 160rpm. The extent of heavy metal removal was investigated separately by changing adsorbent dose, contact time of shaking and changing pH of the solution. After attaining the equilibrium adsorbent was separated by filtration using filter paper and aqueous phase concentration of metal was determined with atomic adsorption spectrophotometer (Varian AAA 220 FS).

Adsorption isotherm studies

At the optimum conditions of adsorbent dose and pH, the synthetic solutions of Pb ions were agitated for one hour at various initial concentrations and amount of unadsorbed lead in the filtrate were analysed. The values were fitted into Langmuir and Freundlich adsorption isotherms.

In this study the following linearised form of the Langmuir isotherm was used.

$$C_{eq} / C_{ads} = bC_{eq} / K_L + 1/ K_L$$

and $C_{max} = K_L/b$

Where
C_{ads} = amount of metal ion adsorbed (mg/g)
C_{eq}= equilibrium concentration of metal ion in solution (mg/dm^3)
K_L =Langumir constant (dm^3/g)
b = Langumir constant ($dm^3.mg$)
C_{max}= maximum metal ion to adsorb onto 1g chitosan (mg/g).

The Freundlich equation which is used is expressed as:

$$C_{ads} = P\, C_{eq}^{1/n}$$

In and linearised form of the Freundlich equation was used.

$$\log C_{ads} = \log P + 1/n \log C_{eq}$$

where
C_{ads} = amount of metal ion adsorbed (mg/g)
C_{eq}= equilibrium concentration in solution (mg/dm^3)
1/n = Freundlich constant (mg.g^{-1})
P = Freundlich constant (g.dm^{-3})

Kinetics Studies
In the present study kinetics were calculated for both pseudo-first order, the pseudo second order kinetic models applied and expressed as follows.

Pseudo-first order kinetics
Rate expression is

$$\log(q_e-q_t) = \log q_e - \frac{K_1}{2.303}t$$

q_t and q_e are the amounts of ion adsorbed at time t and at equilibrium (mg/g).
k_1 = rate constant (min^{-1})

Pseudo-Second order Kinetics
Rate expression is

$$t/q_t = 1/k_2q_e^2 + t/q_e$$

where
k_2 = second order kinetic constant (gmg^{-1}min^{-1}).

RESULTS AND DISCUSSION

FTIR studies
Figure-1 and 2 shows the FT- IR spectrum of the Carboxymethyl chitosan and Carboxymethyl chitosan/2,3-dimethoxy benzaldehyde Schiff base. The spectrum shows a broad peak at 3420 and 3418 cm^{-1} for CMC and CMC-SB, which indicates the intermolecular hydrogen bond O-H, N-H stretching and polymeric association. Compared with pure CMC the broad peak was shifted to the lower region, this reduction in the peak position indicates that the functional groups of CMC and 2,3-dimethoxy benzaldehyde were involved in the participation of non-covalent interaction. The asymmetric C-H stretching was indicated by the peak at 2918 cm^{-1} for CMC and 2921 cm^{-1} for CMC-SB, this corresponding peak shift to the higher position reveals the incorporation of aromatic C-H bonds of aldehyde [6].

