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RESEARCH ARTICLE

PERFORMANCE OF CROSS-LINKED CHITOSAN BASED HYBRID TERNARY BLEND FOR SEPARATION OF CADMIUM

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ABSTRACT

Treatment A series of Chitosan(CS)/Poly(vinyl alcohol)(PVA)/ Methylcellulose(MC) hybrid ternary blend with crosslinked of glutaraldehyde (G) was fabricated by a solution casting method, in order to be used as a potential sorbent material for toxic soft metal of cadmium (Cd). The fabricated crosslinked CS/ PVA / MC hybrid ternary blend film were characterized by FT-IR, X-ray diffraction (XRD) and Scanning electron microscopy (SEM). Effect of time, pH, adsorbent dose and adsorbate concentration on the adsorption of Cd (II) was investigated in batch process and pseudo-first and pseudo-second-order kinetic models was also evaluated. The data was analyzed on the basis of Lagergren pseudo first order, and pseudo-second order. Regardless of the metal ion species, the adsorption capacity rapidly reached and adsorption followed second order kinetic equation. The equilibrium adsorption obeyed Langmuir and Freundlich isotherms were calculated. The maximum monolayer adsorption capacity of CS/PVA/MC-G blend film as obtained from Langmuir adsorption isotherm was found to be 100.15 mg g⁻¹ for Cd (II) ions. The experimental results demonstrated that CS/PVA/MC-G blend film could be used for the removal of Cd (II) ions from aqueous medium through adsorption. The regeneration study indicates that CS/PVA/MC-G blend film could be used repeatedly without significantly changing their adsorption capacities and desorption percentage.

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INTRODUCTION

Over the past decades, rapid increase in global industrial activities have led to tremendous increase in the use of heavy metals, which resulted in an increasing discharge of toxic and polluting heavy metals, such as Cu, Pb, Ni, Zn and Cd into the aquatic environment. Heavy metal contamination of the various water resources is of great concern given the toxic effect on humans as well as the biota present in the environment [1]. Unlike most other toxic pollutants, metals can accumulate throughout the food chain due to their non biodegradability and thus have potentially detrimental effects on all living species. The major sources of heavy metal pollutants are several industrial activities including mining, metal plating, oil refining, electronic device manufacturing, printing, and the production of chemicals, dyes and paints, pulp and paper, textiles, petrochemicals, leather, fertilizers and pesticides [2,3]. Thus, the removal of such toxic metal ions from wastewater is a crucial issue. Different technologies and processes are currently used. Biological treatments, membrane processes, advanced oxidation processes, chemical and electrochemical techniques and adsorption procedures are the most widely used for removing metals from industrial effluents [4, 5]. Among all the treatments proposed, adsorption using sorbents is one of the most popular methods. It is now recognized as an effective, efficient and economic method for water decontamination applications and for separation to analytical purpose. The great advantage of this method over others is the low generation of residues, easy metal recovery and the possibility for the reuse of

the adsorbent. Studies have been carried out to develop more effective and selective adsorbent materials, which are abundant in nature and require minimal processing in order to the decrease cost [6, 7]. A new development in recent years for heavy metal removal is to use chitosan (CS) as the adsorptive material. CS is a natural biopolymer with a high content of the amine (-NH₂) functional group and is inexpensive and abundant, widely available from seafood-processing wastes and have high binding capacities for many heavy metal ions [8]. Blending of synthetic with natural biopolymers is considered as a new class of materials that is of particular significance [9]. Recently, the study and development of blends formed by three or more components has raised the attention of both the industrial and the academic world. Blending of CS with PVA and ternary blends of CS/PVA/gelatin, CS/PVA/pectin has been already reported in literature [9, 10]. Furthermore, cross-linking treatment has emerged as another important strategy to improve the performance of ternary blends. It has been reported that CS and PVA could be well cross-linked with some PVA- and CS-based cross-linkers [11].

We have fabricated and comprehensively investigated the physical and chemical properties of polymer blends based on CS/PVA/MC and chemically crosslinked with glutaraldehyde [12]. The objective of the present study is focused on the development of CS/PVA/MC ternary blend films reticulated with glutaraldehyde (G) and investigated the adsorption behaviors and performance of the ternary blend films for cadmium ion removal. The choice of using cadmium ions as the model heavy metal species in the study was based on a consideration that the relative priority pollutants and that is often difficult for further effective treatment by conventional technologies. The effect of pH, adsorbent dose, and initial concentration of Cd²⁺ adsorption and

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time on adsorption capacity was investigated. The characterization of adsorption kinetics and isothermal adsorption were also studied in order to provide a new method and theoretical evidences for wastewater treatment.

