Preparation and Characterization of Chitosan (CN)/Polyethylene glycol (PEG) binary blend for Heavy metal Chromium removal

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INTRODUCTION
Rapid industrialization has resulted in the discharge of large amounts of heavy metal–contaminated wastewater into natural ecosystems pose a serious problem to the environment and the life forms [1]. Among the various industries, the textile based industries use large volumes of water in their operations and therefore discharge large volume of wastewater into the environment, most of which is untreated. Chromium is one of the most hazardous heavy metal and cause adverse effects to human life. Chromium is commonly found in two oxidation states; hexavalent Cr(VI) and trivalent Cr(III). The hexavalent form is 500 times more toxic to aquatic life than trivalent one [2]. Various methods used for the removal of chromium from aqueous solutions include chemical precipitation, reverse osmosis, ion exchange and adsorption [3]. The biopolymer chitosan is a natural, safe, and cheap produced from chitin, and it is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acyetylated unit, an organic strain of polymer) which is extracted naturally from the living things, such as the shells of shrimps, crabs and other crustaceans and some fungi by using alkali sodium hydroxide[4]. Chitin has been recommended as an excellent adsorbent in many research papers, because of its unique properties such as biodegradability, chelating capacity, flocculating ability and its possibilities of regeneration in a number of applications [5]. Another polymer used in our study is Polyethylene glycol (PEG). It is a water-soluble, waxy solid that is used extensively in wastewater treatment as a surfactant constituent [6, 7] or as catabolic products of these. The present study concentrates on the preparation of binary blend of Chitosan with polyethylene glycol of ratio (1:1) and has been used for the removal of heavy metal chromium, adsorption study was carried out and was fitted to Langmuir isotherm model.

MATERIALS AND METHODS
Material
Chitosan of 92% deacetylated was purchased from India Sea Foods, Cochin, Kerala. Polyethylene glycol was purchased from Sigma Aldrich, Bangalore, India. All other chemical used were of analytical grade and used as received.

Preparation of Chitosan, and polyethylene glycol solution

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One gram of chitosan was dissolved in 100 ml of 10% acetic acid by stirring for 20 minutes and the viscous liquid was used for further reaction. 1 gram of polyethylene glycol (400) was dissolved in 20ml of deionised water.

**Preparation of Chitosan/PEG blend**

Solutions of chitosan and polyethylene glycol were mixed in weight ratio of 1:1 and stirred for 30 minutes in an electrical stirrer and poured into polystyrene petri dishes and allowed to dry for the preparation of binary blends.

**Characterization of Polymer blends**

**FT-IR spectroscopy (FTIR)**

The Fourier transform infrared (FTIR) investigation was carried out using PERKIN ELMER spectrometer in the range of 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). The IR spectrum was recorded in a solid state using KBr pellet method.

**X – Ray Diffraction Studies**

It was carried out using (XRD – SHIMADZU XD – D1) a Ni – filtered Cu Ka X-ray radiation source. The blends were scanned within the range of 10\(^{\circ}\) - 90\(^{\circ}\) (2\(\theta\)) at a scanning rate of 5\(^{\circ}\)/min.

**Thermo Gravimetric Analysis (TGA)**

Thermo gravimetric analysis (Perkin Elmer Model, USA) was used having unit of microprocessor temperature control with TA data station. The sample mass generally in the range of 2 - 3 mg was used. An equipment consist of both sample pan with balance system was placed in temperature ranges from 25°C to 800°C with 50 cm\(^3\)/min flow rate of nitrogen. The mass of sample pan was recorded constantly as a function of temperature.

**Differential Scanning Calorimetry (DSC)**

The differential scanning calorimetry (DSC) measurements were performed with NETZSCH DSC 200 PC in a pan Al, pierced lid in the N\(_2\) atmosphere at a heating rate of 20 K/min.

**Scanning electron microscopy (SEM)**

To observe the surface morphology of the prepared blend, Field Emission Scanning Electron Microscopy was used. By using sputter coated with a 5 nm thick gold, the samples were sprinkled.

**Adsorption studies**

The metal solutions with different initial concentrations were taken in stoppered bottles and agitated with the prepared adsorbents separately at 30\(^{\circ}\)C in orbit shaker at fixed speed of 160 rpm. After attaining the equilibrium the adsorbent was separated by filtration using filter paper and aqueous phase concentration of metal was determined with atomic absorption spectrophotometer (Varian AAA 220 FS).