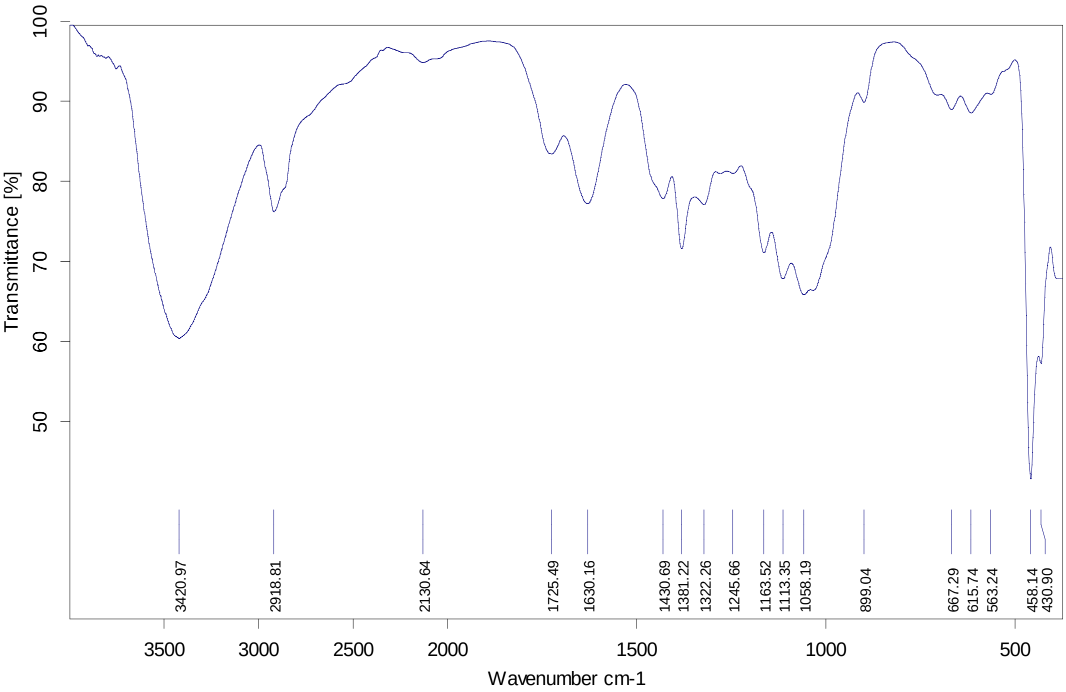

Figure 1: FTIR spectrum of Carboxymethyl Chitosan

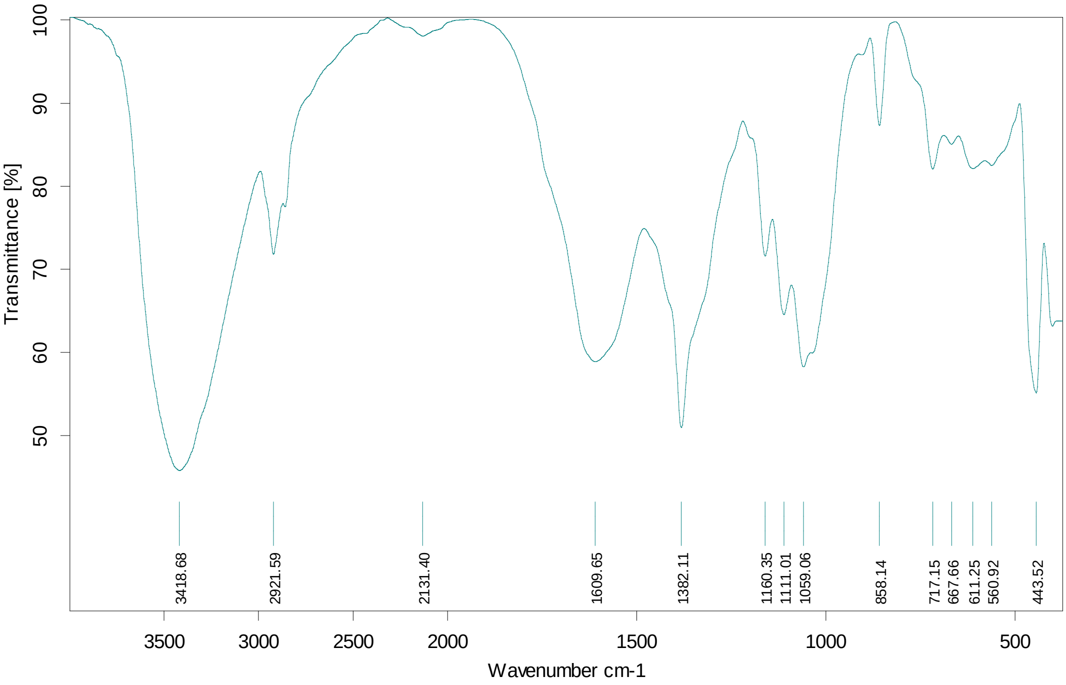

Figure 2: FTIR spectrum of Carboxymethyl Chitosan/2, 3-Dimethoxy Benzaldehyde Schiff base derivative

A characteristic peak observed at 1725 and 1630 cm^{-1} indicates the presence of C=O (COO^{-}) groups and NH$_2$ group of CMC and this peak was shifted to around 1609 cm^{-1} in the case of CMC-SB which indicated the overlapping of C=N and C=C group confirming the formation of carboxymethyl chitosan/2,3-dimethoxy benzaldehyde Schiff base compound[7]. Peaks obtained at around 1382, 1245, 1160, 1111 and 1069 cm^{-1} are due to C-H bending, OH bending, NH bending, C-O stretching, glycosidic bonds, C-O-C stretching respectively.

