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Removal of Chromium (VI) from aqueous solution using chitosan - Starch blend

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ABSTRACT

The removal of Cr (VI) ions from aqueous solutions has been investigated using chitosan/Starch blend under different experimental conditions of initial chromium concentration, adsorbent dose and pH. The adsorption efficiency has been explained in terms of Langmuir and Freundlich equations. The results have revealed that the adsorption of Cr (VI) onto chitosan/Starch blend, which were found to well fit by the Freundlich isotherm. The result indicates that under the optimum conditions, the maximum adsorption comply that the chitosan/Starch blends is an effective adsorbent for chromium.

Key words: Chromium, Adsorption, chitosan, starch, glutaraldehyde.

INTRODUCTION

Water pollution is becoming a major problem endangering all living beings. This problem is not only currently acute but it is also becoming regressive day by day. The effects of water pollution strongly impact the gentle balance of nature. Basically the pollutants of water are classified as organic and inorganic pollutants. The inorganic pollutants consists mainly the heavy metals (metallic elements). Metals and metalloids due to their extensive use represent an important fraction of the pollutants [1]. Heavy metals like iron, manganese, lead, mercury, chromium, cadmium, nickel, cobalt, beryllium and copper are present in both natural and contaminated environments. They act as the minerals when they are present in the permissible limits. In well balanced natural environments, they occur at low concentrations. However these are present at high concentrations as is the case in contaminated environments. They occur naturally as ions, compounds and complexes (speciation) in the environment in a variety of forms [2]. Heavy metals may be released into the environment from metal smelting and refining industries, scrap metal, plastic and rubber industries and various consumer products and from burning of waste containing these elements.

The release of large quantities of hazardous materials into the natural environment has resulted in a number of environmental problems due to their nonbiodegradability and persistence, can accumulate in the food chain, and thus may pose a significant danger to human health. They disrupt bodily functions by accumulating in vital organs and glands in the human body such as in the heart, brain, kidney, bone and liver. They also displace vital nutritional minerals from the co-enzymes in the body and impede biological functions.

Chromium is one of the toxic element which is first to remove. Chromium (Cr(VI)) does not occur in nature, but is present in ores, primarily in the form of chromite. Chromium generally exists in two oxidation states, Cr (III) and Cr (VI). Chromium plays an important role in glucose and cholesterol metabolism and is an essential element to man and animals but at higher levels is toxic to both. The hexavalent form is 500 times more toxic to aquatic life than trivalent one [3].

A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion – exchange and adsorption. Most of these methods suffer with high capital and regeneration costs of the materials [4]. Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments. Cost is an important parameter for comparing the sorbent materials. The spent adsorbent themselves pose huge disposal issues. On the other hand, biosorption techniques could represent a new, less expensive way to remove toxic heavy metals even in dilute conditions from industrial wastewaters [5].

Chitosan is a well know biopolymer which is typically obtained by deacetylation of chitin under alkaline conditions, the most abundant organic materials, being second only to cellulose in the amount produced annually by biosynthesis. Chitosan displays interesting properties such as biocompatibility, biodegradability [6, 7] and its degradation products are non-toxic, non-immunogenic and non-carcinogenic [8, 9]. Therefore, chitosan has prospective applications in many fields such as biomedicine, waste water treatment, functional membranes and flocculation. However, chitosan is only soluble in few dilute acid solutions, which limits its applications.

Among the many kinds of candidates for use in biopolymers, starch is one of the most promising materials for biodegradable plastics because it is a versatile biopolymer, with immense potential and low price for use in non-food industries [10]. Rice starch and its major components, amylose and amylopectin, are biopolymers which are attractive raw materials for use as barriers in packaging materials. They have been used to produce biodegradable films to partially or entirely replace plastic polymers because of their low cost and renewability, as well as possessing good mechanical properties [11]. However, compared to common synthetic polymers, the biodegradable products based on starch, unfortunately, still reveal many disadvantages which are mainly attributed to the highly hydrophilic character of starch polymer.

