Equilibrium, thermodynamic and kinetic studies for removal of Chromium from aqueous solution by Grafted copolymer

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ARTICLE INFO

ABSTRACT

The graft co-polymer of binary monomers ethyl acylate (EA) and acrylonitrile (AN) onto natural cellulosic fiber using ceric ammonium nitrate as initiator has been studied for the removal of Chromium from aqueous solution. FTIR analysis and Boehm titration were used to identify and estimate the surface functional groups. Point of zero charge for the cellulosic fiber between 4.25 to 4.45 respectively. The maximum adsorption capacity of onion skin (76.9 mg/g) was slightly higher (pH = 5.3, T = 303K). The pseudo second order kinetic model fitted the batch data adequately. The rate constant of the kinetic model for cellulose fiber in absence of diffusional resistance was estimated to be 0.07 mg/g/min respectively at 303 K. Estimated thermodynamic parameters indicated the biosorption process to be endothermic.

1. Introduction

Heavy metals are known to cause toxicological problems to environment and human health. Recent scientific researches mainly focus upon sustainable way of development using techniques that are environment friendly as well as cost-effective and practical. Based on the aforesaid criteria, investigations are being carried out to extract heavy metal ions from wastewater using biological waste. Chromium metals are major components of stainless steel and their salts are used extensively in electroplating industries.chromium is being released in huge quantities in industrial waste water leading to pollution and contamination of the environment. Industries like metal cleaning, electroplating and metal processing, etc. are the main sources of chromium emanation to the environment Amrita et al. 2005, Although chromium (III) is an essential nutrient to produce various biochemical processes, chromium (VI) is reported as toxic element. It has been reported that both nickel and chromium (VI) can cause an increase triglyceride and phospholipids in serum associated with liver necrosis (Das et al, 2001; Kaufman et al, 1970; Kumar et al., 1981). A study by Kumar *et* demonstrated that there is increased accumulation of lipids in liver of rats after orally exposed to chromium (VI). Chromium, which initiates lipid peroxidation (LPO), thereby causing oxidative damage to critical macromolecules like proteins, DNA as well as celldamage/ death (Das et al., 2001; Doreswamy et al., 2004). Several biosorbents such as rice husks, tea factory waste (Wasetwar et al., 2008), fish scale Espinosa et al , wheat shell Basci et al, coffee husk (Rahmana et al., 2009) maple sawdust (Kumar et al., 1981) has been investigated for adsorbing heavy metal ion from aqueous solutions.

In this study the effectiveness Cellulosic fiber have been found as a suitable material for preparation of hydrogel by grafting reaction, as its linear structure provides good reinforcing properties to networks. Due to its renewable and abundance in nature it was used for cost effective technologies and hydrogel (**Nada et al., 2007; Sokker et al., 2006; Chauhan et al., 2005**). Cellulose and its derivatives have been used for removal of chromium from aqueous solutions was investigated.

2.0 Materials and methods

2.1. Biosorbent preparation

Several agricultural product and byproduct are natural source of cellulose. Among them, cotton, hemp, flax, rice husk, sugarcane bagasse, sawdust of wood, wheat straw,

onion skin, palm kernel husk, peanut skin, pinus bark, corncobs, cane stick, jute stem, banana fiber, papyrus, rapia, etc., have been tested as efficient adsorbent for heavy metal ion, especially adsorbent for divalent metal cation (Espinosa et al., 2001; Nada et al., 2006**).** But the raw fiber material used in this study was purchased from Himachal Krishi Vishwavidyalaya, Palampur, H. P, and India. The purification of the fiber was done by the soxhlet extraction with acetone for 72 hours and the resultant fiber was dried at room temperature. Acrylonitrile (AN), zinc nitrate, magnesium nitrate, dimethyl formamide (DMF), acetone, nickel nitrate (S.D. Fine), ethyl acylate (EA), ceric ammonium nitrate (Merck, India) and Nitric acid (Nice Chemical Ltd) were used as received.