The FTIR spectrum of CMC and carboxymethyl chitosan Schiff base showed its characteristic peaks and the absorption band of Schiff base formation were in the range of 1598 – 1650 cm^{-1}, confirming the presence of C=N (imine) bond which was formed between the NH group the carboxymethyl chitosan matrix and with the C=O group of corresponding aldehyde. There was the reduction in the intensity of the peak for NH_2 group content which indicates the participation of the amino group of the polymer matrix with the aromatic aldehyde to form Schiff bases [8].

XRD studies

X- ray diffraction patterns of various samples were measured to investigate the change of the crystalline nature of solids. **Figure 3 and 4** shows the XRD diffractogram of Carboxymethyl chitosan and Carboxymethyl chitosan/2,3-dimethoxy benzaldehyde Schiff base. The peaks of CMC obtained at 2θ = 20°, 29° and 46° were broad. For CMC-SB the peak was shifted to 2θ = 30°, 48° and 56°, this indicates the formation of Schiff base. The peaks are broad, which indicates that the prepared schiff base has semi crystalline nature. The weak diffraction peak centered at diffraction angle 2θ-10° and sharp diffraction peak at 20° are indicative of high degree of crystalline morphology of chitosan [9], but after derivatization the crystallanity tends to decreases for CMC and further decreases for CMC-SB which makes the material suitable for wastewater treatment.