**RESULTS AND DISCUSSION**

**FTIR spectroscopy of Chitosan/PEG binary blend**

The FTIR spectral details of Chitosan and the binary blend prepared using Chitosan/PEG of ratio 1:1 were depicted in Figure 1 and 2. The IR spectra of Chitosan showed a prominent peak at 3454.75 cm\(^{-1}\) for –OH stretching, which overlaps the NH stretching in the same region and the presence of intra molecular hydrogen bonding. A peak observed at 2923.08 cm\(^{-1}\) was typically due to aliphatic –CH asymmetric stretching. The absorption in the range of 1628.87 cm\(^{-1}\) to 1540.02 cm\(^{-1}\) represents the amide I carbonyl stretch as the shoulder on the broad amine deformation [8] and the peak at 1421.52 cm\(^{-1}\) shows the presence of CH\(_2\) deformations and OH deformation [9]. The peak at 1384.01 cm\(^{-1}\), 1322.23 cm\(^{-1}\) shows the presence of C-O stretching and O-H in plane bending vibration. The peaks at 1098.72cm\(^{-1}\) and 1021.37cm\(^{-1}\) show the presence of C-N stretching coupled vibrations, glycosidic bonds in the pyranose ring. The peaks at 776.38 cm\(^{-1}\), 674.35 cm\(^{-1}\) and 472.23 cm\(^{-1}\) shows the presence of CH\(_2\) rocking, OH out of plane bending and C-C bending [10].

Figure 2, shows the FTIR spectrum of Chitosan/PEG of ratio 1:1 displayed a characteristic peak at 3434.4 cm\(^{-1}\) shows the presence of inter molecular hydrogen bonding, NH stretching, O-H stretching and confirms the polymeric association [11], the peaks at 2946.0 cm\(^{-1}\) and 2860 cm\(^{-1}\) corresponds to asymmetric and symmetric C-H stretching vibrations, and the peaks at 1382.4 cm\(^{-1}\) and 1117.3 cm\(^{-1}\) confirms the presence of OH in plane bending, C-O stretching and C-N stretching vibrations. The frequencies were disappeared or shifted during blending confirm the formation of polymer blends [12].

**X-Ray Diffraction studies (XRD) of Chitosan/PEG binary blend**

Figure 3 shows the XRD spectrum of CS/PEG blend (1:1) shows two broad peaks at 2\(\theta\) =15\(^{\circ}\) and 2\(\theta\) =
40°. The two broad peaks obtained at different 2θ values indicates that the blend has semi crystalline nature and the crystallinity of the binary blend is lower than pure chitosan which confirms that amorphous nature increases during the blending of polymeric mixture [13].

**Thermogravimetric Analysis of Chitosan/PEG binary blend**
Thermogravimetric analysis (TGA) is a thermal analysis technique, used to determine the sample stability and loss of weight in diverse temperature [14]. Thermal details of binary blend of Chitosan/PEG of ratio 1:1 are discussed below. From the figure 4a and 4b it is found that the heating rates were suitably controlled at 10°C min⁻¹ under nitrogen atmosphere, and the weight loss was measured from the ambient temperature up to 800°C.

The thermal analyses for CS/PEG binary blend showed a slight weight loss up to 240°C, which probably was due to the adsorbed water molecules. Significant weight loss for CS/PEG blend was noticed between 240°C and 370°C, were attributed to the decomposition of chitosan and polyethylene glycol polymer blends. Around 96.4% of the specimen had broken down toward the end of the analysis deserting 3.60 % of the blend as a deposit.

**DSC of Chitosan/PEG binary blend**
DSC is an analytical tool which helps to understand the thermal behavior of polymers and polymer blends. To get more insight on the thermal behavior of the blend samples, DSC measurements were performed and the results are shown in Figure 5. The peaks for pure chitosan are read at around 107°C and 125°C. For binary blend of CS/PEG a broad endothermic peak was observed at around 150°C, as we add PEG to chitosan the peak was shifted to higher temperature region which was in agreement with the study performed by Ling-hao He [15]. Two glass transition temperatures were observed for the blend at 137.8°C and 200°C. A broad endothermic peak was observed at around 150°C was due to crystallization of blend. The figure shows that the blend is stable till 350°C.

**Scanning Electron Microscopic Analysis**
Scanning Electron Microscopy is a versatile tool to study the morphological features of materials particularly very complex polymeric materials. The surface morphology of chitosan characterized by SEM indicates a microporous and fibrous structure [16].

SEM observations of CS/PEG (1:1) blend revealed almost smooth surface (Figure - 6) with very fine microvoids. The cross sectional morphology of the same composite (Figure - 7) shows the fine interaction of the two polymers in a very fine manner resulting in a highly miscible homogenous polymer blend with higher stability. The pores in the blend and the microvoids in the cross section are effective in increasing the functional surface in the composite which enable the same to be used as a good adsorbent.

