Lowcost bio-sorbent 'maize bran' for the removal of cadmium from wastewater

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A novel biosorbent maize bran has been successfully utilised for the removal of cadmium(II) from wastewater. The maximum removal of cadmium(II) has been found to be 94.5% at pH 8.6, initial Cd^{II} concentration 1.25 mg L^{-1} and temperature 20°C. The effect of different parameters such as contact time, adsorbate concentration, pH of the medium and temperature have been investigated. Dynamics of the sorption process were studied and the values of rate constant of adsorption, rate constant of intraparticle diffusion and mass transfer coefficient were calculated. Various thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 have also been evaluated and critically discussed. It has been concluded that the reaction was spontaneous and exothermic in nature. The applicability of Langmuir isotherm suggests the formation of monolayer coverage of the adsorbate on the surface of adsorbents.

Removal of toxic heavy metals from industrial wastewater is essential from the standpoint of environmental pollution control. Cadmium is one of them and the permissible limit of cadmium(II) in drinking water as per World Health Organisation (WHO) is 0.005 mg L^{-1}. Ingestion of cadmium(II) above its permissible limit causes various types of acute and chronic metabolic disorders such as *itai-itai* disease, renal damage, emphysema, hypertension and testicular atrophy[1]. Many physico-chemical wastewater treatment processes viz. oxidation-reduction, precipitation, ion exchange and liquid membrane have been used for Cd^{II} removal. However, all these processes have the limitations of technical and/or economical viability. Adsorption is a simple and attractive method for the removal of metal from the effluents due to its high efficiency, easy handling and being economically feasible. Some conventional chemisorbents have been utilized for the removal of heavy metals. Many non-conventional biosorbents viz. banana pith, wood saw dust, orange peel, bamboo dust, peanut shell, coniferous bark, waste tea leaves, soyabean hull etc.[2] have also been utilised for the removal purpose. We have chosen maize bran as a biosorbent, which is low cost, easily available and mostly biodegradable.

Materials and methods :

Physico-chemical analysis of the adsorbent :

Maize bran was collected from M/s. S. K. Industries (Flour mill), Narayanpur, Mirzapur (U.P.) and was used in experiments with double washing with double-distilled water to remove soluble lighter materials and drying at 60°C

in an oven and crushing and sieving to < 178 μm. It is biodegradable.

Various physical properties of maize bran are given in Table 1. Chemical analysis of the maize bran shows the presence of various oxides of Al, Si, Mn, Fe etc.

IR studies (Table 2) of maize bran shows that major constituents are carbon while quartz, carbon hexagonal, Fe-O, Mn-O, Si-C, Ca_2SiO_4, Ca-P and alumina has also been found (18.41%).

The present work deals with adsorption studies of Cd^{II} ion on maize bran at different concentration, temperature and pH. The adsorption dynamics, rate constant of adsorption, rate of intraparticle diffusion and mass transfer coefficient have been evaluated. The adsorption equilibrium for the investigation of suitability of the adsorption isotherm model has also been discussed.

Experimental

In the present investigation batch mode of operation was selected in order to measure the progress of adsorption. The same was carried out by shaking 1.0 g of desired grade of adsorbent (maize bran) with 50 ml aqueous solution of adsorbate (cadmium chloride) of desired concentration at different temperatures and pH in different glass bottles in a shaking thermostat at a constant speed of 125 rpm. The pH of the adsorbate solution was adjusted by adding HCl or NaOH.

The progress of adsorption was noted at different time

intervals till the attainment of saturation. At the completion of predetermined time intervals, the adsorbate and adsorbent were separated by high speed centrifugation at 15000 rpm and the supernatant liquid was analysed by Orion Ion Selective pH meter, Model No. 960 (USA) to find out the residual concentration of cadmium ion.

Blank samples were run under similar conditions of concentration, pH and temperature but without the adsorbent in all the cases to correct for any adsorption on the internal surface of the bottles.

