Batch adsorptive removal of copper (II) using carboxymethyl cellulose (CMC), polyethylene glycol (PEG) and montmorillonite (MMT) clay ternary blend

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ABSTRACT

Heavy metal contamination of water resource is of great concern because of the toxic effect to human beings, and other animals and plants in the environment at even very low concentrations. Polymer blending is a very important and widely used method for the modification of polymer materials. In the present work ternary blend of Carboxymethyl cellulose, Polyethylene glycol and Montmorillonite clay was prepared with the crosslinker glutaraldehyde by sol gel method in 1:1:1 ratio and characterized using FTIR spectroscopy, X-Ray diffraction studies, Thermo gravimetric analysis, Differential scanning analysis and Scanning Electron microscopic analysis. Removal of heavy metal copper from aqueous solution using the prepared ternary blend was carried out and the adsorption efficiency was analyzed by varying initial metal ion concentration, adsorption dose, contact time and pH. Isotherm models such as Langmuir and Freundlich were used and equilibrium kinetics studies were also done. The studies revealed that the adsorption data fitted well in Freundlich adsorption isotherm and found to follow pseudo second order.

Keywords: Carboxymethyl cellulose, Polyethylene glycol, Montmorillonite clay, Isotherm model, kinetics studies.

INTRODUCTION

Water pollution is one of the life threatening problems all over the world. Water gets polluted due to the natural and anthropogenic process. The main pollutants are the untreated effluents containing toxic heavy metals from various industrial wastewaters such as metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the glass production industry. Among the various contaminants of water, heavy metals are getting importance for their non-degradable nature and often accumulate through tropic level causing deleterious biological effect [1].

Owing to the toxic effects of heavy metals, the industries are advised to treat the wastewaters systematically to remove/minimize the metal contents in their wastes [2]. Various methods were reviewed by recent researchers for the removal of heavy metals such as chemical precipitation [3], ion exchange, reverse osmosis, electro dialysis, membrane process [4], adsorption, nanofiltration, coagulation and flocculation [5], floatation [6] etc. As a result, recent research has been focused on development of cost effective alternatives. Adsorption [7] processes have been investigated as an efficient low cost [8], easy operation and little use of chemical additives, as well as the possibility of reusing the adsorbent materials and efficient method to remove heavy metals from aqueous solution. Biosorption is one such technique wherein the heavy metals are adsorbed and assimilated by biomaterials which occur in nature. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement, and regeneration of biosorbent and the possibility of metal recovery [9].
The natural polymers, cellulosic are envisioned as the most suitable ways to solve the environment related issues. The components which are present in natural fibers are cellulose (α-cellulose) hemicelluloses, lignin, pectin and waxes [10]. Generally the chemical or thermo chemical modifications have done with cellulosic raw materials which render them more effectively for the collection and binding of various metal ions.

Polyethylene glycol is a polyether compound also been known as polyethylene oxide (PEO) or polyoxyethylene (POE) has many unique properties which make it an ideal choice. The addition of inorganic fillers into polymers is well known as an economical way to improve the properties of the polymers [11].

The inorganic clay such as kaolin, mica, vermiculite, bentonite, sepiolite, diatomite and rectorite have been introduced into polymeric network to form organic inorganic composite. Clay minerals possess excellent properties such as low or null toxicity, good biocompatibility, and promise for controlled release, thus give rise to the incessant interest to their development for biological purposes. These applications are mainly based on high cation exchange capacity, excellent swelling property, remarkable hydration ability, and structural plasticity of the cationic clays.

Clay is a cheap natural raw material that has been widely used for many years as inorganic filler for plastics and rubbers to reduce the polymer consumption and cost.

Montmorillonite is a 2:1 layer-type clay mineral and its basic structural unit is composed of two tetrahedrally coordinated sheets of silicon ions surrounding a sandwiched octahedrally coordinated sheet of aluminum ions [12]. It is chemically hydrated sodium calcium aluminium magnesium silicate hydroxide (Na, Ca) 0.33(Al, Mg) 2(Si4O10) (OH) 2·nH2O. Its advantages of a high surface area, large aspect ratio and a platelet thickness of 10 Å make it suitable for reinforcement purposes [13]. The parallel layers in these structures are linked together by weak electrostatic forces. With many outstanding properties such as high specific surface area, high cation exchange capacity, layered structure, chemical and mechanical stability [14-17].

