



Heavy Metal Uptake by Agro based Waste Materials

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Biosorption is one such emerging technology which utilized naturally occurring waste materials to sequester heavy metals from industrial wastewater. The aim of the present study was to utilize the locally available agricultural waste materials for heavy metal removal from industrial wastewater. The wastewater containing hexavalent chromium was treated with biomass prepared from corn stalks. It was found that a time of one hour was sufficient for sorption to attain equilibrium. The equilibrium sorption capacity after one hour was 0.375 mg.g⁻¹. The optimum pH was (2-2.5) for chromium. Ion exchange was the major removal mechanism along with physical sorption and precipitation. The biosorption data was well fitted to Langmuir adsorption model. The kinetics of biosorption process was well described by the pseudo 2nd order kinetics model. It was concluded that adsorbent prepared from corn stalks can be utilized for the treatment of heavy metals in wastewater.

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Heavy Metal Uptake by Agro based Waste Materials

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Biosorption is one such emerging technology which utilized naturally occurring waste materials to sequester heavy metals from industrial wastewater. The aim of the present study was to utilize the locally available agricultural waste materials for heavy metal removal from industrial wastewater. The wastewater containing hexavalent chromium was treated with biomass prepared from corn stalks. It was found that a time of one hour was sufficient for sorption to attain equilibrium. The equilibrium sorption capacity after one hour was 0.375 mg.g⁻¹. The optimum pH was (2-2.5) for chromium. Ion exchange was the major removal mechanism along with physical sorption and precipitation. The biosorption data was well fitted to Langmuir adsorption model. The kinetics of biosorption process was well described by the pseudo 2nd order kinetics model. It was concluded that adsorbent prepared from corn stalks can be utilized for the treatment of heavy metals in wastewater.

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I. INTRODUCTION

Heavy metals such as chromium have number of applications in basic engineering works, paper and pulp industries, leather tanning, petrochemicals fertilizers, etc. The hexavalent and trivalent chromium is often present in electroplating wastewater [1]. Other sources of chromium pollution are leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication [2].

Heavy metals are toxic to aquatic flora and fauna even in relatively low concentrations. Some metals can be assimilated, stored and concentrated by organisms [3]. Strong exposure of hexavalent chromium causes cancer in the digestive tract and lungs and may cause gastric pain, nausea, vomiting, severe diarrhoea, and hemorrhage [4].

The conventional methods for treatment of chromium wastes include: lime and soda ash precipitation, removing metals from wastewater requires development of new sorbents. A wide range of commercial sorbents including chelating resins and activated carbon are available for metal sorption, but

they are relatively expensive. In recent years, numerous low cost natural materials have been proposed as potential adsorbents. These include moss peat [5], algae [6], leaf mould [7], sea weeds [8], coconut husk [9], sago waste [10], peanut hull [11], hazelnut [12], bagasse [13], rice hull [14], sugar beet pulp [15], plants biomass and bituminous coal [16]. In this research adsorbent prepared from corn stalks was used for treatment of chromium wastes. Effect of operating conditions like temperature, pH and initial metal concentration on chromium adsorption were investigated.

II. THEORETICAL AND EXPERIMENTAL PART

a) Optimization of chromium adsorption

i. Determination of equilibrium time

Batch experiments were carried out to find the equilibrium time for sorption of chromium on corn stalks. All experiments were performed three times and average values were used in all calculations. 1.0 g corn stalks powder of 50 mesh sizes was mixed in 100 ml solutions of chromium. The initial concentration of each solution was 100mg.l⁻¹. It was shaken at 200 rpm and samples were collected at different time intervals. After completion of each batch of experiments the solution was filtered using filter paper. Filtrate was analyzed using atomic absorption spectrophotometer to determine the amount of metal left after sorption. The amount of metal sorbed was calculated by material balance. Sorption capacity q was determined using the formula:

$$q_e = V \cdot \frac{(C_0 - C_f)}{m} \quad (1)$$

Where C₀ and C_f are the initial and final concentrations of metal in solution, V is the volume of solution and m is the mass of adsorbent.

ii. Effect of pH

Keeping the same operating conditions as mentioned previously, pH of solution was varied from 2 to 7.5. The Cr(VI) is present in solution as CrO₄⁻² and Cr₂O₇⁻² at normal pH values but when pH values are reduced below 3 then Chromium exists in the form of HCrO₄⁻. When adsorbent developed from corn stalks is intimately mixed with chromium solution at low pH values then OH⁻ group present in biomass are replaced by chromate ions in the solution.

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b) Adsorption Isotherms

The Biosorption data from experiments were fitted with:

i. Langmuir isotherm [17]

Langmuir adsorption isotherm sheds no light on the mechanistic aspects of adsorption. It provides information on uptake capabilities and also reflects the usual equilibrium process behaviour. The Langmuir non linear equation is:

$$q_e = q_m \cdot \frac{b \cdot C_e}{1 + b \cdot C_e} \quad (2)$$

Where q_e is the amount of metal sorbed per unit weight of biomass at equilibrium, C_e is the residual equilibrium metal, q_m is the maximum possible amount of metal ion adsorbed per unit weight of biomass and b is the equilibrium constant related to the affinity of the binding sites for the metals, lower is b more is the affinity of metal to biomass.

