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Research Article

# REMOVAL OF CADMIUM FROM THE AQUEOUS SOLUTION USING CHITIN/POLYETHYLENE GLYCOL /CARBOXY METHYL CELLULOSE TERNARY BLEND

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**Abstract**

This paper reports the removal of Cadmium ions from aqueous solutions using chitin/polyethylene glycol and Carboxy methyl Cellulose Ternary blend. Effect of various process parameters such as initial metal ion concentration, pH, adsorbent dose and contact time has been studied for the removal of Cadmium. Experimental data were analysed by Langmuir and Freundlich adsorption isotherms. The characteristic parameters and related correlation coefficients have been determined. The isotherm study revealed that the adsorption equilibrium is well-fitted to the Freundlich isotherm. Pseudo-first- and -second-order kinetic models were used for describing kinetic data. The results indicate that under the optimum conditions, the chitin/polyethylene glycol and Carboxy methyl Cellulose Ternary blend was found as a favorable adsorbent for cadmium.

**Keywords:** Cadmium ions, chitin/polyethylene glycol, various process parameters, Freundlich isotherm

## Introduction

Chitin is a long chain polymer of N- Acetyl glucosamine, a derivative of glucose **[1]** second most naturally available material next to cellulose. It is a hard, white, inelastic, nitrogeneous polysaccharide having biodegradability, biocompatibility, non toxicity and metal adsorption properties **[2].** Chitin has involved remarkable consideration in the areas of agriculture, pharmaceuticals, biotechnology and water purification. The major source of chitin is from crab or shrimp shells and fungal mycelia. Chitin is insoluble polysaccharide having the properties same as cellulose in its solubility and less chemical reactivity.

A wide range of natural materials such as seaweed, alginate, dead biomass, rice hulls, chitin, chitosan have been studied because of their ability to adsorb heavy metals and their low- cost **[3 - 7].**

Heavy metals are the *d*-block elements (transition metals) of the periodic table. Many are also known to be toxic to both humans and other living forms, with their accumulation over time causing damage to the kidney, liver, and reproductive system in addition to cancer **[8].** Heavy metals are released into the environment by activities of people and high levels of these metals constitute a great risk for the aquatic ecosystem and human. Heavy metals are dangerous because they tend to *bioaccumulation.* Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment.

Comparatively cadmium is also an extremely toxic heavy metal commonly found in industrial workplaces. The Cd absorption by inhalation or ingestion can cause irreversible damage to several vital organs, among which the most sensitive are the kidney, the bone and the respiratory tract **[9].** Different types of methods have been proposed for the treatment of water and industrial waste water containing heavy metals**[10]** such as biological treatments, procedures using a filtration membrane, advanced oxidation processes, electrochemical methods and adsorption processes have proven to be more viable alternative due to low cost of processing and instrumentation, ease of operation and no need for large facilities **[11].**Considerable amount of world production of chitin, chitosan and derivatives are used in wastewater treatment **[12].** In textile industry, chitin can be used in printing and finishing preparations, while chitosan is able to remove dyes from dye processing effluents **[1, 13].** Consequently chitin may be used in wastewater treatment for the removal of cations such as Cd ions **[14].** One of the most important properties of chitin is its ability to remove metal ion **[15].** Their structure allows excellent complexation capacity with metal ions, particularly transition and post-transition metals **[16].** It was supported that the chelation of a single metal ion by several -NH or $NHCOCH_3$ groups effectively isolates each metal ion from its neighbors **[17].**

The aim of this study is the preparation of chitin/polyethylene glycol and Carboxy methyl Cellulose Ternary blend from chitin biopolymer in controlled experimental condition to use as an adsorbent for the uptake of heavy metal $Cd^{2+}$ ion.

## Materials and Methods

### Materials

Chitin (99%) was obtained from India sea foods, Cochin, Kerala. All the chemicals used in the present study were of analytical reagent grade. Polyethylene glycol and Carboxy methyl Cellulose 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 was prepared in the laboratory by double distillation of deionised water in quartz distillation plant.

### Preparation of chitin/polyethylene glycol and Carboxy methyl Cellulose Ternary blend

The chitin, polyethylene glycol and Carboxy methyl Cellulose Ternary blend was prepared by mixing solutions of chitin with polyethylene glycol and Carboxy methyl Cellulose solution in the various weight ratio at room temperature in moderate agitation for about 30 minutes in the presence of 10 ml glutaraldehyde, cross linking agent. The solution was stirred well and then allowed to dry in a petridish to get chitin/polyethylene glycol/Carboxy methyl Cellulose ternary blend.