Results and discussion

Effect of contact time and concentration :

A series of experiments were performed at different initial adsorbate concentration viz. 1.00, 1.25 and 1.50 mg L^{-1} and time interval and at a temperature of 30°C and pH 8.6. The percentage removal of Cd^{II} was found 94.25, 88.33 and 82.30, respectively. The results showed that the extent of adsorption increased rapidly in the initial stages but became slow in the later stages till the attainment of equilibrium. Equilibrium time for the adsorption of Cd^{II} on maize bran at various adsorbate concentration was found to be 100 min, which indicated that equilibrium time was independent of initial adsorbate concentration. Extent of removal was highly dependent on the concentration of the adsorbate. The removal curves thus obtained were single smooth and continuous suggesting the formation of monolayer of adsorbate on the surface of the adsorbent[3].

Table 1. Physical and chemical properties of biosorbent maize bran

Surface area (m^{2}g^{-1})	437.00
Bulk density (g cm^{-3})	0.2432
Particle size (µm)	<178
Average particle diameter (cm)	1.95 × 10^{-2}
Porosity (fraction)	0.37
Proximate analysis (%) :	
Moisture	7.97
Volatile matter	42.34
Fixed carbon	31.28
Total ash	18.41
Oxides of Al, Mn, Si, Fe, etc.	11.49
Remaining oxides	6.92

Adsorption dynamics :

The rate constant for the adsorption (k_{ad} min^{-1}) of cadmium ion was evaluated in the light of Lagergreen rate equation[4],

$$\log (q_e - q) = \log q_e - \frac{k_{ad}}{2.303} .t \qquad (1)$$

where q and q_e are the amounts of adsorbate (mg g^{-1}) at time t (min) and at equilibrium respectively. The linear

plots of log ($q_e - q$) vs t (Fig. 1) suggested the first order kinetics of the uptake of Cd^{II}. The values of k_{ad} at different temperatures was calculated from the slopes of these lines and are represented in Table 3.

Table 2. IR bands of maize bran alongwith their possible assignments

Band position (cm^{-1})	Assignment
3410	-OH str.
2950	-C=C-H str.
1746	-C=O str.
1556, 1518	Aromatic ring
1487	>N-H str.
945	Fe-O
841	Mn-O
773	-C-H str.
746	Al-O
682, 550	Si-O stretch
493	Fe-O
470	Si-O-Ca bend
450	Si-O bend

During the batch mode of operation, there is a possibility of intra particle pore diffusion of adsorbate, which is often the rate controlling step[5]. Thus, the rate constant of intraparticle diffusion (k_{id}) at different temperatures was determined by using Weber and Morris relationship[6] [$q = k_{id}$ $t^{1/2}$] by plotting amount of the adsorbate adsorbed (q) vs $\sqrt{T}$. The values of k_{id} were obtained from the slopes of the respective plots and are represented in Table 3.

Table 3. Rate constants for adsorption, thermodynamic parameters and Langmuir constants for cadmium(II) ion

Temp.(°C)	20	30	40
k_{ad}. min^{-1} (×10^2)	5.896	5.343	4.836
k_{id} (mg g^{-1} min$^{-1/2}$) (×10^3)	10.8	9.83	8.05
$\bar{D}$ (cm^2 s^{-1}) (×10^9)	4.712	3.600	2.826
β_1 S_s (min^{-1}) (×10^2)	4.685	4.254	3.726
$-\Delta G^0$, kcal mol^{-1}	1.662	1.218	0.926
$-\Delta H^0$, kcal mol^{-1}	–	14.684	10.055
$-\Delta S^0$ cal mol^{-1} K^{-1}	–	44.444	29.165
Q^0 (mg g^{-1}) × 10	0.771	0.743	0.720
b (dm^{-3} mg^{-1})	34.17	22.43	12.63
R_L	0.0191	0.0288	0.0502