In the present investigation polymeric blends of CMC/PEG/MMT were synthesized, characterized and has been used as the adsorbent for the sorption process of copper from aqueous solution. It includes batch adsorption equilibrium to study the effect of pH, contact time, adsorbent dose and metal ion concentration.

**EXPERIMENTAL SECTION**

Carboxymethyl cellulose, Polyethylene glycol and Montmorillonite clay were purchased from Sigma Aldrich, Bangalore and all the other chemicals were of analytical grade and used as received without further purification.

**Preparation of carboxymethyl cellulose / polyethylene glycol / montmorillonite clay ternary blend with glutaraldehyde (1:1:1)**

1gm of Carboxymethyl cellulose and 1gm of polyethylene glycol were dissolved in minimum amount of water. 1gm of montmorillonite clay mixed in water was also added. The three were mixed and stirred for 20 minutes. 5ml of the cross linking agent glutaraldehyde was added to the above mixture and stirred for 30 minutes. The solution was cast on plastic weighing boats and dried in vacuum for 10 h to remove the formic acid.

**Characterization of the polymer blends**

**FTIR studies**

Fourier Transform Infra-Red spectra of the ternary blend of carboxymethyl cellulose were recorded in the frequency range of 400–4000 cm⁻¹ using Thermo Nicolet AVATAR 330 spectrophotometer. The sample was pressed into pellets with KBr.

**X – ray diffraction studies**

X – ray diffractograms of powdered samples were obtained using an X - ray powder diffractometer (XRD – SHIMADZU XD – D1) with Ni – filter, Cu Ka, radiation source. The relative intensity was recorded in the scattering range 20 of 10 – 90°.

**Thermo gravimetric analysis**

Thermo gravimetric analysis of the ternary blend of carboxymethyl cellulose was conducted by SOT Q600. V8.0 Build 95 to measure the weight loss at different temperatures with the heating range 20-850°C and rate 20°C per minute.
Differential scanning calorimetric analysis
The thermal behavior of the blend was studied using NET 2 SCH DSC thermal analyzer. The sample was inserted into the Al pan and DSC scan was made from 30 – 300°C in nitrogen atmosphere at a heating rate of 20°C min⁻¹. The results were recorded and analyzed.

Heavy metal removal by batch adsorption studies
Synthetic solution of Cu (II) ions was taken in stoppered bottles and agitated with blend films at 30°C in orbit shaker at fixed speed of 160 rpm. The extent of heavy metal removal was investigated separately by changing absorbent 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).

RESULTS AND DISCUSSION

FTIR studies
As shown in Figure 1, the spectrum of CMC/PEG/MMC – GLU (1:1:1) shows a broad band at 3442 cm⁻¹ which is due to the OH stretching vibration. The band at 1604 cm⁻¹ is assigned for the C=O stretching. The bands at 2919 and 2850 cm⁻¹ are due to asymmetric and symmetric CH stretching modes of vibration. The band at 1416 cm⁻¹ corresponds to CH₂ bending. Compared with the pure CMC, the peaks of the prepared blends were shifted which indicates the physical versus chemical interaction would have taken place during blending.

![Figure 1: FTIR spectrum of CMC/PEG/MMC – GLU (1:1:1)](image)

XRD studies
![Figure 2: XRD diffractogram of CMC/PEG/MMC – GLU (1:1:1)](image)
The change in the crystalline nature of the prepared CMC/PEG/MMC – GLU blend was studied in the X-ray diffraction studies. The XRD pattern of the CMC/PEG/MMC – GLU (1:1:1) blend (Figure-2) shows peaks at various 2θ values such as 18.55°, 22.7°, 31.5°, 33.25° and 42°. The broad peak at around 2θ = 42° reveals the lower percentage degree of crystallinity values, which confirms the amorphous nature and the suitability for adsorption process.

TGA analysis

![TGA thermogram of CMC/PEG/MMC – GLU (1:1:1)](image)

The TGA thermogram of CMC/PEG/MMC – GLU (1:1:1) blend was represented in the Figure-3. Initially the degradation takes place in the range of 30°C -100°C shows about 4 - 5% weight loss due to the evaporation of loosely bound water molecules from the samples. The second stage is a predominant one, were the maximum weight loss which has taken place indicating the elimination of small molecules. The maximum decomposition takes place at the temperature range from 150 to 300°C. In the third stage, the breakdown of the polymeric backbone takes place at around 350 to 800 °C. At the end of the experiment around 36.8% of the sample remains as the residue confirming that the prepared blend has higher thermal stability.