Experimental section

Reagents

Chitosan (92% deacetylated) was the kind gift of India seafoods Cochin, Kerala, India. PVA, MC, and glutaraldehyde (analytically pure) were purchased from S&D fine Chemicals, Mumbai, India.

Preparation of crosslinked ternary blend

Crosslinked ternary blend film of CS/PVA/MC was fabricated and characterized as described in our earlier works [12]. 1 g CS powder was added into a 100 mL of formic acid and stirred to form a 1 wt% clear CS solution. Meanwhile 1 g PVA powder was charged into 100 mL purified water while stirring to form a 1 wt% clear PVA solution. Then CS and PVA were blended together to form a homogeneous CS/PVA binary blend solution. 1 g MC was charged into 100 mL purified water and stirred to form 1 wt% MC solution. Finally CS, PVA, and MC solutions in the weight ratio (1:1:1) was mixed and stirred. Then the cross-linker reagent glutaraldehyde (G) 0.75% (v/v) was slowly added under constant stirring. Further the solution was poured into plastic molds and allowed to dry for 72–120 h at room temperature (25°C) in the desiccators followed by additional 24 h in an oven at 40°C, in order to remove the residues of water and formic acid.

Film Characterization

The infrared spectra were recorded on Thermo Nicolet AVATAR 330 spectrophotometer in 4000 – 400cm⁻¹ wavelength range using KBr pellet method. X-ray diffraction (XRD) studies were performed using X-ray powder diffractometer (XRD – SHIMADZU XD – D1) using a Ni – filtered Cu K α X-ray radiation source. The morphology of the blend membranes was examined by a scanning electron microscopy (JEOL) Model JSM-6390LV.

Adsorbate solution

Synthetic stock solution 50 mgL⁻¹ of heavy metal was prepared by dissolving required quantity of Analar grade salt in the demineralised water. Cadmium chloride used as source for Cd(II) for the preparation of stock solution. The stock solution was further diluted with demineralised water to desired concentration for obtaining the test solutions.

Batch mode adsorption experiments

The adsorption of heavy metal on CS/PVA/MC-G was studied by batch technique. The general method used for this study is described as below:

A known weight of adsorbent (e.g. 0.5–1.0 g) was equilibrated with 50 ml of the heavy metal solution CdCl₂ with a known starting concentration in plastic bottles at a room temperature in a thermostatic mechanical shaker (WIDSONS Scientific) for a known period (5 min–24 h) of time. After equilibrium, the suspension of the adsorbent was separated from solution by filtration using Whatman filter paper No. 1. The concentration of heavy metal ion remaining in solution was measured by atomic absorption spectrophotometer (Varian AAA 220 FS). The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using hydrochloric acid, sodium hydroxide and buffer solutions when required. Adsorption of metal ion on the walls of glass flasks determined by running the blank experiments was found negligible. The results of these studies were used to obtain the optimum conditions for maximum heavy metal removal from aqueous solution.

The adsorption capacity Q (mg g⁻¹) of CS/PVA/MC-G was calculated as follows

$$qe = \frac{(C_0 - C_t)}{m} V \quad (1)$$

where C_0 and C_t are the concentrations of Cd²⁺ ions before and after adsorption, respectively (mg l⁻¹), V the total volume of the aqueous solution (L), and m is the dry weight of CS/PVA/MC-G (g).

Adsorption kinetics

For kinetic measurements, 1.0 g CS/PVA/MC-G was added into 100mL solution containing heavy metal ion Cd(II) with the initial concentrations 50mg/L under the condition of pH 5. Then 0.5mL of the supernatant was withdrawn at a given time interval by using a 1mL pipette and used for the residual metal analysis and the pH was measured. In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the first- and second-order equations were used to fit the experiment data. The first-order kinetic equation and second order kinetic equation are expressed as (2) and (3), respectively [13]:

$$\log \left(\frac{q_e}{q_t} \right) = \log q_e - \frac{k_1}{2.303} \times t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t are the amounts of metal ion adsorbed on adsorbent (mg/g) at equilibrium and at time t , respectively, and k_1 is the rate constant of first-order adsorption (min⁻¹). The straight line plots of $\log(q_e - q_t)$ against t were used to determine the rate constant k_1 ; k_2 is the rate constant of second-order adsorption (g mg⁻¹ min⁻¹), it can be obtained from the straight-line plots of t/q_t against t .