Mass transfer analysis :

The mass transfer analysis for the adsorption of cadmium(II) ion was determined at various temperatures (20, 30 and 40°C) using the Mckay *et al.* equation[7],

$$\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mK} \right) = \ln \left(\frac{mK}{1 + mK} \right) - \left(\frac{1 + mK}{mK} \right) .\beta_1.S_s.t \qquad (2)$$

where, C_0 is the initial adsorbate concentration, C_t is the adsorbate concentration after time t, m is the mass of the biosorbent per unit volume, K is the Langmuir's constant obtained by multiplying Q^0 and b, β_1 is the mass transfer

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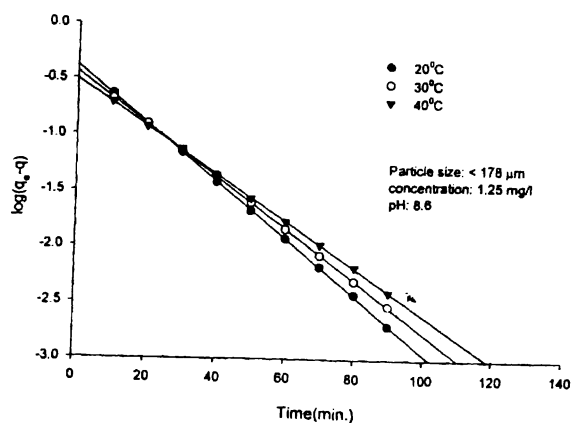coefficient, S_s is the outer specific surface of the adsorbate per unit volume.

Fig. 1. Rate constant plot for adsorption of Cd^{II} on maize bran at different temperatures.

The mass transfer coefficient (β_1) was determined from the slopes and intercepts of the plots of $\ln (C_t/C_0 - 1/1 + mK)$ vs t (Fig. 2). The values of rate parameter (β_1, S_s) are given in Table 4 obtained by multiplying β_1 and S_s and were similar to the adsorption rate constant (K_{ad}). However, it may be mentioned that the deviations of some points from the linearity of the plots (Fig. 2) supported the varying extent of mass transfer at the initial and final stages of the adsorption. This result also supported the proposition that the intraparticle pore diffusion is rate controlling step.
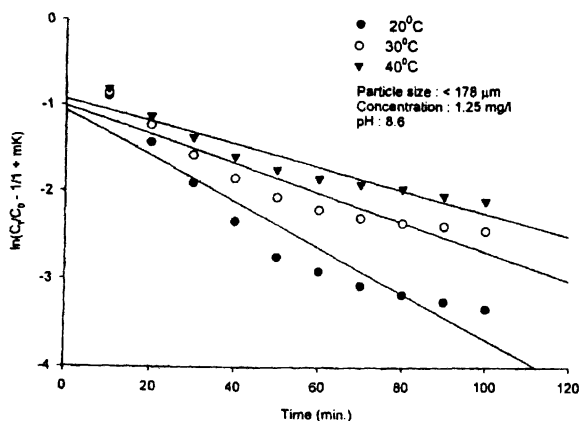

Fig. 2. Mass transfer plot for the adsorption of Cd^{II} on maize bran at different temperatures.

Effect of temperature :

Adsorption studies were carried out at temperatures 20, 30 and 40°C. The percentage of adsorption decreases from 94.50 to 81.50 with rise of temperature from 20 to 40°C at concentration 1.25 mg L^{-1} and pH 8.6. Equilibrium time for 20, 30 and 40°C was found to be 100 min. The results reveal the exothermic nature of the adsorption. The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the ac-
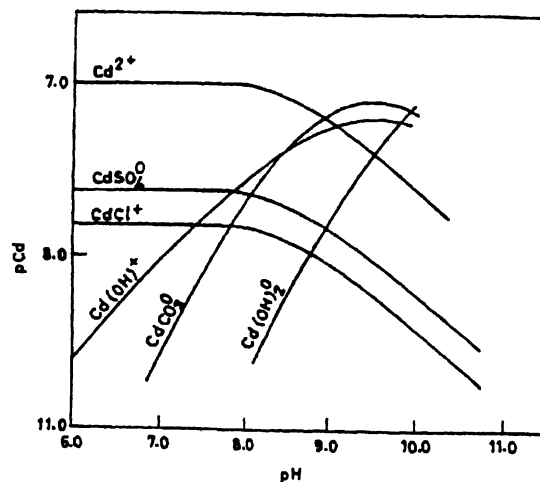