DSC studies

![DSC thermogram of CMC/PEG/MMC – GLU (1:1:1)](image)
The Figure 4 shows the DSC thermogram of CMC/PEG/MMC – GLU (1:1:1) blend. Broad endothermic peak was observed at the temperature of 112.4 °C indicates the crystallization of the blended polymers as well as evaporation of water in the films. The single glass transition temperature was appeared at 200°C which shows the polymer miscibility and compatibility of the prepared material. There is no exothermic peak till 300°C showing the improved thermal stability of the blend.

Effect of adsorbent dose
The effect of adsorbent dose on the removal of copper (II) ion was investigated by varying the amount of CMC/PEG/MMC – GLU (1:1:1) blend from 1 to 6 g, while keeping other parameters such as pH, initial metal ion concentration and contact time as constant. From Figure-5, it was evident that the removal percentage of copper (II) ion increases with increasing the adsorbent dose from 1g to 5g.

Effect of contact time
The effect of contact time on the adsorption of Cu $^{2+}$ ions onto the synthesized CMC/PEG/MMC – GLU (1:1:1) blend was represented in figure-6. The increase in initial adsorption rate of copper was observed at the beginning until 360 min, thereafter, the adsorption rate became constant. Further increase in contact time does not show that much increase in metal ion uptake. The progressive increase in adsorption and consequently the attainment of
equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of synthesized CMC/PEG/MMC – GLU (1:1:1) blend [20]. The obtained results clearly indicate that Cu (II) removal was increased from 38.2% to 91.6% with the contact time variation from 60 to 360 min, respectively. The observed results illustrated that the optimum contact time for maximum removal of Cu (II) was 240 minutes.

Effect of pH
The pH of aqueous solution strongly affects the uptake and percentage removal of metals from the aqueous solution [21,22]. The effect of pH on adsorption process was investigated by varying the pH of the metal solution from 4 to 8, while keeping other parameters constant. Figure 7 shows the influence of solution pH on the adsorption of CMC/PEG/MMC – GLU (1:1:1) blend for Cu$^{2+}$ ion from aqueous solution. The results revealed that the adsorption increases with an increase in pH of the metal ion solution initially (from pH: 4 to 5) but thereafter it declines (pH>5). The optimum pH for removal of Cu (II) ion was found to be 5. At pH 4, minimum adsorption occurs due to the H$^+$ adsorption compared to M(II) ions. After pH 5, the drastic decrease in adsorption was attributed to the formation of soluble hydroxyl complexes which will ultimately lead to the reduction in sorption capacity of metal ions.

![Figure 7: Effect of pH of CMC/PEG/MMC – GLU (1:1:1)](image)

Adsorption isotherms
Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and kinetics. An equilibrium studies gives the capacity of the adsorbent. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. The data of the present study by varying the initial concentration of the metal solutions were fitted in isotherms such as Freundlich and Langmuir models.

Langmuir isotherm
Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site.

The linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation:

$$C_{ads} = \frac{(KLC_{eq})}{(1 + bC_{eq})} \quad (1)$$

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

$$\frac{C_{eq}}{C_{ads}} = \frac{bC_{eq}}{K_{L}} + \frac{1}{K_{L}} \quad (2)$$

And
Cmax = KL/b  

where:

\[ \text{Cads} = \text{amount of Cr (VI) adsorbed (mg·g}^{-1}) \]

\[ \text{Ce}_\text{eq} = \text{equilibrium concentration of Cr (VI) in solution (mg·dm}^{-3}) \]

KL = Langmuir constant (dm³·g⁻¹)

b = Langmuir constant (dm³·mg)

Cmax = maximum Cr (VI) to adsorb onto 1 g blend (mg·g⁻¹)

The constant b in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant KL can be used to determine the enthalpy of adsorption [23]. A plot of Ceq/Cads vs Ceq confirming the applicability of the Langmuir adsorption isotherm (Figure 8).