Adsorption isotherms

Keeping the other conditions constant and changing the Cd²⁺ initial concentration, adsorption behavior of metal ions onto CS/PVA/MC-G surface was described by Langmuir isotherm plots and Freundlich isotherm plots. The equations are shown as Eqs. (4) and (5) [4, 14]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \quad (4)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (5)$$

where C_e is the equilibrium concentration of the metal ion in solution (mgL⁻¹), q_e the equilibrium adsorption capacity (mg g⁻¹), Q the monolayer saturated adsorption capacity (mg g⁻¹), and b (Lmg⁻¹), k_f (mgg⁻¹) and n are the constants.

Desorption and reusability

In order to determine the potential reusability of the crosslinked ternary blend film, consecutive sorption–desorption cycles were repeated three times using the sorbent prepared following the procedure described in adsorption experiments. Desired amount of adsorbent for adsorption of Cd(II) was taken in a conical flask for a fixed time (24 h), then treated with 50 ml of each 0.1M HCl, 0.1M HNO₃, 0.1M NaCl, and 0.01M EDTA solution. The amount of Cd(II) desorbed was then determined by back EDTA titration [15]. Percentage of desorption of Cd(II) calculated from the following expression:

$$\text{Percentage of desorption} = m_d/m_a \times 100\% \quad (6)$$

where m_d is the amount of Cd(II) ions desorbed (mg) and m_a is the amount of Cd(II) ions adsorbed (mg).

RESULTS AND DISCUSSION

Characterization of Cd-CS/PVA/MC-G

The FTIR spectra of the CS/PVA/MC-G ternary blend film, before and after adsorption of Cd(II) ions was recorded and presented in Fig.1. The stretching frequency at $1168\text{--}1188\text{cm}^{-1}$ indicates the formation of acetal ring by crosslinking. The strong broad band at 3435cm^{-1} is the characteristic of the N-H and -OH stretching vibration. The significant decrease in transmittance in this band from 3435cm^{-1} to 3431cm^{-1} after adsorption of cadmium indicated that the bonding of metals with NH_2 group was occurred. Thus the nitrogen atom of chitosan moiety acted as main adsorption site and it that the adsorption of Cd(II) ions on the surface of the Cd-CS/PVA/MC-G was either through complexation or through physical way which might be through electrostatic interaction and Vander Waals forces[16]. The FTIR spectra also showed that the N-H bending vibrations at 1718 and 1538cm^{-1} shifted to 1713 and 1557cm^{-1} after the adsorption of Cd(II), which suggested that the interactions between Cd(II) and $-\text{NH}_2$ groups. Since Cd(II) can act as Lewis acid and $-\text{NH}_2$ is a Lewis base, therefore coordination is possible by electron transfer.

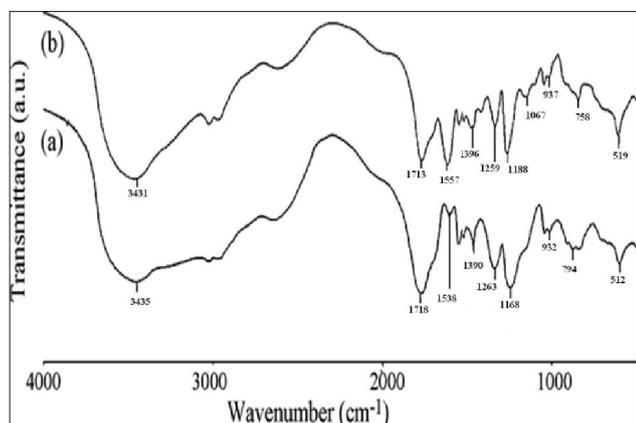


Fig. 1. FTIR spectra of (a) CS/PVA/MC-G films before adsorption of Cd(II) and (b) CS/PVA/MC-G films after adsorption of Cd(II).