The experimental studies were carried out in duplicate. Point of zero charge (PZC) was determined using the mass titration method described by Basci et al., 2009**.** Initially three aqueous solutions were prepared of pH 3, 6 and 10. Increasing amount of biosorbents (0.05%, 0.1%, 0.5%, 1.0%, 3.0%, 7.0% and 10.0% w/w) were added in 20ml of each solutions and allowed to equilibrate in a temperature controlled shaker incubator for 24h in 30ºC and 120 rpm. The equilibrium pH was measured for each solution using a digital pH meter. The pH versus biosorbent mass curve gives the PZC range for both the biosorbents.

Fourier transform infrared spectroscopy (FTIR) was used to identify the chemical groups present in the fiber. Solutions of $NaHCO_3$ (0.1 mol/L), Na_2CO_3 (0.05 mol/L), NaOH (0.1 mol/L), and HCl (0.1 mol/L) were prepared with deionized water. 1 g of cellulose were added to a volume of 50mL of these solutions and shaken at 100 rpm for 24h to reach equilibrium. After filtration, excess of base or acid was then determined by back titration using NaOH (0.1 mol/L) and HCl (0.1 mol/L) solutions.

2.2. Biosorption studies

The copper solution was prepared by dissolving its sulfate salt (Merck) in deionised water. Equilibrium sorption studies were conducted in 250 mL Erlenmeyer flask in a temperature controlled shaker incubator at 120 rpm for 24 h. For these studies, 0.2 g cellulose fiber contacted with the desired concentrations of chromium solution at defined initial pH and temperature.

Batch studies were carried out in a vessel of diameter 12 cm with 500 mL of solution and specified amount of biosorbent. A mechanical stirrer (1500 rpm) was used to agitate the system. Concentration of chromium metal ions in the solution was measured by Atomic absorption spectrophotometer (Perkin Elmer A Analyst 200). The amount of metal uptake by the biosorbent was calculated using the following equation:

$$q_t = V\left(C_i - C_t\right)/W \qquad (1)$$

where q_t and C_t is amount of metal ion biosorbed per gram of biomass and solution concentration at time t, C_i is the initial solution concentration, V is the volume of metal solution and W is the weight of biosorbent.

3 Results and discussion

3.1. Characterization of biosorbent

The IR spectrum of the grafted copolymer was determined by using KBr Technique. When the traditional KBr pellet technique is used we obtain information about both the polymer grafted on the surface of the fibrils and also about the polymer grafted inside the fibrils. The attenuated total reflectance technique (ATR) is a useful method to detect the surface structural Mao et al. In special case FTIR may also be used to study the form of binding of the adsorbed species to the poymer. The FTIR spectrum of grafted adsorbent was shown in Figure 1.
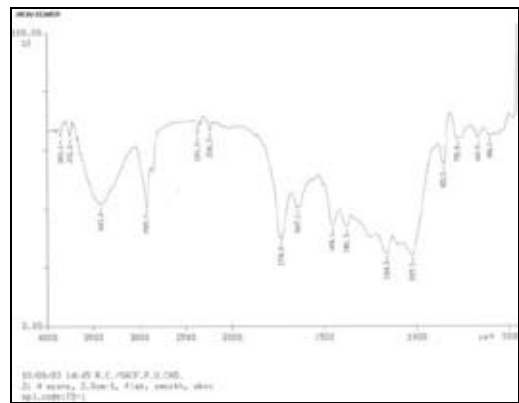

Fig. 1: FTIR spectrum of grafted adsorbent

3.2. Effect of pH

The effect of initial pH on adsorption capacity of cellulose is shown in the Fig. 3. Diluted *HCl* was added to the solutions to get the desired pH values. The uptake increased with change in initial pH from 3 to 5.3 for the adsorbent. Experiments were restricted to pH 5.3 as at higher pH chromium precipitates out in the form of insoluble chromium hydroxide.

An increase in pH results in more negative charges on the adsorbent surface that is likely to attract the positively charged chromium ions to bind to its surface resulting in increased uptake. At low pH, the approach of positively charged Cr cations will be inhibited due to the overall surface positive charge caused by protons that would restrict access to ligands by metal ions as a result of repulsive forces. It is also likely that these protons will compete with Cr ions for the ligands and thereby decrease the interaction of metal ions. In order to prove the aforesaid fact, PZC for celluse fiber were determined. It clearly interprets that to ensure a completely negatively charged surface on the biosorbents, the pH must be

maintained above 4.75 to achieve the maximum adsorption.