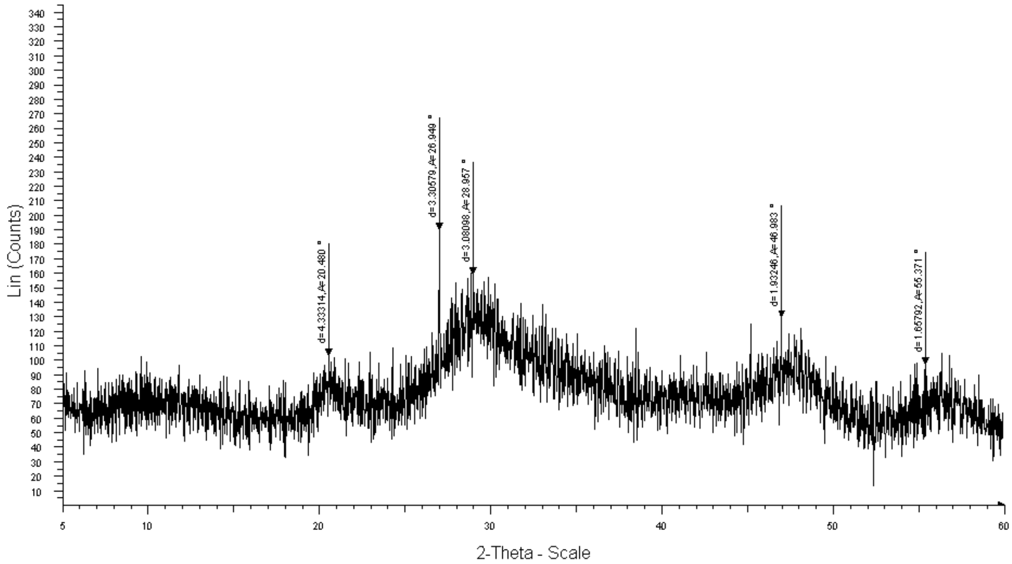

Figure 3: XRD pattern of Carboxymethyl Chitosan

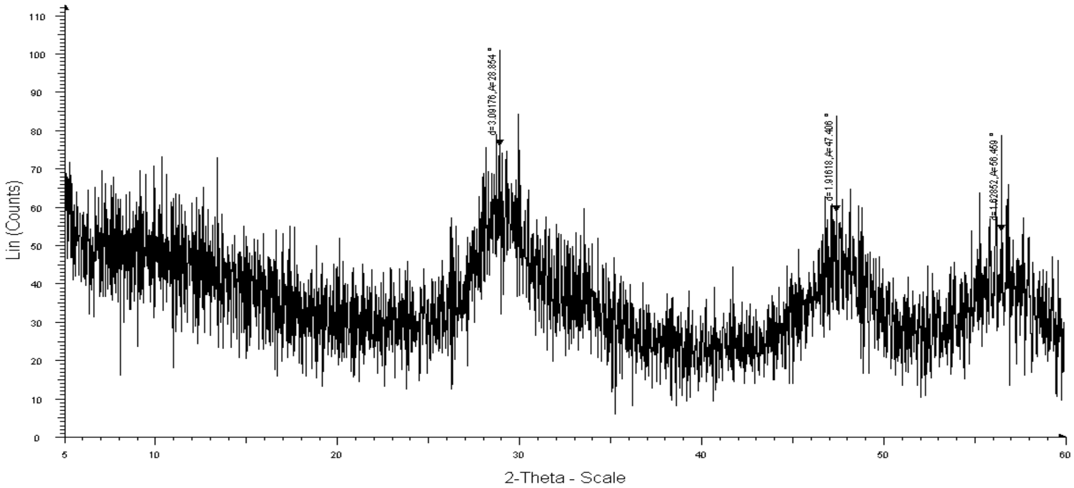

Figure 4: XRD pattern of Carboxymethyl Chitosan/2, 3-Dimethoxy Benzaldehyde Schiff base derivative

Removal of lead(II) ions

Optimum metal adsorption were determined by investigating the parameters such as initial concentration of metal ions, sorbent dosage, contact time and pH of solution at constant temperature. The equilibrium data were fit into Langumir and Freundlich adsorption isotherms. The kinetic studies were investigated using Lagergren (1898). Ho and Mckay (1998) equations. The results are discussed

Effect of adsorbent dose

The effect of the amount of adsorbent on the removal of Pb^{2+} ions is depicted in the Figure - 5. It is observed that the removal of metal ions increases with an increase in the amount of adsorbent. The amount of adsorbent dose was varied from 1 g – 6 g. The minimum percentage removal was 32.3% for a dose of 1gm and maximum value of 82.1% for the dose of 6 g. With increasing adsorbent dosage, more surface area is available for adsorption due to an increase in active sites on the adsorbent [10].

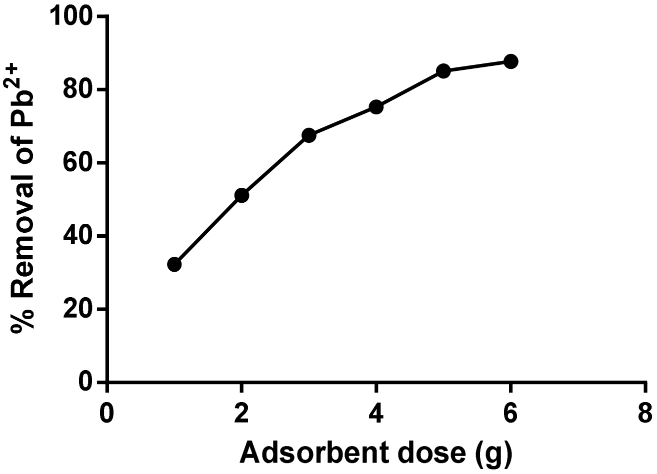

Figure 5: Effect of adsorbent dose on the removal of Pb^{2+}

Effect of pH

The effect of pH on the removal of lead (II) ions was shown in the **Figure 6**. The pH is an important parameter which obviously influences the removal efficiency of metal ions from the solution. The optimum removal was obtained at pH 5. Initially at lower pH the adsorption is very minimum, this can be explained on the basis of a competition between proton and metal ions. While on increasing the pH the adsorption increases with decrease in the concentration of H^+ ions, which compete the metal ions at lower pH. After reaching the maximum removal the decrease in adsorption at higher pH was observed this is due to formation of soluble hydroxyl complexes.