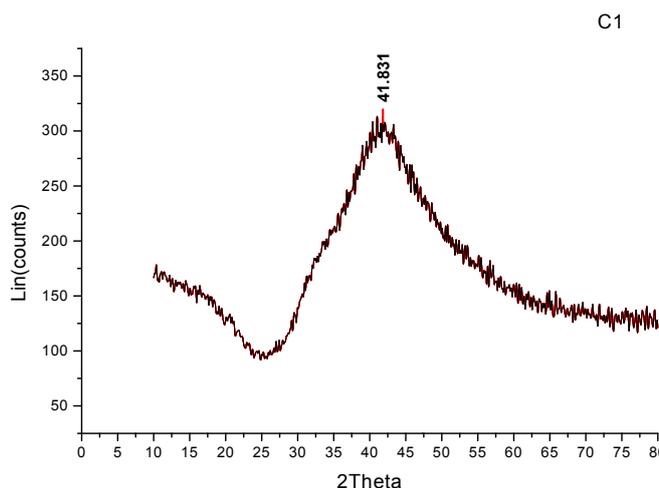


Fig. 2. XRD pattern of the CS/PVA/MC-G films

XRD pattern of the CS/PVA/MC-G is shown in Fig.2. this showed amorphous nature of chitosan/PVA/MC-G films. In Fig.2. CS/PVA/MC-G the peak at 20° becomes flat and broad gradually to higher diffraction value of 41° is proved by the chemical crosslinking. The average crystallinity index (ratio of the areas) of

pure chitosan was reduced when the ternary blend was reticulated with glutaraldehyde. So the cross-linking inhibits close packing of the polymer chains by reducing the degree of freedom in the 3-D conformation, preventing the formation of crystalline regions [12]. This reduction of crystallinity would play a crucial role on influencing the blend degradability, water absorption and swelling. The SEM images of the CS/PVA/MC-G ternary blend film before and after adsorption Cd(II) are shown in Fig. 3. The results are shown in Fig. 3(a, b). From Fig. 3(a), shows that the structures of the CS/PVA/MC-G blend film are highly porous before adsorption, which obviously shows that after adsorption of cadmium causes significant changes in film structure Fig. 3(b). The SEM images clearly showed the reaction of Cd(II) ions with CS/PVA/MC-G made the surface more rough and protrusions than that of CS/PVA/MC-G ternary blend film observed in Fig. 3(b).

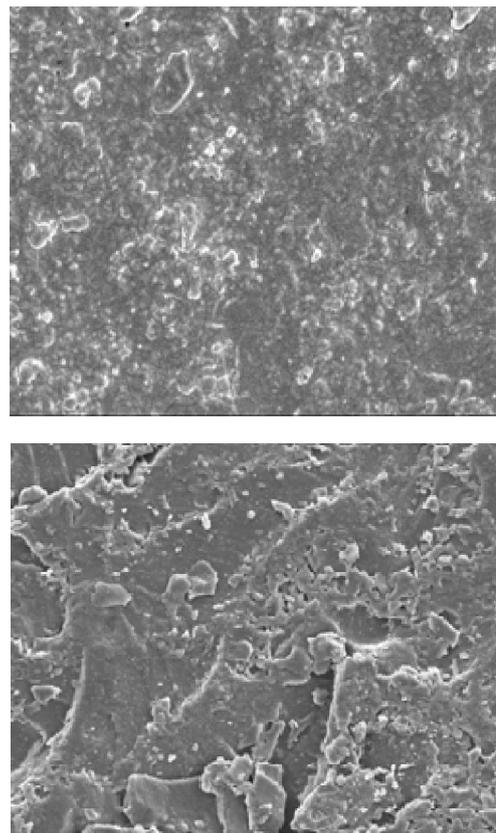


Fig. 3. SEM images of (a) CS/PVA/MC-G films before adsorption of Cd(II) and (b) CS/PVA/MC-G films after adsorption of Cd(II)

Effect of the initial concentration of metal ions

Crosslinked CS/PVA/MC-G blend films was an effective adsorbent over a wide range of adsorbate Cd(II). At lower Cd(II) concentration, CS/PVA/MC-G blends showed close to 96% percentage removal, which reduced slowly with the increase in initial Cd(II) concentration (Fig. 4.). At 50mg L^{-1} Cd(II) concentration, 70% adsorption was observed, which reduced steeply with further increase in Cd(II) concentration up to 500mg L^{-1} . These data can be used effectively for the maximum utilization of adsorbent for the removal of Cd(II) concentration from the metal solution. High adsorption (close to 94%) of Cd(II) by crosslinked CS/PVA/MC-G blend films indicates that its potential application for the removal of Cd(II) from metal solution. At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal

ions concentration. The difference in percentage removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent. Furthermore, one has to optimize the dose of adsorbent depending on the concentration of adsorbate for the removal of heavy metals up to maximum extent and complete utilization of adsorbent.