### Preparation of metal solution

200 mg/L concentration of cadmium chloride stock solution was prepared. Cadmium chloride was used as the source of Cd(II) ion in the synthetic wastewater. The solubility of Cadmium chloride in water is due to the formation of complex ions such as $[CdCl_4]^{2-}$. Because of this behavior, $CdCl_2$ is a mild Lewis acid **[18].** 1:1 Hydrochloric acid and 2N 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.

### Adsorption experiment

Batch adsorption studies were performed to investigate the extent of cadmium removal using know weight of chitin/polyethylene glycol and Carboxy methyl Cellulose Ternary blend in contact with known volume of synthetic heavy metal solution by varying the parameters such as pH, adsorbent dose, contact time and initial concentration of metal ion solution. Synthetic solution of Cd(II) ion taken in Stoppard bottles and agitated with the blend films at 30°C in orbit shaker at fixed speed of 160 rpm. After attaining the equilibrium adsorbent was separated by filtration using filter paper and aqueous phase concentration of metal was determined with atomic absorption spectrophotometer (Varian AAA 220FS).

The change in Cadmium ion concentration due to adsorption was determined using Atomic Absorption Spectrophotometer (AAS). The percentage removal of Cd was calculated using the equation

$$\text{Percentage Cd removal} = ((Co-Ce)/Co)*100$$

Where Co and Ce are the initial and equilibrium concentration of Cd(II) solution (mg/L) respectively.

## Results and Discussion

### Effect of adsorbent dose

The dependence of the dosage of adsorbent used on the adsorption of Cd(II) ions was studied and the results are shown in Fig. 1. The amount of adsorbents used were varied from 1 g to 6 g while the other parameters such as pH, agitation period and agitation rate are kept constant. The percentage of Cd(II) ions removal increases with an increase in the adsorbent's dosage. This may be due to by increasing the adsorbent's dosage, the number of adsorption sites available for adsorbent–adsorbate interaction is increased as well **[19].**

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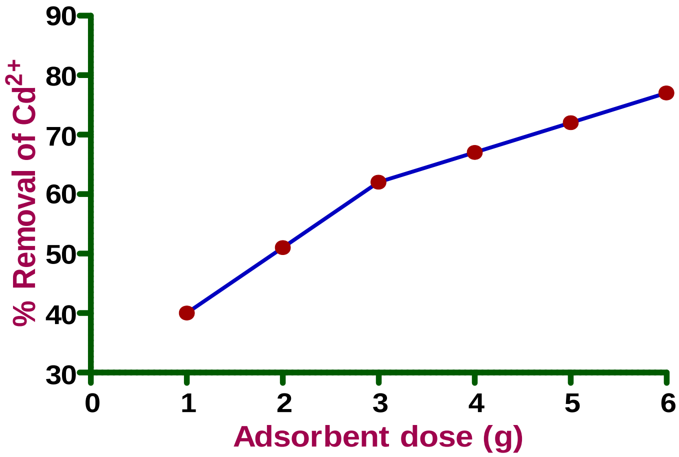


**Figure 1: Effect of adsorbent dose on the removal of Cd(II) ion using Ternary blend**

The adsorption capacity tends to a decrease after certain extent, which is due to an increase in the adsorbent's dosage at constant Cd (II) ions concentration and volume, will lead to Un-saturation of the adsorption sites and also due to the particulate interaction such as aggregation resulting from high adsorbent dosage contributes to this observation. Moreover, the surface metal ions concentration (on adsorbent) and the solution metal ion concentration come to equilibrium with one another **[20, 21].**

**Effect of pH**

The adsorption of Cd (II) ions onto the adsorbents varies with initial pH, due to the nature of chemical interactions with the functional group present on the chitin matrix. Effect of pH on the adsorption characteristics was determined in the pH range 4-8, and the studies shows that the system is strongly pH dependent. The adsorption capacity of Cd(II) ions onto the adsorbent increased with an increase in the initial pH value of the solution. At PH =6 its shows maximum adsorption

