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# Studies on adsorption behavior of Cadmium onto nanochitosan-carboxymethyl cellulose blend

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## ABSTRACT

*This paper reports the removal of Cadmium ions from aqueous solutions using nanochitosan(NC)/carboxymethyl cellulose(CMC) blend. Effect of various process parameters, viz., initial metal ion concentration, pH, and adsorbent dose has been studied for the removal of Cadmium. The adsorption data have been explained in terms of Langmuir and Freundlich equations. The results revealed that the adsorptions of Cadmium onto NC/CMC blend, was found to fit well with the Freundlich isotherm. The results indicate that under the optimum conditions, the NC/CMC blend was found as an effective adsorbent for cadmium.*

**Key words:** Nanochitosan, Carboxymethyl cellulose, blend, Cadmium, Adsorption.

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## INTRODUCTION

Contamination of wastewater with metal ions such as cadmium, chromium, arsenic, nickel and zinc is an ongoing problem due to their toxicity. These metals are toxic even at very minute concentrations [1]. Presence of metal ions is of special concerns they can accumulate in different components of the environment. It is well known that heavy metals can damage nerves, liver and bones and also interfere with the normal functioning of various metallo-enzymes [2–5]. The adverse effects of cadmium on human beings include high blood pressure, kidney damage, destruction of testicular tissues and red blood cells. Cadmium ions can replace Zn (II) ions in some metallo-enzymes, thereby affecting the enzyme activity [6]. From electro-plating industries, batteries, phosphate fertilizers, mining, pigments, stabilizersand alloys, cadmium finds its way to the water streams through wastewaters [7, 8]. The permissible limits of cadmium for the discharge of wastewater is 0.1 mg $L^{-1}$ in India. From wastewater, heavy metals are usually removed by precipitation technology using hydroxides, carbonates and sulphides [9–11]. Each method has its own benefits and limitations [12, 13]. A variety of microbial and other biomass types has been reported to have good biosorption potential and such materials have been suggested for use in wastewater treatment for metal removal [14–18]. Efficient and environment friendly adsorbents are still needed to reduce heavy metal content in wastewaters to acceptable level at affordable costs.

Recently numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. The removal of metal compounds and particularly from solution by biological material is recognized as an extension to adsorption and is named as biosorption [19]. Among the polysaccharide compounds such as chitin [20], starch [21] and their derivatives chitosan [22] deserve particular attention. These polysaccharides are abundant, renewable, and biodegradable, low-cost and are the best choice in water treatment and useful tool for protecting the environment.

Chitosan is a well known solid sorbent for transition metals because the amino groups on chitosan chain can serve as coordination sites [23, 24] In addition to binding ability, it has a high content of functional groups and is produced very cheaply, since chitin is the second abundant biopolymer in nature next to cellulose [25, 26].

In this present work, we explore the novel sorbent nanochitosan (NC) and carboxymethyl cellulose (CMC) blend which has a high affinity for Cd (II) ions and fully exploit its ability in a wide range of metal concentrations. The efficient removals of metal ion by the sorbent were studied as function of pH, adsorbent dosage and contact time. The equilibrium studies of the adsorption process are evaluated.

## MATERIALS AND METHODS

### Materials

All chemicals used in the present study were of analytical reagent grade. Chitosan (from crab shells) was procured from India Seafood's, Cochin, Kerala, Carboxymethyl cellulose (CMC) was purchased from Sigma Aldrich, India. Analytical grade cadmium chloride was purchased from S.D. Fine Chemicals, Cadmium (II) ion source. Hydrochloric acid and sodium hydroxide were from Chemical Drug House Ltd., India. Millipore water is prepared in the laboratory by double distillation of deionised water in quartz distillation plant.

### Preparation of nanochitosan (NC)/carboxy methyl cellulose (CMC) blend with Glutaraldehyde as crossling agent

10 g chitosan was dissolved in 2000 ml of 2.0 % (v/v) acetic acid. 100 ml of 0.75 mg/ml TPP was dropped into the beaker. Then the solution was filtered to remove the residual TPP. The nanochitosan was washes several times in water and freeze dried. About 10 grams of CMC were slowly added to 200 ml of water stirred well and allowed to dissolve.

The NC/CMC blends were prepared by mixing NC and CMC in the weight ratio 30:1 and 10 ml of cross linking agent glutaraldehyde was added with stirring for 2 hours.

Formation of nanochitosan was proved by Scanning Electron Microscopy studies using SEM analyzer (JSM 6400; Joel. Tokyo, Japan) studies. Particle size distribution was analysed using Nanotrac 150 particle size analyzer which works based on dynamic light scattering.