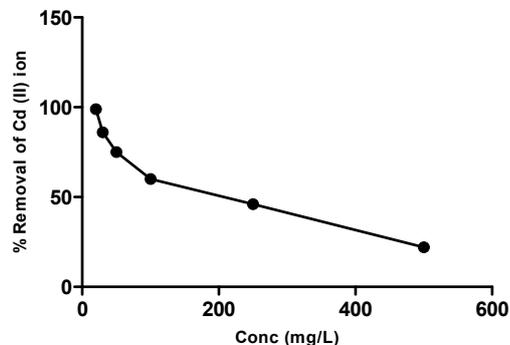


Fig. 4. Effect of initial Cd(II) concentration on its adsorption (%) by CS/PVA/MC-G films

Effect of adsorbent dose

The dependence of Cd(II) sorption on CS/PVA/MC-G was studied by varying the amount of the adsorbent from 1.0 g to 6.0 g while keeping the other parameters such as pH, metal solution volume (50 mL), concentration (100 mg L^{-1}), and contact time (6 h) constant. The removal percentage increases with increasing adsorbent dose (Fig. 5.) from 40% to 74.5% of Cd(II). The reduction in adsorption capacity may be due to the fact that some of the adsorption sites remain unsaturated when adsorbent dose is increased. Large amount of Cd(II) was adsorbed as the number of available adsorption sites are increased, resulting in the overall increase in the removal efficiency [17].

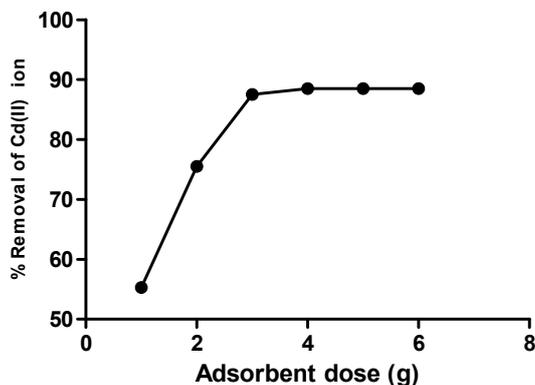


Fig. 5. Effect of adsorbent dose for Cd(II) (50 mg l^{-1}) adsorption on CS/PVA/MC-G films

Effect of pH

The effect of pH on the adsorption of Cd(II) ions by the CS/PVA/MC-G blend films is illustrated in Fig. 6. Metal-ion adsorption is known to be dependent on the pH of solution. The amount of adsorption increased significantly as the pH increased from 2 to 8 and then leveled off at pH 5–7, pH over 7 was not taken into account to avoid precipitation [18]. Metal ion uptake capacities at lower pH were more dependent than those at higher pH. Adsorption of Cd(II) with 50 mg l^{-1} initial concentration at pH 2.0 was observed about 58%, which further increased up to 87% at 5.0 attained a

maximum value. The adsorption increases with increasing pH of the solution. This could be explained by the fact that at low pH, more protons will be available to protonate amine groups to form groups $-\text{NH}_3^+$, whereas in acidic medium ($\text{pH} < 7$) due to high H^+ concentration, active sites of the adsorbent were protonated and leads to the prevention of metal ions adsorption [19].