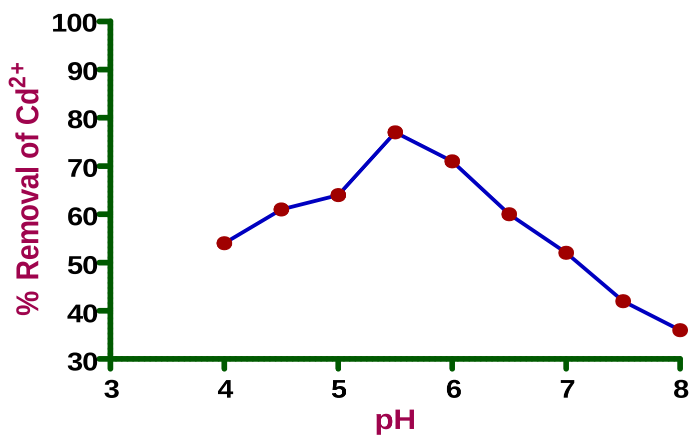


**Figure 2: Effect of pH on the removal of Cd (II) ion using Ternary blend**

As shown in Figure 2, the optimal uptake of free ionic Cd occurs at pH 5.5 and then declining at higher pH. At pH 6, the strong electrostatic interaction with the positively charged functional groups of chitin and will cadmium occur, therefore increases Cd(II) uptake. At pH values higher than 7, precipitation of Cd (II) ions as Cd $(OH)_2$ occurs simultaneously and could lead to inaccurate interpretation of adsorption.

**Effect of contact time**

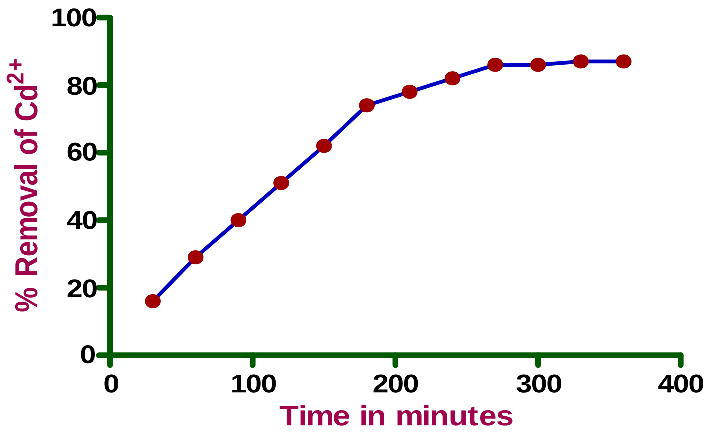


**Figure 3: Effect of contact time on the removal of Cd(II) ion using Ternary blend**

The amount of time required for an adsorption process was studied to know the optimum time required for Cd(II) ion removal. The time factor is also an important parameter which increases the adsorption efficiency of the adsorbent to attain economic compatibility. It can be seen form Figure 3 that there was a rapid uptake with increasing the contact time and adsorption equilibrium was attained within 210 min. Therefore, 210 min of contact time was chosen as the optimum contact time for chitin/polyethylene glycol binary blend.

**Equilibrium kinetics study**

In order to investigate the mechanism of adsorption, the pseudo-first order and pseudo-second order model were used to study the experimental data obtained. The pseudo-first order model of Lagergren is given as

$dq_t / d_t = k_1 (q_e - q_t)$ -------- (1)

where $k_1$ is the first-order-rate constant. Integrating Eq. (1) with respect to integration conditions

$\log (q_e - q_t) = \log q_e - k_1 t/2.303$ ------------- (2)

where $q_e$ and $q_t$ (mg/g) are the amounts of cadmium adsorbed on the adsorbent at equilibrium and time $t$, in mg/g, and $k_1$ ($min^{-1}$) is the rate constant of first-order adsorption. The slope and intercept of the plot of $\log(q_e - q_t)$ versus $t$ (Figure 4) for both the bio-sorbents were used to determine the values of $q_e$ and $k_1$ as shown in Table 1. The coefficients of correlation for the first-order-kinetic model were not high. Also, the estimated values of $q_e$ calculated from the equation differed from the experimental values (Table. 1), which shows that the model is not appropriate to describe the adsorption process.

The pseudo-second order equation **[22]** may be expressed as

$t/q_t = 1/k_2 . qe^2 + 1/q_e$ ---------(3)

where $k_2$ is the rate constant of second order adsorption (g $mg^{-1}$ $min^{-1}$). The straight line plots of t/qt against t have been tested to obtain rate parameters and it suggests the applicability of this kinetic model to fit the experimental data (Figures 5).