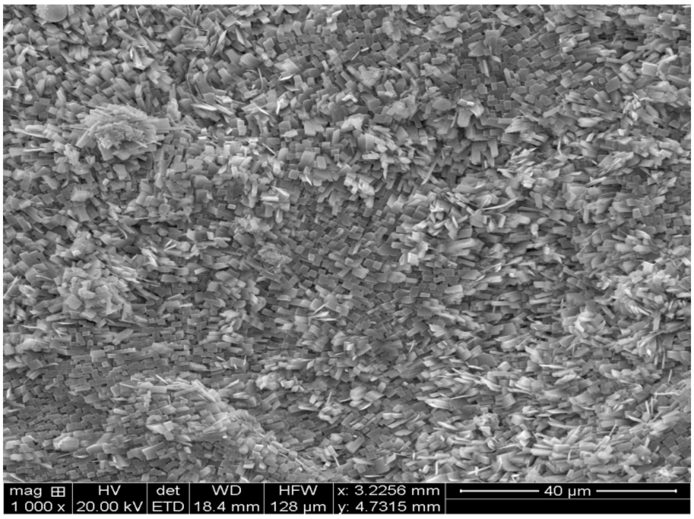


**Figure – 1: SEM image of nanochitosan**

## Preparation of Cadmium chloride solution

The stock solutions of Cd(II) was prepared to get a concentration of 200mg/L of cadmium as cadmium chloride. 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. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

## Experimental

Batch studies were performed with different concentrations of cadmium chloride to investigate the extent of adsorption. Synthetic solution of Cd (II) ion taken in stoppered bottles and agitated with the blend films at 30° C in orbit shaker at fixed speed, 160rpm. The extent of heavy metal removal was investigated separately by changing adsorption 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 220FS).

# RESULTS AND DISCUSSION

## Effect of time

The effect of contact time shows the kinetic behavior of Cd (II) ion sorption onto the sorbent NC/CMC blend. The removal efficiency of the adsorbent for Cd (II) ion is illustrated in Figure 1. The rate of Cd (II) removal was quite rapid initially, but it gradually becomes slower with passage of time reaching a maximum in 150 minutes. The initial faster rate may be due to the availability of the uncovered surface area of the adsorbent initially, since adsorption kinetics depends on the surface area of the adsorbent. In addition, the variation in the amount of Cd (II) ion removed by the adsorbents could be related to the nature and concentration of the surface groups (active sites) responsible for interaction with the cadmium ions.

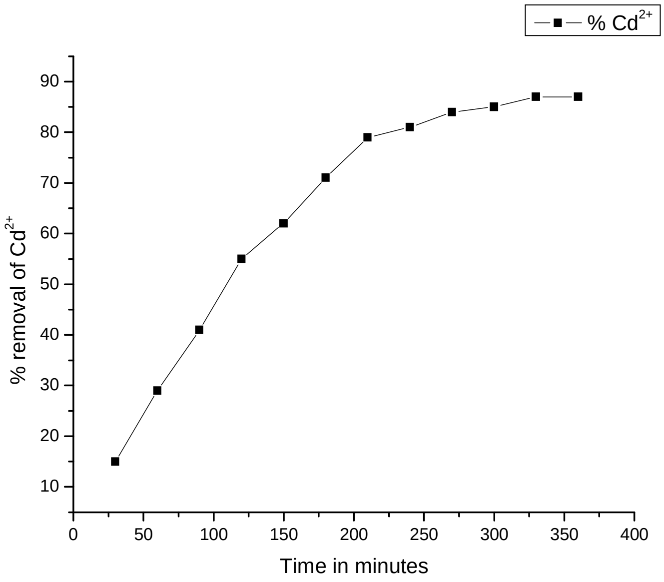


**Figure 2: Percentage removal of cadmium ion using nanochitosan/carboxymethyl cellulose blend at different time intervals**