To overcome the disadvantage of the individual properties of the chosen biopolymers, the polymer blending technology is used, which represent a more versatile approach for the development of new membrane materials in that the material properties of blends can be varied over a wide range. Relative to a single-component polymeric material, a blend enjoys several degrees of freedom that allow tailoring of the material to meet the membrane requirements suitable to effective adsorption process.

In this aspect, the present research work is carried out by preparing chitosan(CS)/starch(ST) blend (1:1) in the presence of glutaraldehyde as the crosslinking agent, used as novel low cost biosorbent for the subsequent removal of heavy metals especially chromium. The most convenient means of determining metal uptake abilities is through a batch reaction process.

MATERIALS AND METHODS

Chitosan with degree of deacetylation, DD = 92%, was obtained from India Sea Foods, Cochin, Kerala, Starch was purchased from Sigma Aldrich, India. All other reagents and solvents were used in this study were analytical grade and purchased from commercial sources. Millipore water is prepared in the laboratory by double distillation of deionized water in quartz distillation plant.

Preparation of chitosan/starch blends

About 10 grams of chitosan was slowly added to 2000 ml of acetic acid with constant stirring. 10 gram of the starch was dissolved in 1000 ml of water at 80°C. Blends of Chitosan/Starch was prepared by mixing the two polymers in the weight proportions of 1:1 and 10 ml of crosslinking agent glutaraldehyde was added with stirring for 2 hours.

Preparation of potassium dichromate solution

The stock solutions of Cr (VI) were prepared to get a concentration of 200mg/L of chromium as potassium dichromate. 1:1 Hydrochloric acid and 1% 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.

Experimental

Batch studies were performed with different concentrations of potassium dichromate to investigate the extent of adsorption. Synthetic solutions of Cr (VI) ion were taken in stoppered bottles and agitated with the 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 adsorption 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 220FS).

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time was studied for the chromium adsorption using CS/ST – glu blend. The plot reveals that the rate of percent removal of chromium is higher at the beginning. This is probably due to availability of more adsorption sites for the adsorption of chromium ions, the maximum removal was attained for about 250 min of shaking time and then it attains the equilibrium.

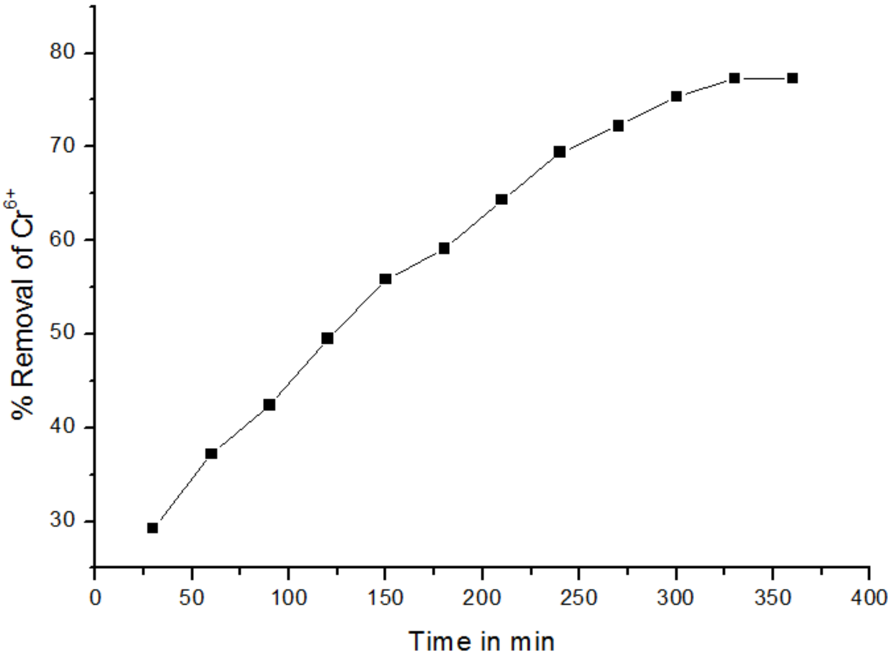

Figure 1: Percentage removal of chromium ion using Chitosan/Starch blend at different time intervals