The Langmuir isotherm is limited in its application to adsorption in monolayer. It applies well to chemical adsorption and to physical adsorption when saturation is approached [24].

\[ \text{Ceq} = \frac{\text{Cmax}}{\text{KL}} b \]

(Figure 8: Langmuir adsorption isotherm)

**Freundlich isotherm**

Freundlich equation plot of log Cads vs. log Ceq yielded a straighter line as shown in Figure 9. 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:

\[ \text{Cads} = KF C_\text{eq} / n \]

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

\[ \log \text{Cads} = \log KF + l/n \log \text{Ce}_\text{eq} \]

where:

\[ \text{Cads} = \text{amount of Cu (II) adsorbed (mg·g}^{-1}) \]

\[ \text{Ce}_\text{eq} = \text{equilibrium concentration in solution (mg·dm}^{-3}) \]

\[ l/n = \text{Freundlich constant (mg·g}^{-1}) \]

\[ KF = \text{Freundlich constant (g·dm}^{-3}) \]

From Figure-9 It is evident that the values of 1/n and KF, which are rough measurements of the adsorption intensity and adsorption capacity of the adsorbent, have been determined by the least square fit.

**Table 1: The Langmuir and Freundlich parameters**

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_L (dm³/g)</td>
<td>b (dm³/mg)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.6779</td>
<td>0.002584</td>
</tr>
</tbody>
</table>
To examine the relationship between adsorption and aqueous concentration at equilibrium, various biosorption isotherm models are widely employed for fitting the data. The Freundlich isotherm is originally empirical in nature [25], 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 [26]. The value of $n$, of this model, falling in the range of 1–10 indicates favorable biosorption [27]. 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 [28]. The present study results indicate that the Freundlich model fit the experimental data well (Table 1). The adsorption data provided an excellent fit to the Langmuir isotherm. The dimensionless separation factor ($R_L$) value indicates that Cu (II) biosorption of biosorbent in this study is favorable.

**Kinetics studies**

Investigating the mechanism of adsorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been exploited to analyze the experimental data. Pseudo-first-order and pseudo-second-order models have been applied to find out the adsorption mechanism. The equation of these kinetic models is expressed as follows

**Pseudo first order equation**

$$\log(qe - qt) = \log qe - (k_1/2.303)t$$

(7)

where $q_e$ and $q_t$ refer to the amount of metal ions adsorbed per unit weight of adsorbent at equilibrium and at any time $t$.

The plots of $\log (q_e - q_t)$ versus $t$ were straight lines (Figure 10). The correlation coefficients ($R^2$) which was calculated for the removal of Cu$^{2+}$ ion were 0.8695. The slope and intercept of plots of $\log (q_e - q_t)$ versus $t$ were used to determine the first-order rate constant ($k_1$) and equilibrium adsorption density $q_e$. 

![Figure 9: Freundlich adsorption isotherm](image)

![Figure 10: Pseudo-first-order kinetics for copper adsorption](image)
Pseudo second order
Using the pseudo-second-order equation also, the adsorption process may be described [29]. The differential equation is the following
\[
\frac{dq}{dt} = k(q_e - q)^2
\]  
(8)
Integrating the above equation and applying the boundary conditions gives
\[
\frac{1}{q_e - q} = \frac{1}{q_e + kt}
\]
(9)
On rearranging the equation (9) we get a linear form [30,31]. It can be represented as follows
\[
\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}
\]
where \( h = k_2 q_e^2 \) (mg g\(^{-1}\) min\(^{-1}\)) which can be regarded as the initial adsorption rate as \( t \) tends to 0 and \( k_2 \) is the rate constant of second order adsorption (g mg\(^{-1}\) min\(^{-1}\)). The straight line plots of \( t/q_t \) against \( t \) have been tested to obtain rate parameters and it suggests the applicability of this kinetic model to fit the experimental data (Figure 11)

![Figure 11: Pseudo-second-order kinetics for copper adsorption](image)

Table 2: Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Pseudo-first-order kinetic model</th>
<th>Experimental value</th>
<th>Pseudo-second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>qe (mg/g) k_1 (min(^{-1})) R(^2)</td>
<td>qe (mg/g) k_2 (g mg(^{-1}) min(^{-1})) R(^2)</td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>410.43 0.006464 0.8695</td>
<td>150.4 156 0.00392 0.9835</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 lists the computed results obtained from both the first order and second-order kinetic model. The correlation coefficients for the second-order kinetic model obtained were nearing 1 when compared to the pseudo first order. The calculated \( q_e \) values also agree well with the experimental data. These indicate that the adsorption system studied follows the pseudo-second-order [32].

REFERENCES