3.3. Biosorption isotherms

The adsorption isotherm for ethyl acrylate at temperatures of 293 K, 303 K and 313 K. The Langmuir, Freundlich, Temkin and D-R isotherm models were employed to describe the uptake of Chromium by natural fiber grafted co-polymer.

Langmuir

$$q_e/q_{max} = K_L C_e/(1+K_L C_e) \qquad (2)$$

Freundlich

$$q_e = K_F C_e^{1/n} \qquad (3)$$

Temkin

$$q_e = \frac{RT}{b} \ln(AC_e) \qquad (4)$$

Dubinin-Radushkevich

$$q_e = q_{max} \exp^{-\beta\varepsilon^2} \qquad (5)$$

In the above equations q_e and C_e is the amount of the metal adsorbed per unit mass of adsorbent and metal concentration in the solution at equilibrium respectively, q_{max} is the Langmuir constant related to the maximum monolayer adsorption capacity and K_L is the Langmuir constant related to the affinity of the binding sites. The terms K_F and n in Eq. (3) are related to binding energy and adsorption capacity and to the intensity of adsorption respectively. In Eq. (4), $B = (RT/b)$ is related to the heat of the adsorption process. *A* and *B* are Temkin constants. For D-R model in Eq.5, β is a coefficient related to the mean free energy of adsorption (mol^2 J^{-2}), and $\varepsilon = RT \ln(1+1/C_e)$ is the Polanyi potential (J mol^{-1}).

The estimated value of these constants obtained by fitting the model expressions to the experimental data along with R^2 are listed in Tab. 1. Out of the 4 isotherm models studied, the higher values of R^2 obtained from the fitting to Langmuir and Freundlich isotherm expression indicate that these give good fit to the

Table 3(a)
Pseudo-first-order Kinetic rate constants related to the biosorption of chromium biosorption onto Cellulose fiber

Table 1 compares the values of q_{max} obtained in this study with that of other biosorbents reported in the literature. It is seen that the adsorption capacity of the skin of onion and garlic are higher than that of many other biosorbents for this metal ion.

	Celluose fiber			
Metal concentration (mg L^{-1})	$(q_e)_{cal}$ (mg g^{-1})	$(q_e)_{exp}$ (mg g^{-1})	K_2 (mg g^{-1} min^{-1})	R^2
20	3.61	3.38	0.114	0.999
35	7.54	7.5	0.061	0.999
50	10.1	10.8	0.05	0.999
Biosorbent dosage (g)		(2)		
0.5	28.2	25.9	0.013	0.999
0.75	21.3	20.5	0.018	0.998
1	18.2	16.4	0.021	0.999
1.5	12.9	13	0.035	0.998
2	10.1	10.8	0.05	0.999
3	8.1	8.1	0.047	0.999

Table 1. Comparison of Langmuir based maximum adsorption capacity of several biosorbents for Cr (IV) adsorption

3.4. Biosorption kinetics studies

Experiments were carried out to obtain the variation of adsorbed amount with time at different biomass amount (initial metal concentration = 50 mg/L) and initial concentration of metal ion (biosorbent = 2g) at 303 K.

3.5.1. Intrinsic rate constant

Biosorbent	q_{max} (mg/g) (T (K)/pH)	Reference
Tectona grandis	15.4 (298/5.0)	[3]
Fish scale	58.5 (-/ -)	[8]
Cellulose	80.6 (303/5.3)	Present study
Wheat shell	8.3 (298/5.0)	[10]
Coffee husk	7.5 (298/4.0)	[11]
Sugar beet pulp	31.4 (298/4.0)	[21]

Table 2. Pseudo-second-order Kinetic rate constants related to the biosorption of Chromium biosorption onto grafted fiber

The kinetic data for the studied biosorption process was analyzed by fitting pseudo first-order and pseudo second-order kinetic model to the experimental data. The linear form of the model expression is:

Pseudo first-order model

$$\log_{10}(q_t - q_e) = \log_{10} q_e - K_1 t \qquad (6)$$

Pseudo second-order model

$$t/q_t = t/q_e + 1/K_2 q_e^2 \qquad (7)$$

where K_1 and K_2 are the rate constant of the pseudo first-order and second-order equation respectively.