Low values of parameter b indicate that corn stalks have high affinity for chromium. The table 1 presents linear equations of Langmuir model.

The essential characteristic of a Langmuir isotherm can be expressed as a dimensionless constant, defined as the separation factor:

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (3)$$

ii. Freundlich isotherm [18]

The Freundlich non linear equation is:

$$q_e = K_F C_e^n \quad (4)$$

Where, K_F and n are constants indicating adsorption capacity and adsorption intensity, respectively. The constants were obtained from the plots of the linearized equations:

$$\log q_e = \log K_F + n \cdot \log C_e \quad (5)$$

Another use of the results is to plot the variation of the distribution coefficient K_d as a function of q_e in logarithmic scale:

$$\log K_d = \left(\frac{1}{n}\right) \cdot \log K_F + \left[\frac{(n-1)}{n}\right] \cdot (\log q_e) \quad (6)$$

c) Kinetic Models

To determine order of the adsorption kinetics, first-order and second-order kinetic models were tested to fit the experimental metal removal data and to assist water treatment process design.

i. First order model

The model of the first order is generally expressed by [19]:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (7)$$

Which carry out, after integration, to [20]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (8)$$

ii. Second order model

It is an equation which is often employed on the representation of kinetics of adsorption. It is presented in the form [21]:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (9)$$

The integration of the equation (14) permits to obtaining the equation [22]:

$$\frac{1}{q_t} = \frac{1}{K_2 \cdot q_e^2} \cdot \frac{1}{t} + \left(\frac{1}{q_e}\right) \quad (10)$$

This presents the linearization of the second class equation; It is the equation which helps us to extract the parameters of the second order kinetic model.

III. RESULTS AND DISCUSSIONS

a) Optimization of chromium Biosorption

i. Determination of equilibrium time

As shown in Figure 1 about 55% removal was attained in first 15 min and concentration became almost constant after 90 min. The fast initial uptake was due to the accumulation of metal ions on surface of adsorbent which is a rapid step. More time was consumed on diffusion of ions to binding sites. It was concluded that one hour was sufficient for sorption to attain equilibrium. The equilibrium capacity obtained after one hour of sorption was $0.375 \text{ mg} \cdot \text{g}^{-1}$ for chromium.

ii. Effect of pH

Figure 2 shows the adsorption of chromium at different value of pH. The sorption was pH dependent and optimal pH was [2-2,5] for chromium. Main removal mechanism was ion exchange between metal anions and hydroxyl ions in case of hexavalent chromium. This fact is indicated by the change of pH at the end of adsorption process.

b) Adsorption Isotherm

i. Langmuir isotherm

The values of equilibrium relation parameter, R_L were calculated for five Langmuir linearizations. As shown in Table 2, R_L values lie between 0 and 1 which indicate favourable sorption isotherm for chromium metal. Low values of parameter b indicate that corn stalks have high affinity for chromium.

ii. Freundlich Isotherm

The values of equilibrium relation parameter, n were calculated for two Freundlich model's, the results

is shown in table 3, n values is high than 1 so the adsorption of chromium adsorption was not well fitted with Freundlich model and The low values of maximum adsorption capacities obtained from the Freundlich model, confirm that the molecule of Methylene Blue is not strongly adsorbed inside the pores because of its size.

c) *Kinetic Models*

First and second order equation accounting both with theoretic and experimental point of view was used to describe the adsorption kinetics of Chromium onto Corn stalks.

i. *First order model*

The experimental q_e values are lower than the theoretic value. The values of K_1 , q_e and regression coefficients provided in Table 4, demonstrate that chromium adsorption by Clay are not first-order.

ii. *Second order model*

The correlation coefficient (R^2) for this plot is superior than 0.9 (Table 5). The experimental q_e values were compared to theoretic q_e values determined by second order rate kinetic models. The q_e values calculated from the pseudo second order kinetic model

exhibit excellent agreement with the experimental q_e values (Table 5). Thus, the sorption process is pseudo-second order. The pseudo-second order model is based on the assumption that the rate-limiting step is a chemical sorption between the adsorbate and adsorbent. This provides the best correlation of the data.