Effect of Adsorbent dosage

The effect of the adsorbent dose was studied by varying the sorbent amounts from 1 to 6 g/L at room temperature, fixing the initial concentration, pH and contact time. From the figure it is evident that the adsorption of chromium increases rapidly with increase in the amount of CS/ST - glu blend due to greater availability of the surface area at higher concentration of the adsorbent. The significant increase in uptake was observed when the dose was increase from 1 to 3 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles.

Effect of pH

Aqueous solution pH is a critical parameter as it strongly affects metal biosorption, surface charge of the adsorbent, the degree of ionization and the speciation of adsorbate species [12]. The chromium adsorption was carried out to optimize the pH for maximum removal efficiency, the pH of the solution is varied from 4 – 8, at constant initial concentration, contact time and temperature. The maximum removal was found to be at pH 5. The further increase in the pH the insoluble precipitates formed [13].

Due to further increase in pH up to 6.0, the percentage adsorption was decreased, because OH− ions increased the hindrance of diffusion as well as some of the trivalent cations may react with OH− ion and precipitated and there by decreased the free metal ions available in the solution. The site dissociation and solution chemistry of the heavy metals such as hydrolysis, complexation by organic and/or inorganic ligands, redox reactions and precipitation are strongly influenced by pH and, on the other side, strongly influence the speciation and the biosorption availability of the heavy metals [14].

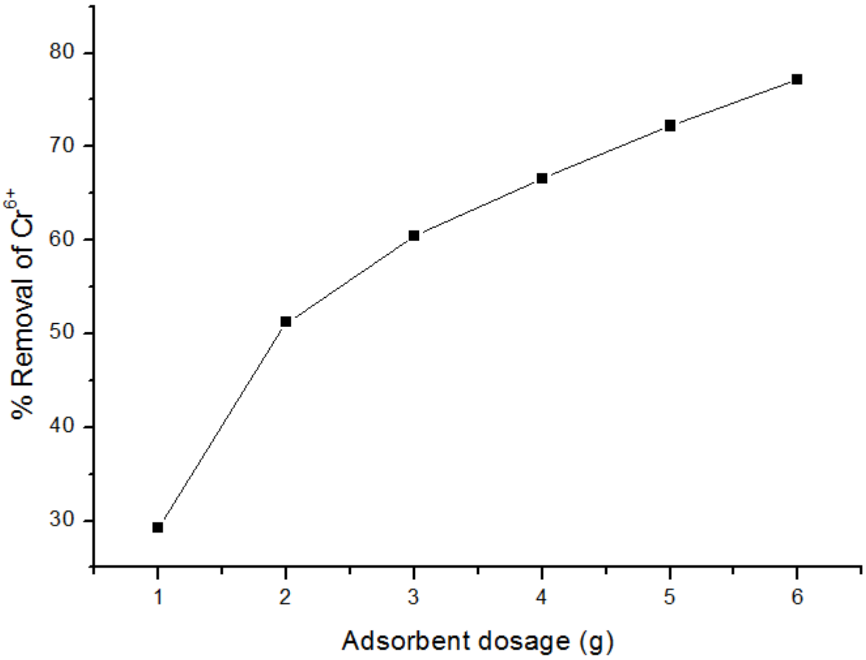

Figure 2: Percentage removal of chromium ion using Chitosan/Starch blend at different adsorbent dose

Equilibrium model

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate metal uptake per unit mass of adsorbent, qe, to the equilibrium adsorbate concentration in the bulk fluid phase Ce.