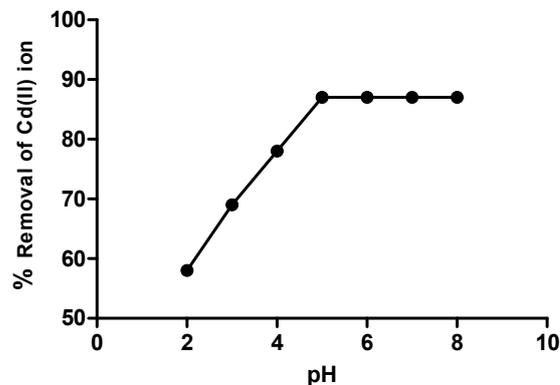


Fig. 6. Effect of pH for Cd(II) (50 mg l^{-1}) adsorption on CS/PVA/MC-G films

Effect of contact time

The effect of contact time on the adsorption of Cd(II) at 50 mg L^{-1} initial concentration is shown in Fig. 7. Initially, rate of adsorption was faster up to 4 h and 82.5% maximum removal of Cd(II) occurred. Time for equilibrium was observed 5 h, and beyond this time no change in adsorption was occurred. Thus, the equilibrium time was maintained 5 h in subsequent adsorption studies. It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of heavy metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained. In the beginning fast adsorption, may be explained due to the availability of more number of adsorption sites [20]. After initial adsorption of adsorbate, the available sites in the adsorbent reduced and thus rate of adsorption further decreased [21], which attained a limiting value at equilibrium. Rate of adsorption is of great significance for developing the adsorbent-based water technology [22]. These results are important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

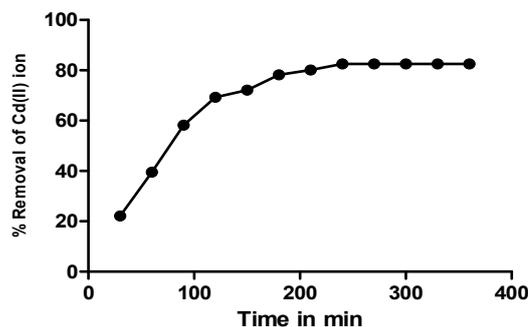


Fig. 7. Effect of time on the adsorption Cd(II) (50 mg l^{-1}) on CS/PVA/MC-G films at pH 5

Adsorption kinetics

Fig. 8(a, b) shows the time profile of metal ions adsorption onto crosslinked CS/PVA/MC-G blend film with the initial concentration of 50 mg L^{-1} . The results obtained from the experiments were used to study the kinetics of Cd^{2+} ion adsorption. The values of the pseudo first and second order rate constants and correlation coefficient (R^2)

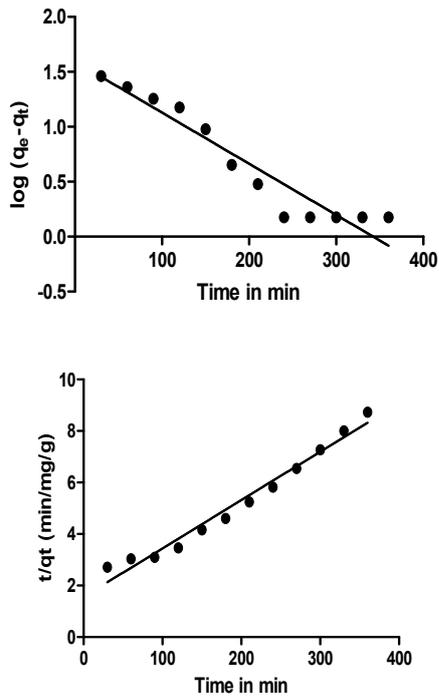


Fig. 8. (a) Pseudo-first-order, and (b) Pseudo-second-order plots for Cd(II) adsorption on CS/PVA/MC-G films at different concentrations: adsorbent dose at pH 5

monolayer adsorption where as the Freundlich isotherm is an empirical model that is based on sorption on heterogeneous surface. Langmuir adsorption isotherm plot for C_e/q_e versus C_e is shown in Fig. 9(a, b) gives the Freundlich adsorption isotherm plot of $\log q_e$ versus $\log C_e$.

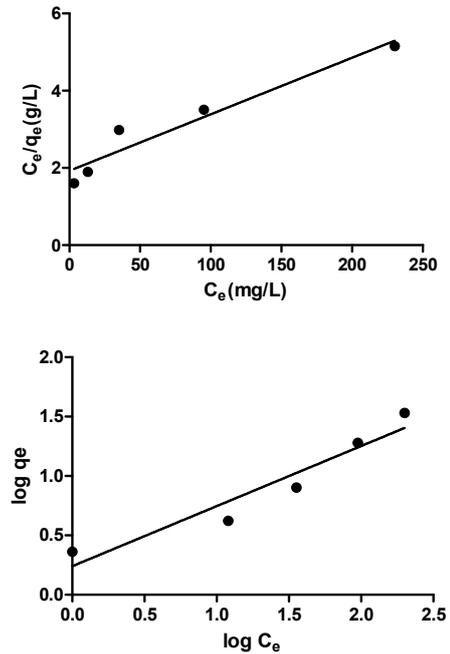


Fig. 9. (a) Langmuir plot and (b) Freundlich plot, for Cd(II) adsorption on CS/PVA/MC-G films