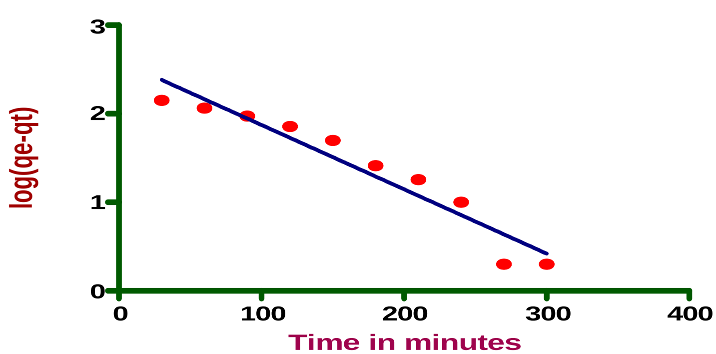


**Figure 4: Pseudo-first-order kinetics of Cd(II) ion removal using chitin/PEG/CMC blend**

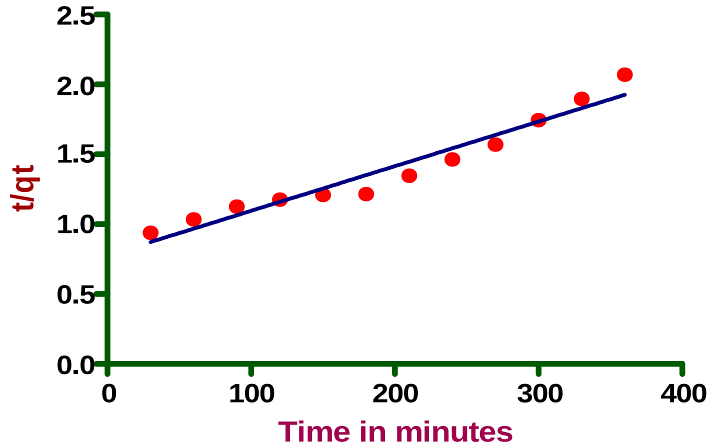


**Figure 5: Pseudo-second-order kinetics of Cd(II) ion removal Using chitin/PEG/CMC blend**

**Table – 1. Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Cd (II) sorption by chitin/polyethylene glycol blend**

| **Metal ion** | **Pseudo-first-order kinetic model** | | | **Experimental value** | **Pseudo-second-order kinetic model** | | |
|---|---|---|---|---|---|---|---|
| | **qe (mg/g)** | **$k_1$ ($min^{-1}$)** | **$R^2$** | **qe (mg/g)** | **qe (mg/g)** | **$k_2$ (g $mg^{-1}$ $min^{-1}$)** | **$R^2$** |
| Cd(II) | 350.54 | 0.007149 | 0.9496 | 164 | 170.52 | 0.003694 | 0.9504 |

The value of correlation coefficient $R^2$ for the pseudo-second-order adsorption model is relatively high, and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of $R^2$ for the pseudo-first-order are not satisfactory. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of cadmium by **chitin/PEG/CMC** blend.

## Adsorption isotherms

Adsorption isotherms are the mathematical models that explain the relationship between the adsorbent and adsorbate. The equilibrium data are plotted in the form of an adsorption isotherm. Based on a set of assumptions, that is related to the heterogeneity/homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate species. Most adsorption works adopt either the Langmuir or Freundlich isotherm (or both) for adsorption data correlation. The Langmuir isotherm is valid for dynamic equilibrium adsorption–desorption processes on completely homogeneous surfaces with negligible interaction between adsorbed molecules that exhibit the form

$C_{ads} = (K_L C_{eq})/(1 + bC_{eq})$ ------ (4)

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

$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L$ ------- (5)

And

$C_{max} = K_L/b$ --------- (6)

where:
$C_{ads}$ = amount of Cd (II) adsorbed ($mg \cdot g^{-1}$)
$C_{eq}$ = equilibrium concentration of Cd (II) in solution ($mg \cdot dm^{-3}$)
$K_L$ = Langmuir constant ($dm^3 \cdot g^{-1}$)
$b$ = Langmuir constant ($dm^3 \cdot mg$)
$C_{max}$ = maximum Cd (II) to adsorb onto 1 g chitosan ($mg \cdot g^{-1}$).

The constant $b$ in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant $K_L$ can be used to determine the enthalpy of adsorption. A plot of $C_{eq}/C_{ads}$ vs. $C_{eq}$ yielded a straight line (see Fig. 6), confirming the applicability of the Langmuir adsorption isotherm.