**Adsorption study**
The adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium [17]. The data of the present study by varying the initial concentration of the metal solutions were fitted in isotherm model Langmuir. The chromium adsorption on to Chitosan/PEG blend was carried out by changing the initial metal ion concentration and thus verified for fitting in the Langmuir adsorption isotherm model.

The Langmuir equation has been often used to give the sorption equilibrium [18]. The Langmuir model assumes that the adsorption of metal ions occurs on a homogenous adsorbent through a monolayer adsorption without any interaction between adsorbed ions [19]. Langmuir model follows unimolecular adsorption and from the linear Langmuir isotherm the calculation of adsorption capacities and Langmuir constant by the following equations were done:

\[
C_{ads} = \frac{(K_L C_{eq})}{(1 + b C_{eq})} \quad \text{-------(1)}
\]

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

\[
\frac{C_{eq}}{C_{ads}} = \frac{b C_{eq}}{K_L} + \frac{1}{K_L} \quad \text{-------(2)}
\]

\[
C_{max} = \frac{K_L}{b} \quad \text{-------(3)}
\]

where: \(C_{ads}\) = amount of Cr (VI) adsorbed (mg·g⁻¹)
\(C_{eq}\) = equilibrium concentration of Cr (VI) in solution (mg·dm⁻³)
\(K_L\) = Langmuir constant (dm³·g⁻¹)
\(b\) = Langmuir constant (dm³·mg)
C_{max} = maximum Cr (VI) to adsorb onto 1 g chitosan (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 \( K_L \) can be used to determine the enthalpy of adsorption.

A plot of \( C_{eq}/C_{ads} \) vs \( C_{eq} \) confirms the applicability of the Langmuir adsorption isotherm.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter \( R_L \) indicate the nature of the isotherm, if the conditions are (\( R_L > 1 \), \( R_L = 1 \), \( 0 < R_L < 1 \) and \( R_L = 0 \)) are unfavorable, linear, favorable and irreversible respectively [20].

The separation factor, \( R_L \) is defined by:

\[
R_L = 1/ (1+bC_f)
\]

Where \( C_f \) is the final Cr (VI) concentration (ppm) and \( b \) is the Langmuir adsorption equilibrium constant (dm\(^3\) mg\(^{-1}\)).
Table 1. \( R_L \) values based on Langmuir adsorption

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Initial concentration ( C_0 ) (mg/dm(^3))</th>
<th>Final concentration ( C_f ) (mg/dm(^3))</th>
<th>( R_L ) values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI) ion</td>
<td>1000</td>
<td>295</td>
<td>0.555088</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>130</td>
<td>0.738984</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>50</td>
<td>0.880398</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>23</td>
<td>0.941184</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9</td>
<td>0.976131</td>
</tr>
</tbody>
</table>

From Table 1 it was evident that the observed \( R_L \) values are in the range of 0 < \( R_L \) < 1. Since the calculated \( R_L \) values are in the range of 0–1, it was concluded that the Chitosan/PEG blend was found to be the favorable adsorbent [20].

Fig 8. Langmuir isotherm for Chromium
Table 2. Adsorption isotherm constant, C_{max} and correlation coefficients

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_L (dm^3/g)</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>1.346</td>
</tr>
</tbody>
</table>

The linear Langmuir plot indicates the formation of monolayer coverage of adsorbate on the surface of adsorbent. Table 2 shows the isotherm constant, C_{max} value and the correlation coefficient values are 495.40 mg of chromium per gram and 0.7706 respectively for CS/PEG blend. Moreover the values of the constants related (b-values) to adsorption energy of adsorption much close to zero, indicating that the monolayer adsorption has taken place [21]. From the R^2 and b values it may hence be deduced that the adsorption process closely follows the Langmuir isotherm model confirmed the monolayer coverage of Cr (VI) at the outer surface of binary blend.

CONCLUSION

In this study, the Chitosan/PEG binary blend was prepared in the ratio of (1:1) and was characterized using analytical techniques such as FTIR, XRD, TGA and DSC. From the FTIR results, it was found that the the peaks were shifted to higher wave number during blend formation which confirms the Chitosan was effectively bound with polyethylene glycol. XRD studies elucidate that the prepared blend was highly amorphous and suitable for adsorption process. TGA and DSC results indicate that the blend have excellent thermal stability and compatibility. The morphology as well as the compatibility of the blends has been studied using SEM and XRD methods. The removal of heavy metal chromium was successfully fitted with Langmuir model. It was concluded from the above results that the binary blends were highly suitable for heavy metal removal and fits with Langmuir unimolecular adsorption.

ACKNOWLEDGEMENT
Nil.

CONFLICT OF INTEREST
No conflict of interest.

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