The values of the model constants for different operating parameters is tabulated **in Tab. 3(a) and 3(b).** The value of the experimental equilibrium adsorption $(q_e)_{\text{exp}}$ was determined by the intercept of adsorption isotherm and the overall mass balance equation. The calculated value of q_e i.e. $(q_e)_{cal}$ from the pseudo first-order model was obtained through an iterative procedure such that the value of R^2 is maximized whereas the model parameters of eq. (7) was determined using linear regression technique. The higher values of R^2 for pseudo second-order kinetic model implied that the biosorption process is best described this approach.

Non linear regression of original form of the pseudo second order expression

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \qquad (8)$$

was stated to be more appropriate. The non-linear optimization method available with Microsoft Excel 2007 version (solver) was used in this study to determine the model constants of the above equation. The value of $(q_e)_{cal}$ and K_2 for garlic skin are shown within the bracket of Tab. 3(b). It is seen that there is no significant difference in the value of the parameters obtained with the two techniques. Similar result was also obtained with onion skin biosorbent.

The intrinsic rate of reaction refers only to the rate at which one chemical species is converted into another. The measurement of this can be achieved by making the process independent of physical processes such as heat, mass and momentum transfer. The change in the value of K_2 with variation of biomass amount and initial feed concentration suggests that it is not the intrinsic reaction rate. Qualitatively, increase of metal loading in biomass implies greater penetration of the sorbate into the adsorbent thereby increasing the intraparticle mass transfer resistance.

The weight of the biomass gives good representation of the external surface area. As W tends to infinity, the product of bulk phase mass transfer coefficient and surface area also tends towards infinite and the mass transfer resistance for transport of metal ion from the bulk solution to the biosorbent-solution interface towards zero. Further the intraparticle mass transfer resistance can be neglected as the reaction can be assumed to occur at the surface of the biosorbent itself. The value of K_2 in absence of mass transfer resistances was obtained from the intercept of the curve shown on extrapolation to $1/W \to 0$ (W is infinite). The desired value of K_2 for onion and garlic scale are 0.07 mg/g/min ($R^2 = 0.94$) and 0.075 mg/g/min ($R^2 = 0.89$) respectively.

3.6. Thermodynamic parameters

The chemical equilibrium constant of a reversible reaction can be related to temperature by the following expression:

$$\ln K_a = -\Delta G^0 / RT = -\Delta H^0 / RT + \Delta S^0 / R \quad (10)$$

where K_a is the equilibrium constant, ΔG^o is the change in standard Gibbs free energy, ΔS^o is the standard entropy change, ΔH^o is the standard enthalpy change, T is the temperature and R is the universal gas constant. The free energy change for the process was determined by using the equilibrium constants obtained from Langmuir isotherm model. Thermodynamic parameters of ΔH^o and ΔS^o were obtained from the slope and intercept of the plot between $\ln K_a$ versus $1/T$.

The negative values of Gibbs free energy (~ -16.0 kJ/mol) indicated that the feasibility of the process. Standard enthalpy change for cellulose was estimated to be 11.8 kJ/mol respectively. The corresponding standard change in entropy was 0.095 kJ/mol/K respectively. The positive values of ΔH^o for Chromium removal indicated that the metal adsorption process was endothermic in nature. The positive values of ΔS^o for Chromium with adsorbent showed an increased randomness at solid solutions interface during the adsorption of Cr on the waste biomass (Basci et al., 2009; Chauhan et al., 2005).

4 Conclusions

The study indicated that natural fiber grafted co-polymer is efficient adsorbents for removal of Chromium from aqueous solution. The high adsorptive capacity of this cellulose fiber implies that it can be looked as an alternative to costly adsorbents like activated carbon, resins etc. The proposed new technique for estimation of reaction rate constant in absence of mass transfer resistances provide a means of delineating the influence of reaction kinetics and diffusional resistances on the uptake rate and result in improving contactor design.

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