Table 1 : Linear equations of Langmuir model

Forms	Equations
Langmuir 1	$\frac{1}{q_e} = \frac{1}{C_e} \frac{1}{bq_m} + \frac{1}{q_m}$ (3)
Langmuir 2	$\frac{C_e}{q_e} = C_e \frac{1}{q_m} + \frac{1}{q_m \cdot b}$ (4)
Langmuir 3	$q_e = -\frac{1}{b} \frac{q_e}{C_e} + q_m$ (5)
Langmuir 4	$\frac{q_e}{C_e} = -bq_e + bq_m$ (6)
Langmuir 5	$\frac{1}{C_e} = bq_m \frac{1}{q_e} - b$ (7)

Table 2 : Langmuir adsorption parameters for chromium biosorption

Forms	b	q_m	r^2	R_L	R
Langmuir I	-1,37	0,02	0,965	0,127	0,128
Langmuir II	-1,368	0,02	0,9863	0,127	
Langmuir III	-1,397	0,0196	0,9962	0,125	
Langmuir IV	-1,325	0,0194	0,9962	0,131	
Langmuir V	-1,3372	0,0198	0,965	0,13	

Table 3 : Freundlich adsorption parameters for chromium biosorption

Forms	Log K_F	K_F	n	R^2	$q_m(mg \cdot g^{-1})$
Freundlich 1	-2,5571	0,0775	1,9019	0,9376	0,0036
Freundlich 2	-2,539	0,0789	2,028	0,9928	0,0030

Table 4 : First order parameters for chromium biosorption

C_0	m_s	r^2	q_e	$q_e(\text{Theoric})/q_e(\text{experimental})$	K_1
0,5	1	0,9464	0,0271	1,01	0,0015

Table 5 : Second order parameters for chromium biosorption

C_0	m_s	r^2	q_e	$q_e(\text{Theoric})/q_e(\text{experimental})$	K_2
0,5	1	0,9939	0,31	0,998	0,718

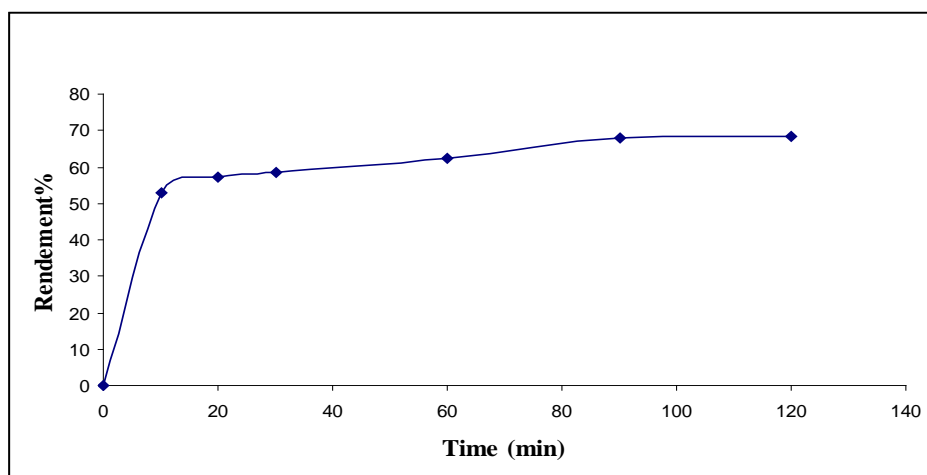


Figure 1 : Equilibrium time of chromium adsorption on Corn Stalks

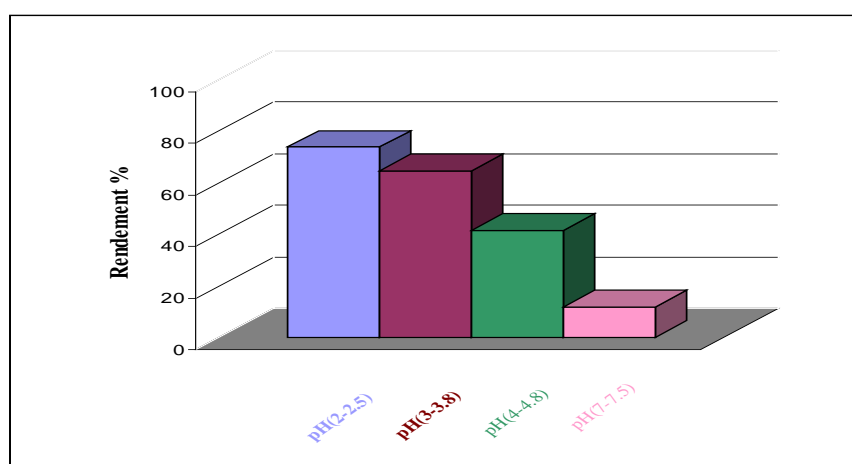


Figure 2 : Effect of pH on the adsorption of chromium on Corn stalks

IV. CONCLUSION

Corn stalks powder was found to be a very good adsorbent for hexavalent chromium. It has good sorption capacity for both metals. The sorption capacity for hexavalent chromium was $0,375 \text{ mg.g}^{-1}$. The sorption was pH dependent and optimal pH was [2-2,5] for chromium. Main removal mechanism was ion exchange between metal anions and hydroxyl ions in case of hexavalent chromium. This fact is indicated by the change of pH at the end of adsorption process. Physical sorption and precipitation also contributed to removal of metals. The adsorption process followed Langmuir model which indicated that ion exchange took place in a monolayer at the surface of adsorbent.

The kinetics of adsorption process was represented well by pseudo 2nd order kinetic model. We can conclude that this adsorption of chromium on corn stalks is a favourable chemisorption.

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