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Biodegradable polymer based ternary blends for removal of trace metals from simulated industrial wastewater

N Prakash [a,*], S Arungalai Vendan [b]

[a] Department of Chemistry, Thangavelu Engineering College, Chennai, India
[b] Industrial Automation and Instrumentation Division, SELECT, VIT University, Vellore

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ABSTRACT

The ternary blends consisting of Chitosan (CS), Nylon 6 (Ny 6) and Montmorillonite clay (MM clay) were prepared by the solution blending method with glutaraldehyde. The prepared ternary blends were characterization by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Thermo gravimetric analysis (TGA), Differential scanning calorimetry (DSC) and Scanning electron microscope (SEM). The FTIR results showed that the strong intermolecular hydrogen bondings were established between chitosan, nylon 6 and montmorillonite clay. TGA showed the thermal stability of the blend is enhanced by glutaraldehyde as Crosslink agent. Results of XRD indicated that the relative crystalline of the pure chitosan film was reduced when the polymeric network was reticulated by glutaraldehyde. Finally, the results of scanning electron microscopy (SEM) indicated that the morphology of the blend was rough and heterogenous. Further, it confirms the interaction between the functional groups of the blend components. The extent of removal of the trace metals was found to be almost the same. The removal of these metals at different pH was also done and the maximum removal of the metals was observed at pH 4.5 for both trace metals. Adsorption studies and kinetic analysis have also been made. Moreover, the protonation of amine groups is induced an electrostatic repulsion of cations. When the pH of the solution was more than 5.5, the sorption rate began to decrease. Besides, the quantity of adsorbate on absorbent was fitted as a function in Langmuir and Freundlich isotherm. The sorption kinetics was tested for pseudo first order and pseudo second order reaction. The kinetic experimental data correlated with the second order kinetic model and rate constants of sorption for kinetic models were calculated and accordingly, the correlation coefficients were obtained.

1. Introduction

Recently, natural polymers have been viewed as a biological and biomedical resource due to their unique properties including non toxicity [1], bio degradability and biocompatibility [2,3]. However, natural homopolymer by itself is inadequate to meet the diversity of demands for biomaterials. Biocompatibility had been considered as 'the ability of a material to perform with an appropriate host response in a specific application [1], taking into account the interactivity between the biomaterial and the host. Some of the prominent applications for biomaterials are: controlled drug delivery [4,5] discussed water treatment and recycling techniques. [6] Presented a super selectivity potentiometric methodology, using an ion-selective electrode, for determination of mercury ion (II) in aqueous solution, orthopedic devices [7], sutures, cardiac pacemakers, and vascular grafts. Natural polymers such as konjac glucomannan [8], chitosan [9] and gelatin [10] have remained attractive as they offer features viz., economical, easy availability, potentially degradability and compatible nature. Chitosan was also blended with several polymers such as polyamides, polyurethane foam, poly (acrylic acid), gelatin, silk fibroin and cellulose to enhance mechanical properties [11–13].

[14] synthesized Alumina-coated multi-wall carbon nanotubes are characterized by scanning electron microscopy, X-ray diffraction, and FTIR. They were used as an adsorbent for the removal of lead ions from aqueous solutions in two modes, batch and fixed bed. Chromium and cadmium are highly toxic heavy metals and have to be removed from the water sources. These metals are from various industrial effluents such as tanneries, electroplating and paints. The Chromium toxicity is mainly induced from its hexavalent form, Cr (VI) and easy solubility in water. Its concentration should not exceed 0.05 mg/L in drinking water and it

* Corresponding author. Tel.: +91 4426810111.
E-mail addresses: prakash.nagapillai@gamil.com, k_nprakash1981@rediffmail.com (N. Prakash), arungalaisv@yahoo.co.in (S. Arungalai Vendan).

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Table I
Ternary polymer blends preparation ratio.

S. No	Polymer Blends
1	Chitosan/Nylon 6/Montmorillonite(1:1:1)-Glutaraldehyde
2	Chitosan/Nylon 6/Montmorillonite(1:2:1)-Glutaraldehyde
3	Chitosan/Nylon 6/Montmorillonite(2:1:1)-Glutaraldehyde

is more toxic with potential carcinogenic effects [15]. Cadmium belongs to the hazardous metal group. It is fairly mobile in soil and primarily present as an organically bound, exchangeable and water-soluble species [16,17]. For Cadmium, the upper limit level in drinking water should be 0.01 mg/L or less. It is shown from the toxicological studies that long term effects of Cd (II) damages kidney, liver and blood. Short-term effects include nausea, vomiting, diarrhoea, and cramps. [18] Reported that the dye degradation rates followed pseudo-first order kinetics with respect to the substrate concentration under the prevailing experimental conditions. Parameters namely the temperature, pH and presence of electron acceptor for different experimental trials were investigated. This was followed by analyzing the effect of pH which emphasized inverse dependency. [19] Synthesized manganese dioxide-coated multiwall carbon nano tube (MnO_2/CNT) based nano composite for experimentation and subsequent optimization. The pH range was varied and the optimum removal was attained when the pH was equal to 6 and 7. They also reported that due to slower the flow rates of the feed solution the higher the removal because of larger contact time. [20] Determined optimal parameters by monitoring different attributaries such as effect of pH, effect of concentration of the dye, amount of adsorbents, contact time, and temperature. Differentiation between particle and film diffusion mechanisms operative in their study was carried out. The removal of Cadmium from the wastewater by various techniques such as chemical precipitation, electro deposition, electro coagulation process, ion exchange and emulsion liquid membrane [21–23] have been employed. These techniques are expensive and ineffective at low concentration of metal ions. Adsorption method is reported to be the most suitable method due to low cost and high efficiency even for low concentration of metal ions [24].