Table 1. Pseudo-first order (k_1) and second order (k_2) rate constants for adsorption of Cd(II) on CS/PVA/MC-G films

	Metal ion Pseudo-first-order kinetics			Pseudo-second-order kinetics		
	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	R^2
Cd(II)	0.00554281	0.06	0.9230	0.01877	83.27	0.9753

Table 2. Langmuir and Freundlich constants and correlation coefficients for the adsorption of Cd(II) on CS/PVA/MC-G films

Metal ion	Langmuir			Freundlich		
	Q (mg g^{-1})	b (L mg^{-1})	R^2	k_f (mg g^{-1})	n	R^2
Cd(II)	100.15	0.01964	0.9181	1.3459	1.5863	0.9928

are included in Table 1. In many cases the pseudo first order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [23]. The second order kinetic model assumes that the rate limiting step may be chemical adsorption [24]. In many cases, the adsorption data could be well correlated by second order rate equation over the entire period of contact time [25]. The results indicate that pseudo-second-order kinetic model is better obeyed in compare with the pseudo-first-order kinetic model for the adsorption of Cd(II) on CS/PVA/MC-G blend film since the experimentally calculated values of q_e at various concentration of Cd(II) were in good agreement with theoretical calculated values. Furthermore, the values of correlation coefficients (R^2) for pseudo-first-order kinetic model were slightly lower than the pseudo-second-order kinetic model.

Adsorption isotherms

Analysis of the equilibrium data is important to develop an equation which accurately represents the adsorption process and which could be used for design purposes. Langmuir and Freundlich adsorption isotherms were used to fit the experimental data. To obtain the isotherms, initial concentration of Cd(II) were varied from 50 to 500 mg L^{-1} while keeping the weight of CS/PVA/MC-G blend film, pH and contact time constant. The Langmuir isotherm assumes

The parameters of Langmuir and Freundlich adsorption isotherms, evaluated from the linear plots, are presented in Table 2, along with the correlation coefficient. Both the models are capable of representing the data adequately. The magnitude of the Freundlich constants, K_f and n indicate that the uptake of Cd(II) from aqueous solutions by the CS/PVA/MC-G blend films is feasible. Langmuir constant, Q , represents the maximum monolayer adsorption capacity of the biosorbent. The value is 100.15 mg g^{-1} for Cd(II). The sorbent developed in the present study exhibits higher adsorption capacity compared to chitosan in its natural form and most of the modified forms.

Desorption and regeneration studies

Desorption studies helps to reveal the nature of adsorption process and to recover the Cd(II) ions from crosslinked CS/PVA/MC-G blend film. Desorption studies was carried out by using HCl, HNO_3 , NaCl and EDTA solution. Desorption occurred only with the EDTA solution. About 71.3% desorption of Cd(II) was obtained from crosslinked CS/PVA/MC blend film.

Conclusion

In this study, Crosslinked chitosan/PVA/Mc films with low water content were prepared by solution casting method using

glutaraldehyde as crosslinking agent. The developed films were well characterized by FTIR, SEM and XRD to assess the structure. Crosslinked chitosan/PVA/MC hybrid ternary blend film was as a sorbent for the removal of Cd(II) ions from metal solution. The Langmuir adsorption model and Freundlich equation are used for the mathematical description of the sorption of Cd(II) ions onto crosslinked chitosan/PVA/MC blend. The adsorption isotherm studies clearly indicated that the adsorptive behavior of Cd(II) ions on crosslinked chitosan/PVA/MC satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site. Batch equilibrium results suggest that the adsorption process follows second order kinetic model in both the cases. The examined new material exhibits high adsorption capacity of cadmium can be efficiently desorbed with 0.01 M EDTA solution. Above research findings clearly indicate that the fabricated crosslinked CS/PVA/MC blend film can be efficiently utilized to recover Cd(II) ions from waste water up to high purity.

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