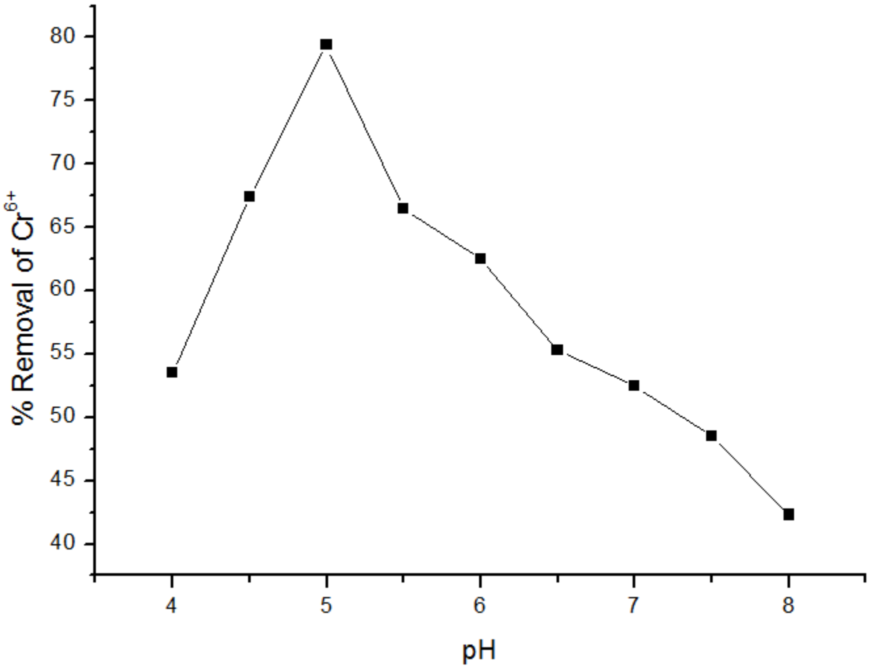

Figure 3: Percentage removal of chromium ion using Chitosan/Starch blend at different pH

Langmuir isotherm

The Langmuir equation has been frequently used to give the sorption equilibrium [15]. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. To get the equilibrium data, initial metal concentration were varied while the adsorbent mass in each sample was kept constant. The linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation:

$$C_{ads} = (K_L C_{eq})/(1 + bC_{eq}) \qquad (1)$$

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

$$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L \qquad (2)$$

And

$$\mathrm{C_{max}} = \mathrm{K_L/b} \qquad (3)$$

where:

C_{ads} = *amount of Cr (VI) adsorbed* $(mg{\cdot}g^{-1})$
C_{eq} = *equilibrium concentration of Cr (VI) 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 .Cr (VI) to adsorb onto 1 g blend* $(mg{\cdot}g^{-1})$

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 [16]. A plot of C_{eq}/C_{ads} vs C_{eq} confirming the applicability of the Langmuir adsorption isotherm.

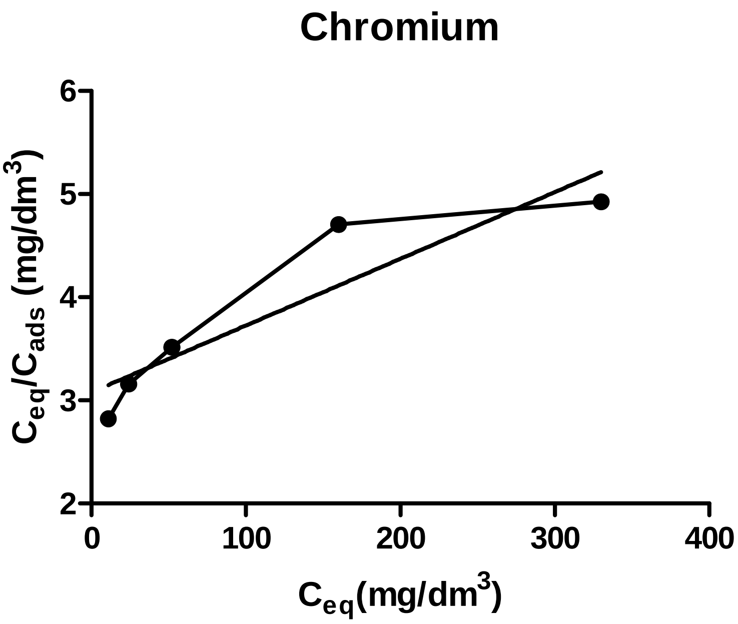

Figure 4: Langmuir plot for the adsorption of chromium ion on to chitosan/starch blend