Fig. 3. Speciation of Cd^{II} species with pH.

tive sites of the adsorbents and adsorbate species and also between the adjacent molecules of the adsorbed phase.

The variation in the extent of adsorption with respect to temperature has also been explained on the basis of thermodynamic parameters viz. changes in standard free energy, (ΔG^0) and enthalpy (ΔH^0) and entropy (ΔS^0). These were calculated by using the following equations,

$$\text{(i)} \quad \Delta G^o = RT \ln K_c \qquad (3)$$

$$\text{(ii)} \quad \Delta H^o = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{K_{C_2}}{K_{C_1}} \qquad (4)$$

$$\text{(iii)} \quad \Delta S^o = \frac{\Delta H^0 - \Delta G^0}{T} \qquad (5)$$

where R, is the gas constant, T is temperature on the absolute scale and K_c, K_{c1} and K_{c2} are the equilibrium constants at temperature T, T_1 and T_2 respectively. The values of these parameters thus calculated are recorded in Table 3. It is obvious from this table that the negative and small values of free energy change (ΔG) was an indication of spontaneous nature of the adsorption process. The negative values of standard enthalpy change (ΔH^o) for the intervals of temperatures were indicating the exothermic nature of the adsorption process and the negative values of ΔS^o for the corresponding temperature intervals suggested the probability of a favourable adsorption.

Adsorption isotherm :

In the present investigation Langmuir isotherm has been found to suit well for explaining, the adsorption process. The basic assumption of Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent. The saturated monolayer can be represented by the following equation,

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \qquad (6)$$

which can be further rearranged as follows

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad (7)$$

where C_e is the equilibrium concentration of the adsorbate, q_e is the amount of the adsorbed adsorbate at equilibrium, Q^0 and b are Langmuir's constants related to the capacity and energy of the adsorption respectively.

The linear nature of the curve is found by the plot C_e/q_e versus C_e at different temperature suggested the applicability of Langmuir isotherm for the present system. The values of Q^0 and b at different temperatures were determined from the slopes and intercepts of the respective plot (Table 3).

The equilibrium parameter R_L which is defined as $R_L = 1/(1 + bC_i)$ in the range $0 < R_L < 1$ reflect the favourable adsorption process. In the present investigation the equilibrium parameter was found to be in the range $0 < R_L < 1$ which is represented in Table 3 indicated that the adsorption process was very favourable and the adsorbent employed exhibited a good potential[8].

Effect of pH :

At 30°C percentage removal of cadmium increased from 38.96 to 88.33% with increase in pH from 4.0 to 8.6 and thereafter the percentage of removal decreased to 16.80 at pH 10.0. The optimum pH for the removal of Cd[II] with maize bran as the adsorbent was 8.6.