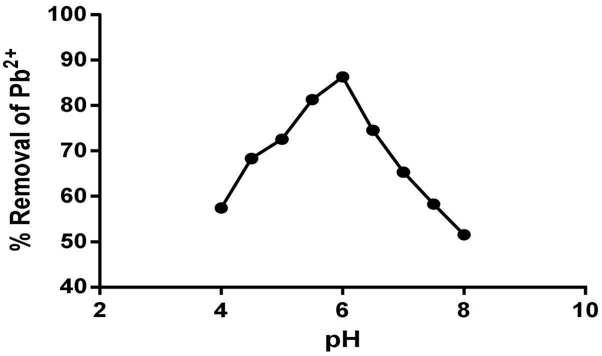

Figure 6: Effect of pH on the removal of Pb^{2+}

Effect of contact time

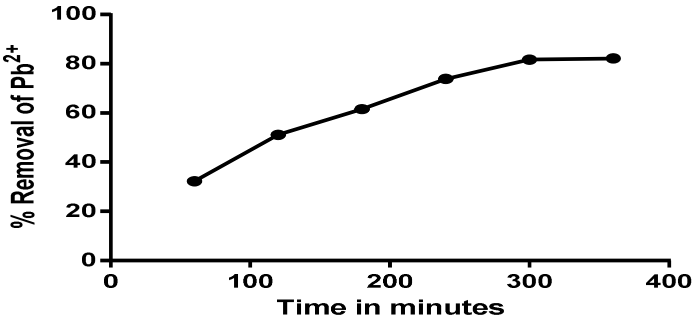

Figure 7: Effect of contact time on the removal of Pb^{2+}

The effect of contact time on the adsorption of Pb^{2+} ions onto CMC-SB was investigated by keeping the other parameters such as adsorbent dose and pH of solution as constant. The observed results are presented in **Figure - 7.** It was found that the removal of metal ions increased with increase in contact time to some extent. Further increase in contact time did not increase the percentage removal of metal ions [11]. The percentage removal of heavy metal ions remains constant after attainment of equilibrium [12]. Thus the results illustrated that the optimum contact time for maximum removal of Pb^{2+} was 360 min.

Langmuir adsorption isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. This monolayer adsorption is reversible and the adsorbed molecule cannot migrate across the surface or interact with neighboring molecules. To get the equilibrium data, initial metal concentrations were varied while the adsorbent mass in each sample was kept constant.

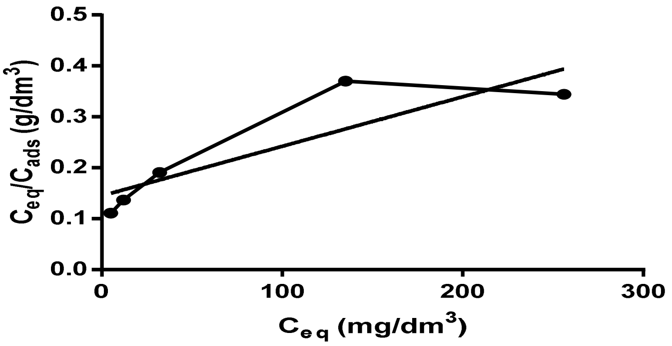

Figure 8: Langmuir isotherm model

The linearised Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant "b" and "K_L". With the help of the slope and intercept of linear plot of C_{eq} /C_{ads} against C_{eq}, the Langmuir constants K_L and b can be calculated and given in the table 1.

Table - 1: Adsorption isotherm constant, Cmax and correlation coefficients

Metal ions	Langmuir constants			
	K_L (dm^3/g)	b (dm^3/mg)	C_{max} (mg/g)	R^2
Pd(II)	0.6901	0.006704	102.94	0.7656

Freundlich isotherm

The linearised Freundlich equation plot of log q_e vs log c_e yielded a straight line as shown in **Figures –9.** The linearity of the plot supports the applicability of the Freundlich adsorption isotherm in this study. The Freundlich isotherm equation is used for the description of multilayer adsorption with the interaction between adsorbed molecules. The model predicts that the adsorbate concentration in the solution will be increasing. The model applies to the adsorption onto heterogeneous surfaces with uniform energy distribution and reversible adsorption.

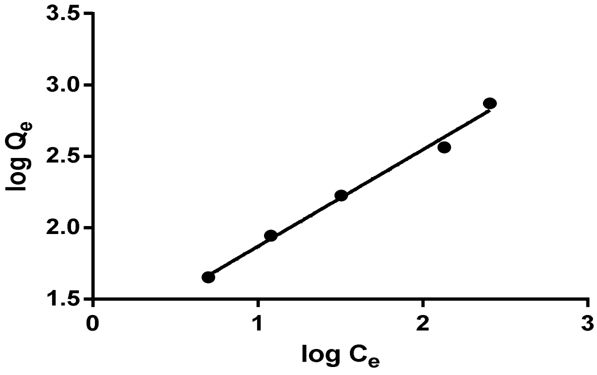

Figure 9: Freundlich isotherm model

Table 2: Coefficients of Freundlich isotherm model

Metal ions	**Freundlich constants**		
	K_F	**n**	**R^2**
Pb(II)	0.07664	1.4773	0.9910

Table 1 and 2 illustrates the linear regression coefficient of two isotherms. On comparing the Langmuir and Freundlich isotherm models, the observed R^2 values of Freundlich isotherm better describes the adsorption process very effectively when compared to the Langmuir model. Hence Freundlich model was followed and multilayer adsorption was suggests for the removal of metal ions by the CMC-SB.