Freundlich isotherm

Freundlich equation plot of log C_{ads} vs. log C_{eq} yielded a straighter line as shown in Fig. 5. 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 are expressed as:

$$C_{ads} = K_F C_{eq}^{1/n} \qquad (4)$$

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

$$\log C_{ads} = \log K_F + 1/n \log C_{eq} \qquad (5)$$

Where:

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

From Fig. 5 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.

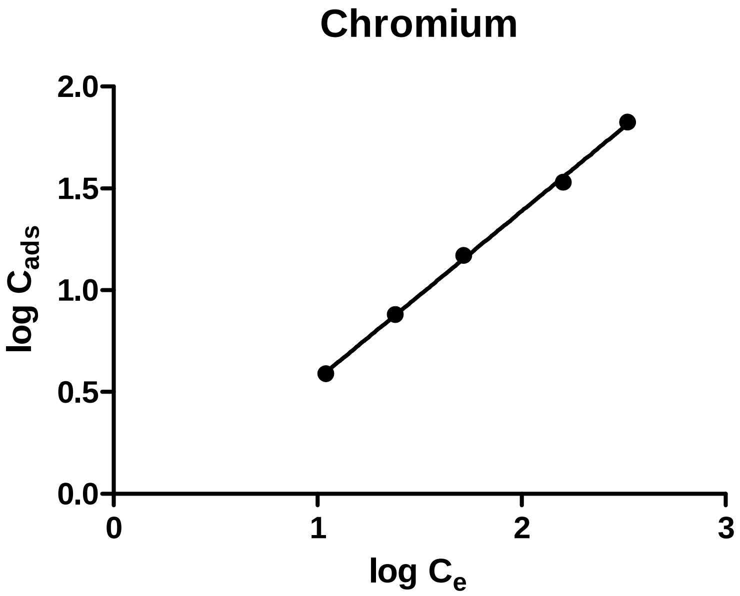

Figure 5: Freundlich plot for the adsorption of chromium ion on to chitosan/starch blend

Table 1: The Langmuir isotherm and Freundlich isotherm parameters of chitosan/starch blend

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**
Cr(VI)	3.0790	0.006465	476.26	0.8424	0.2605	0.8242	0.9989

To examine the relationship between biosorption and aqueous concentration at equilibrium, various biosorption isotherm models are widely employed for fitting the data. The Freundlich isotherm is originally empirical in nature [17], 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 [18]. The value of *n*, of this model, falling in the range of 1– 10 indicates favorable biosorption [19]. 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 [20]. The present study results indicate that the Freundlich model fit the experimental data well. The adsorption data provided an excellent fit to the Langmuir isotherm. The separation factor (R_L) value indicates that Cr (VI) biosorption of biosorbent in this study is favorable. It can be seen from the table, chitosan/starch binary blend used in this study has high biosorption capacity.

CONCLUSION

The adsorption capacity of Chromium (VI) metal ion adsorbed onto the Chitoan/Starch-glu binary blend adsorbent was observed to be related to the solution pH, reaction time, and initial concentration. The functional groups on the biosorbent surface were found to play a role in the entrapment of the target chromium ions. Since biosorbent used in this work is freely, abundantly, locally available, and is expected to be viable for removal of chromium ion from aqueous solution. Results obtained were modeled using Langmuir and Freundlich isotherms. The equilibrium data were well fitted with a Freundlich isotherm equation according to the nonlinear curve fitting regressive analysis, indicating that multilayer maximum adsorption capacity of chromium onto Chitoan /Starch-glu binary blend.

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