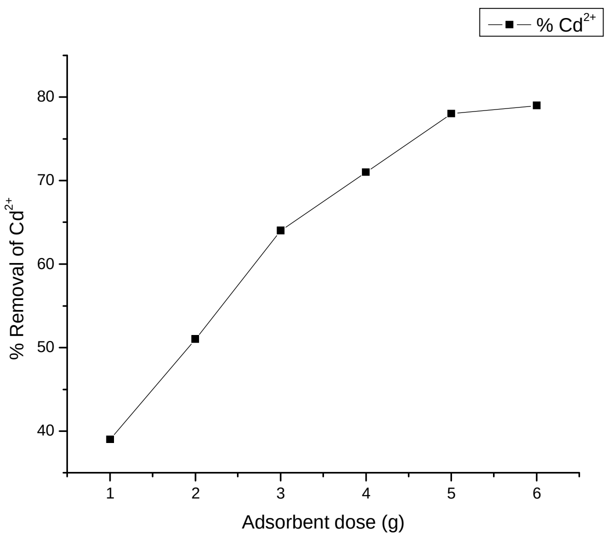


**Figure 3: Percentage removal of cadmium ion using nanochitosan/carboxymethyl cellulose blend at adsorbent dose**

## Effect of adsorbent dosage

The effect of the adsorbent dosage on the cadmium adsorption on nanochitosan/carboxymethyl cellulose blend in the presence of glutaraldehyde as cross linking agent is shown in Figure - 3. The % removal of cadmium (II) increased with the increase of the adsorbent dosage. The increase in adsorption with the increase in amount of adsorbent (NC/CMC blend) dose may be attributed to the fact that more surface area is available for adsorption to occur. The number of available adsorption sites increases by increasing the sorbent and it results an increase in removal efficiency. It can be concluded that by increasing the adsorbent dose, the removal efficiency increases.

**Effect of pH**

The role of hydrogen ion concentration was examined in solutions at different pH [27]. The pH of the solution affects the surface charge of the adsorbents [28]. The hydrogen and hydroxyl ions are adsorbed quite strongly, and therefore the adsorption of other ions is affected by the pH of the solution [29]. It was observed that with the increase in the pH of the solution, the extent of metal ions removal increased for the adsorbent. The maximum adsorption was obtained at pH 5. The concept of increasing metal removal with increasing pH can be explained on the basis of a decrease in competition between proton and metal cations for same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH is due to formation of soluble hydroxyl complexes.

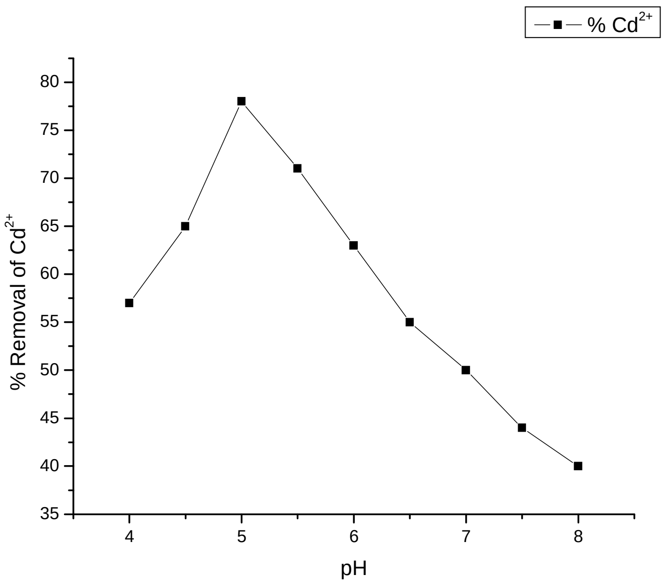


**Figure 4: Percentage removal of cadmium ion using nanochitosan/carboxymethyl cellulose blend at different pH**

**Langmuir**

The Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. This isotherm is based on the assumption that; adsorption is limited to mono-layer coverage, all surface sites are alike and can only accommodate one adsorbed molecule, the ability of a molecule to be adsorbed on a given site is independent of its neighbouring sites occupancy, adsorption is reversible and the adsorbed molecule cannot migrate across the surface or interact with neighbouring molecules [30, 31]. By applying these assumptions and the kinetic principle (rate of adsorption and desorption from the surface is equal), the Langmuir equation can be written in the following hyperbolic form,

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \qquad (1)$$

This equation is often written in different linear forms (Febrianto *et al*., 2009):

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \qquad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L\, q_{max}} \qquad (3)$$

where *qe* is the adsorption capacity at equilibrium (mg/g), *qmax* is the theoretical maximum adsorption capacity of the adsorbent (mg/g) and, as such, can be thought of as the best criterion for comparing adsorptions[32], *KL* is the Langmuir affinity constant (l/mg) and *Ce* is the supernatant equilibrium concentration of the system (mg/l). This isotherm equation has been most frequently applied in equilibrium study of adsorption, however, it should be realized that the Langmuir isotherm offers no insights into aspects of adsorption mechanism [33].