Adsorption Kinetics

Kinetic analysis is required to get an insight of the rate of adsorption and the rate limiting step of the transport mechanism, which are primarily used in the modeling, and design of the process. In order to examine the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, kinetic models were used to test the experimental data.

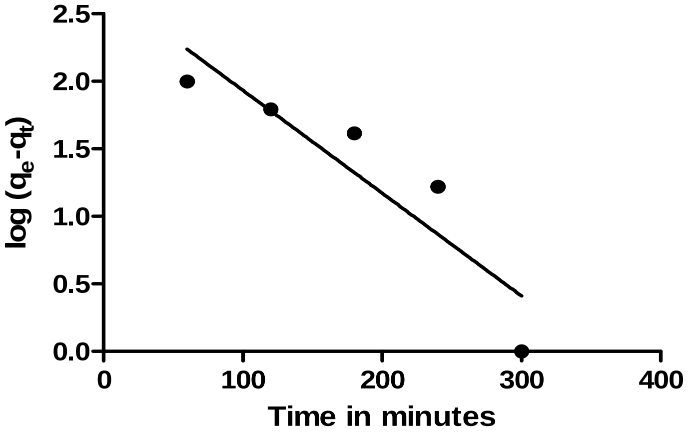

Figure 10: Pseudo-first order kinetics model

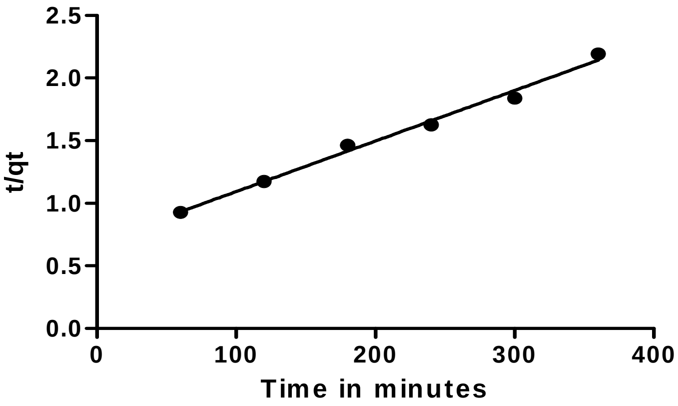

Figure 11: Pseudo-second order kinetics model

The results obtained from pseudo-first-order kinetics demonstrated that the experimental qe (mg. g^{-1}) values did not agree well with the calculated values obtained from the linear plots.

It is clear from the **Table - 3** the correlation coefficient, R^2 of pseudo second order kinetics for Pb (II) showed the better fit than pseudo first order kinetics. This confirmed that the adsorption process follows pseudo second order kinetic model.

Table 3: Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models

Metal ion	**Pseudo-first-order kinetic model**			**Experimental value qe (mg/g)**	**Pseudo-second-order kinetic model**		
	Qe (mg/g)	k_1 (min^{-1})	R^2		qe (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2
Pb (II)	354.04	0.007615	0.8275	180	170.98	0.004035	0.9907

CONCLUSION

Carboxymethyl Chitosan (CMC)/2, 3-Dimethoxy Benzaldehyde Schiff base derivative was synthesized successfully. The FTIR results proves the formation of Schiff base using CMC and with 2,3-dimethoxy benzaldehyde and XRD shows that Schiff base possess semi-crystalline nature. The crystallnity nature tends to decreases for CMC and further decreases for CMC-SB which makes the material suitable for wastewater treatment. The results showed that the adsorbent dose, pH and the contact time had a pronounced effect on the removal of Pb ions from the solution. Freundlich isotherm better describes the adsorption process very effectively and through kinetic studies we confirmed that the adsorption process follows pseudo second order kinetic model.

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