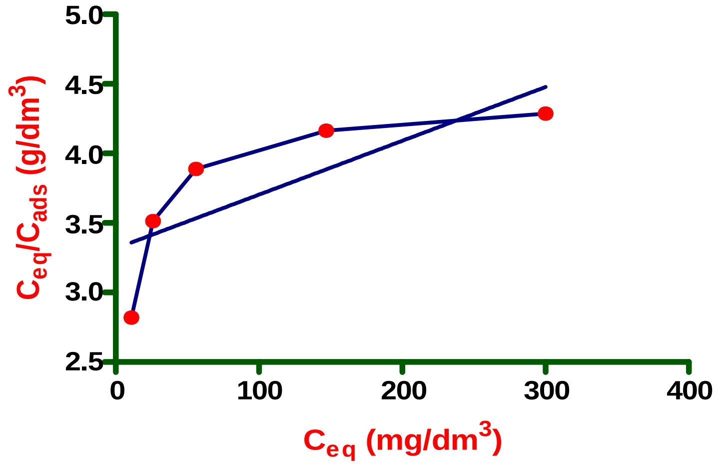


**Figure 6: Langmuir isotherm for Cd (II) ion removal**

The values of $K_L$ and *b* were obtained by a least square fit. Figure 6 shows the Langmuir isotherm fitted on the experimental data. However, a Freundlich equation plot of log $C_{ads}$ vs. log $C_{eq}$ yielded a straighter line as shown in Figure 7. The linearity of the plot supports the applicability of the Freundlich adsorption isotherm in this study. The Freundlich equation which is used to describe heterogeneous surface energies, is expressed as:

$C_{ads} = K_F C_{eq}^{1/n}$ ------- (7)

In this study the following linearised form of the Freundlich equation was used.

log $C_{ads}$ = log $K_F$ + 1/n log $C_{eq}$ ------ (8)

where:

$C_{ads}$ = amount of Cu (II) adsorbed ($mg \cdot g^{-1}$)
$C_{eq}$ = equilibrium concentration in solution ($mg \cdot dm^{-3}$)
1/n = Freundlich constant ($mg \cdot g^{-1}$)
$K_F$ = Freundlich constant ($g \cdot dm^{-3}$)

From Figure 7 it is evident that the values of 1/*n* and $K_F$, which are rough measurements of the adsorption intensity and adsorption capacity of the adsorbent, have been determined by the least-square fit.

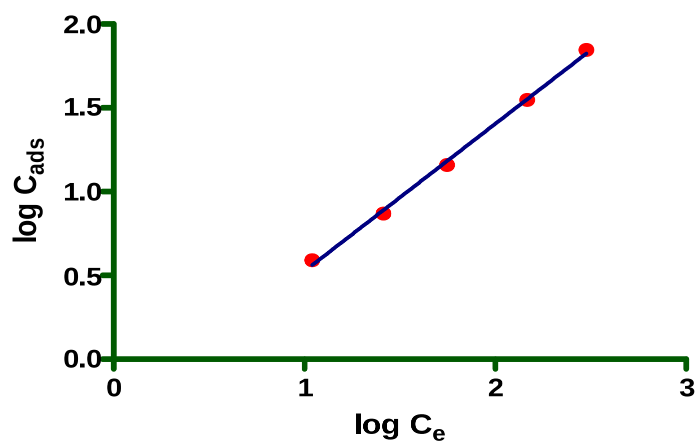


**Figure 7: Freundlich isotherm for Cd (II) ion removal**

**Table 2- Adsorption isotherm constant, $C_{max}$ and correlation coefficients**

| 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) | 0.4057 | 0.0013076 | 310.26 | 0.7240 | 0.5415 | 1.1121 | 0.9989 |

From the table, it is found that the adsorption of Cd (II) ions onto the adsorbent correlates well with the Freundlich equation as compared to Langmuir equation under the various concentration ranges studied. Also, the Freundlich constant n shows the feasibility of heterogeneous adsorption.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, $R_L$ that is used to predict if an adsorption system is “favourable” or "unfavourable" **[23].** The separation factor, $R_L$ is defined by:

$$R_L = 1/(1+bC_f)$$

where $C_f$ is the final metal ion concentration (ppm) and *b* is the Langmuir adsorption equilibrium constant ($dm^3\ mg^{-1}$). The $R_L$ values are calculated and are found in the range of $0 < R_L < 1$, which indicates that the adsorption of Cd (II) onto chitin/polyethylene glycol blend is favourable. Thus, **chitin/PEG/CMC** blend is a good adsorbent.

## Conclusion

The novel **chitin/PEG/CMC** Ternary blend as new bio-sorbent for cadmium was studied. It removes cadmium ions from aqueous solutions, and the sorption capacity was strongly dependent on the adsorbent nature, dosage, initial metal ions concentration and initial pH. The experimental data well fitted to Freundlich and Langmuir equations, with good correlation coefficients. The better fit was with Freundlich isotherm equation indicating the favorability of multilayer adsorption and also it follows pseudo-second-order kinetics. These results can be helpful in designing a wastewater system for the removal of metal ions.

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