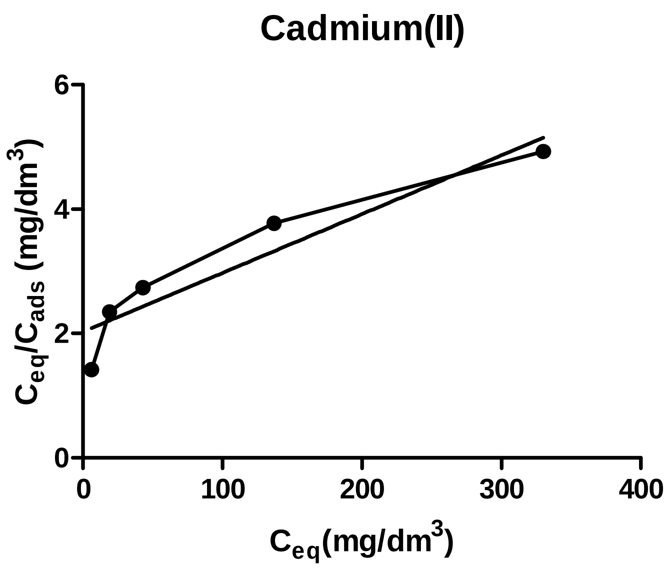


**Figure 5: Langmuir plot for the adsorption of cadmium ion onto nanochitosan/carboxy methyl cellulose blend**

## Freundlich

The Freundlich isotherm was originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation [34]. The Freundlich isotherm can describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents. According to this model the adsorbed mass per mass of adsorbent can be expressed by a power law function of the solute concentration as [35].

$q_e=K_F\, C_e^{\ 1/n}$ - (4)

where $K_F$ is the Freundlich constant related with adsorption capacity (mg/g), $n$ is the heterogeneity coefficient (dimensionless). For linearization of the data, the Freundlich equation is written in logarithmic form:

$\log q_e = \log K_F + (1/\ n) \log C_e$ - (5)

The plot of log *q*e versus log *C*e has a slope with the value of 1/*n* and an intercept magnitude of log $K_F$. On average, a favorable adsorption tends to have Freundlich constant *n* between 1 and 10. Larger value of *n* (smaller value of 1/*n*) implies stronger interaction between the adsorbent and the adsorbate while 1/*n* equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites. Linear adsorption generally occurs at very low solute concentrations and low loading of the adsorbent [36].

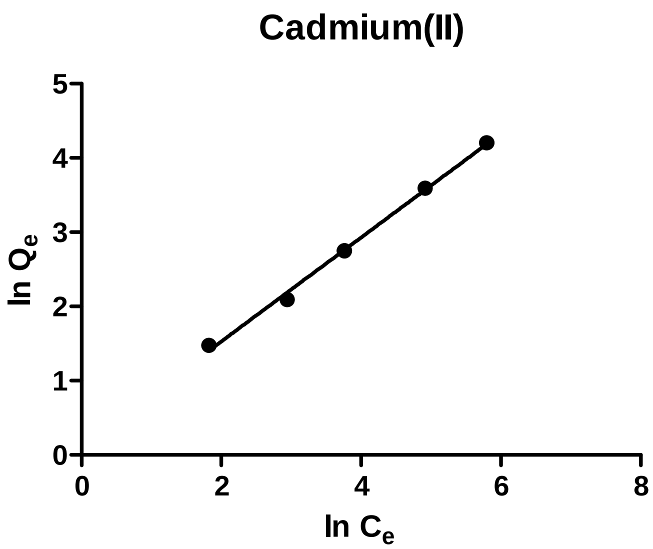


**Figure 6: Freundlich plot for the adsorption of chromium ion onto nanochitosan/carboxy methyl cellulose blend**

**Table 1: The Langmuir isotherm and Freundlich isotherm parameters of nanochitosan/carboxymethyl cellulose blend**

| **Metal ions** | **Langmuir constants** | | | | **Freundlich constants** | | |
|---|---|---|---|---|---|---|---|
| | **$K_L$ ($dm^3$/g)** | **b ($dm^3$/mg)** | **$C_{max}$ (mg/g)** | **$R^2$** | **$K_F$** | **n** | **$R^2$** |
| Cd(II) | 2.028 | 0.009453 | 214.53 | 0.8885 | 1.1384 | 1.4290 | 0.9968 |

Analysis of equilibrium data is important for developing an equation that can be used to design and optimize an operating procedure. To examine the relationship between biosorption and aqueous concentration at equilibrium, various biosorption isotherm models are widely employed for fitting the data. The Freundlich isotherm is originally empirical in nature [35], but was later interpreted as biosorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data [37]. The value of *n*, of this model, falling in the range of 1– 10 indicates favorable biosorption [38]. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations.

This isotherm does not predict any saturation of the adsorbent by the adsorbate. Thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface. The present study results indicate that the Freundlich model fit the experimental data well. The adsorption data provided an excellent fit to the Langmuir isotherm. The separation factor ($R_L$) value indicates that Cd (II) biosorption of biosorbent in this study is favorable. It can be seen from the table, *nanochitosan/carboxymethyl cellulose binary blend used* in this study has high biosorption capacity.

## CONCLUSION

The potential use of NC/CMC as an adsorbent for cadmium was studied. This new biosorbent is able to remove the cadmium ions from aqueous solutions, and the sorption capacity was strongly dependent on the adsorbent nature, and dosage, initial metal ions concentration and initial pH, The experimental data well fitted to Freundlich and Langmuir equations, with good correlation coefficients. These results can be helpful in designing a waste water system for the removal of metal ions.

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