Novel adsorbents prepared from orange peel and Fe_2O_3 nano particles have been used [25] to remove Cadmium from aqueous solutions. The removal of Cadmium from electroplating industry effluent is reported and is shown to have desorption and reusability without loss of efficiency. [26] Assessed the applicability of waste materials-bottom ash and deoiled soya-for the removal of the colorant Congo red from wastewaters. [27] Described the use of bottom ash [a power plant waste] and de-oiled soya [an agricultural waste] as effective adsorbents for the removal of a hazardous azo dye [Chrysoidine Y] from its aqueous solutions. [28] Investigated the removal of the dye-tartrazine by photodegradation using titanium dioxide surface as photocatalyst under UV light. [29] Synthesized carbon nanotube, a composite of multi-walled carbon nanotubes and titanium dioxide (MWCNT/TiO_2) to hybridize the photocatalytic activity of TiO_2 with the adsorptivity. A low cost fertilizer industry waste material, carbon slurry, has been chemically treated, activated and used as adsorbent to remove hexavalent Chromium from aqueous solutions [30] and the kinetics of adsorption follows pseudo second order rate equation based on batch experiments. The removal of lead and Chromium from aqueous solutions has been reported using inexpensive Red mud, an Aluminium industry waste and bagasse fly ash.

[31] revealed from their experimental study a faster kinetics and efficiency of MNP–OPP in comparison to those of MNP and OPP and further confirmed a complexation and ion exchange mechanism to be operative in metal binding. [32] Attempted to degrade aniline in the synthetic effluent by homogeneous and heterogeneous Fenton oxidation process. The kinetic constants and the thermodynamic parameters for the oxidation of aniline in synthetic wastewater were determined. [33] Treated and activated blast furnace dust to prepare low-cost adsorbents. The blast furnace waste generated in steel plants have been used for the removal of lead and Chromium [34] and concluded that the uptake of lead is greater than that of Chromium. [35] studied four isothermal models, Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich, and important thermodynamic parameters were calculated.

The biodegradable polymer using, cross linking treatment has emerged as another important strategy to improve the performance of the blends. In this study, chitosan/nylon 6/montmorillonite clay blends were prepared by the casting process. In order to produce chitosan film with homogeneous dispersion of fine clay Particles, chitosan, the naturally cationic polymer was used as a compatibilising agent for montmorillonite clay modification, glutaraldehyde was added to the blend as a crosslinking agent in various ratios and evaluates the performance of CTS/NY 6/MM clay blend. The hydrophobic behavior and an increase in spacing between the layers of silicate are important factors which make organophilic montmorillonite compatible with most hydrophobic polymers. Clay and silica have already proved to be an effective way to improve the mechanical, electrical, and thermal properties of polymers. This biopolymer can intercalate into the inorganic clay by means of cationic exchange process in the absence of other organic modifiers. The strong interactions between have been clay and chitosan. The enhanced thermal stability properties of chitosan were reported [36]. Modified Ball clay (MBC) and chitosan composite (MBC–CH) was prepared by [37].

In the present study, solution blending of chitosan with nylon 6 and polyurethane foam with and without cross linking agent and subsequent characterization of the obtained blends using IR, TGA, XRD and SEM is reported. Chitosan alone will not have enough strength and it will not have free standing film which will have enough strength to remove the metals. Hence it is blended with silk which is an artificial fiber. This will have a rein forcing effect to hold the chitosan. To improve the strength it is also blended with starch which will have binding effect. This will facilitate the binding of silk and chitosan.

2. Materials and methods

2.1. Chemicals and materials

Chitosan was purchased from India Sea Foods, Cochin, Kerala which is 92% deacetylated. Glacial acetic acids were purchased from Sisco Research Laboratories PVT, LTD, India. Montmorillonite (MM clay) employed in this study was K10 montmorillonite purchased from Sigma-Aldrich. Vermiculite was obtained from Fisher Scientific Pvt Ltd, India. The cross linking agent glutaraldehyde was purchased from SD Fine-Chem Ltd, India.

2.2. Preparation of chitosan/nylon 6/montmorillonite clay blend

Ternary blend films were prepared by casting Methods. Chitosan solutions were prepared by dissolving chitosan in 2% glacial acetic acid solution at room temperature with stirring. Ion-exchanged nylon 6 powder was added to water. Montmorillonite clay dissolved in water was also prepared. Subsequently, the dispersion was mechanically stirred at 1000 rpm for one hour. The product was poured into petri dish and allowed to dry. The same procedure was carried out in presence. The prepared ratios were tabulated below in Table I.