It can be explained on the basis of the nature of sorbent used which contain several metal oxides. These oxides when mixed up with adsorbate solution undergo surface hydroxylations and form hydroxyl compounds on the surface which ultimately gives positively or negatively charged surface as a result of subsequent acid base dissociation according to following scheme[9],

(Basic dissociation)

(Acidic dissociation)
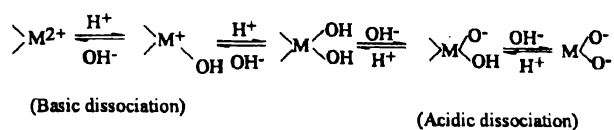
where M denotes Si, Al, Fe, Mn etc. The above scheme clearly indicates that with decrease in the pH of the solution, the positive charge density on the surface increases and hence, the adsorption of Cd[II] decreases. At higher pH the surface is more negatively charged which favours removal of Cd[II].
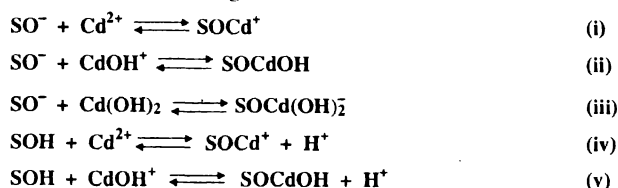
Furthermore, effect of pH can also be explained with the help of cadmium speciation (Fig. 3) where different species of cadmium predominate at different pH of the solution[10].

Conclusion :

Thus the maize bran was found to be a very effective biosorbent for the efficient removal of Cd[II] from wastewater. The removal of cadmium was rapid in initial stages and became slower afterwards; it was also confirmed by mass transfer studies. The double nature of the curves are attributed to the fact that the adsorption in the initial stages was due to the boundary layer diffusion whereas in the later stages adsorption was due to the intraparticle diffusion which is rate controlling step. Thermodynamic studies also confirmed that the process was spontaneous and exothermic. The fitness of the adsorption data into a Langmuir isotherm also confirmed that the monolayer formation of the adsorbate layer took place. The optimum pH for the removal of Cd[II] was found to be 8.6.

Note added :

Note 1. There is given a scheme to understand the acid-base dissociation. The given scheme clearly indicates that with increase in the pH of the solution, negative charge density on the surface increases and hence, the adsorption of Cd[II] increases up to pH 8.6. Possible mechanism through which Cd[II] ions are removed from solution can be understood with the help of cadmium speciation[10] [Fig. 3]. The principal ionic species of hydrated cadmium exist up to pH 8.6. Below pH 7.0 the CdCl⁻ complexes are of significance, but at higher pH values the species Cd(OH)⁺ are increasingly important. According to the James-Healy model 20 (Leckie and James) adsorption of Cd(OH)⁺ may be preferred to Cd²⁺ because solution free energy (which opposes adsorption) increases more rapidly with ionic charge than coulombic free energy (which favours adsorption). Thus, even though Cd(OH)⁺ is present in only small concentrations it could account for significant Cd removal, especially if an equilibrium strongly favouring CdOH⁺(ads) vs CdOH⁺(aq.) exists. When considering cadmium adsorption, account must be taken not only of the bare cation, but also of the hydrolysed species present at any pH. Hence, possible adsorption reactions include the following :

$$SO^- + Cd^{2+} \rightleftharpoons SOCd^+ \qquad (i)$$

$$SO^- + CdOH^+ \rightleftharpoons SOCdOH \qquad (ii)$$

$$SO^- + Cd(OH)_2 \rightleftharpoons SOCd(OH)_2^- \qquad (iii)$$

$$SOH + Cd^{2+} \rightleftharpoons SOCd^+ + H^+ \qquad (iv)$$

$$SOH + CdOH^+ \rightleftharpoons SOCdOH + H^+ \qquad (v)$$

The number of cadmium species in different forms are presented at around pH 8.6 and after that the concentration of various species tends to decrease and resulted in decrease in the adsorption above 8.6. This may be also probably due to soluble hydroxy complexes of cadmium hydroxide.

Note 2. Table 1. Particle size of the adsorbent was 178 µm obtained after sieving the adsorbent. But in the sieved adsorbent, there were different sizes below 178 µm. Average particle diameter is the average of the particle size below 178 µm. The value of average particle diameter is 1.75×10^{-2} cm or 175 µm at the place of 1.95×10^{-2} cm.

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