Sorption Profile of Cd(II) Ions Onto Coconut Husk

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ABSTRACT

The removal of Cd(II) ions by coconut (*Cocos nucifera*) husk has been studied extensively optimising all parameters controlling their accumulation on solid surface. Maximum sorption (84%) of Cd(II) ions (2.29×10^{-5} M) onto sorbent surface is achieved from deionized water in 20 min. using 100 mg of coconut husk/4.5 cm³. The accumulation of Cd(II) ions monitored over a ~ 400-fold concentration (2.30×10^{-6} – 9.18×10^{-4} M) followed Freundlich and Dubinin-Radushkevich (D-R) isotherms. The Freundlich constants $1/n = 0.92 \pm 0.4$ and $C_m = 52 \pm 22$ mmole g⁻¹ and D-R parameters $\beta = -0.0068 \pm 0.0002$ kJ² mole⁻², $X_m = 35.1 \pm 6.8$ mmole g⁻¹ and $E = 8.5 \pm 0.1$ k J mole⁻¹ have been evaluated. The variation of temperature in the range of 278-323 K under optimized conditions yielded thermodynamic entities $\Delta H = 18.1 \pm 0.6$ k J mole⁻¹, $\Delta S = 74 \pm 2$ J mole⁻¹ K⁻¹ and $\Delta G_{298K} = -3.8 \pm 0.04$ k J mole⁻¹. The positive enthalpy and negative free energy reflect the endothermic and spontaneous nature of sorption respectively. Among the ions tested EDTA, borate, oxalate and Eu(III) increased the sorption, while ascorbate, Ce(III) and Sb(III) suppressed the sorption. The investigation regarding selectivity of coconut husk reveals that Cd(II) ions can be separated from Zn(II), Se(IV), Tc(VII) and I(I). This study indicates the potential of coconut husk for the removal of Cd(II) ions from aqueous solutions/industrial effluents.

INTRODUCTION

Cadmium is an important element due to its deleterious effects and useful applications. It is used in metal and alloys plating, in electrodeposited coatings, as stabilizer in plastics, pigments and chemicals, storage batteries, semiconductors, fungicides and in nuclear technology /1/.

Cadmium enters the human body through ingestion and inhalation and accumulates in kidneys. liver, lungs and pancreas. It is one of the most lethal metals because of its 30 years biological half-life in the kidney. It causes renal dysfunction, hypertension, hepatic injury, lung damage, an adverse effect on the reproductive system and bone defects /2,3/. The tolerance limit of cadmium in water is 5 µg L⁻¹; therefore, it must be removed from water for drinking purposes /4/.

The conventional techniques used for the removal of heavy metals from water are filtration, chemical precipitation, reverse osmosis, solvent extraction and membrane techniques /5/. The sorption technique is

superior to them because of its higher efficiency and simple operation. Several low-cost materials have been explored for the removal of cadmium from water /6-9/, but the most efficient and economic sorbent is still required. This paper reports the results of the sorption of cadmium(II) ions onto coconut husk, which is the continuation of our previous work for the exploitation of cheaper materials for the removal of toxic metal ions from aqueous solutions /9-11/.

EXPERIMENTAL

Radiotracer

The radiotracer ^{115}Cd was prepared by irradiating specpure cadmium oxide in the 10 MW swimming pool-type research reactor (PARR-1) of this institute for 12 hours at a neutron flux of $5 \times 10^{13} \text{ n.cm}^{-2} \text{ s}^{-1}$. After 48h cooling the irradiated metal oxide was dissolved in concentrated nitric acid. In order to remove the acid the sample was diluted with deionized water and heated to dryness; this was repeated thrice. After the removal of acid the tracer was diluted to 10 cm^3 with deionized water. The radionuclidic and radiochemical purity was checked on 4k series of 85 Canberra multichannel analyzer coupled with a $25\text{-cm}^3 \text{ Ge (Li)}$ detector and was stored for further use.

Reagents

The reagents used in the present study were of analar grade. Buffer solutions of pH 1-10 having ionic strength of 0.1M were prepared by mixing an appropriate volume of 0.1M solutions of HCl and KCl, CH_3COOH and CH_3COONa and H_3BO_3 and NaOH for buffers of 1-3, 4-6 and 7-10 respectively.

Coconut husk

Coconut husk, which is the by-product of coconut (*cocos nucifera*), was collected from the local market, washed exhaustively with water and finally with deionized water to remove dirt, sand and clay. After washing, it was dried in an oven overnight at 105°C , then it was split into threads and barks. The thread-like portion was reheated again overnight at 105°C . It was ground in a pistil mortar up to 40-mesh size and collected in a bottle.

Sorption measurements

Five cm^3 of an electrolyte of known pH or acid concentration was taken in a glass culture tube with a polyethylene cap. A known concentration of Cd(II) tracer was added to it and mixed thoroughly. An aliquot of 0.5 cm^3 was taken for gross gamma counts (A_0). The remaining solution was shaken with 100 mg of coconut husk for 30 minutes on a Stuart Scientific wrist-action shaker. After shaking, phases were separated

by centrifugation for 3 minutes. Subsequently, 0.5 cm³ of aliquot was withdrawn for radioassay on a Tennenac gross gamma counter equipped with a 30 cm³ well-type Na (Ti) crystal.

The sorbed concentration of ¹¹⁵Cd at equilibrium was calculated by the difference in the activity of aliquot drawn before (A_o) and after shaking (A_e). The percentage sorption and distribution coefficient (K_d) were calculated as

$$\% \text{Adsorption} = \frac{A_o - A_e}{A_o} \times 100 \quad (1)$$

$$K_d = \frac{\text{amount of metal in husk}}{\text{amount of metal in solution}} \times \frac{\text{volume of solution (V)}}{\text{weight of dry husk (W)}} = (\text{cm}^3/\text{g}) \quad (2)$$

The % sorption and the distribution coefficient can be correlated as

$$\% \text{Adsorption} = \frac{100K_d}{K_d + \frac{V}{W}} \quad (3)$$

All the experiments were performed at least in triplicate at 24±2°C or at temperature specified otherwise. The results are the average of at least triplicate independent measurements and precision in most cases is ± 2 %. The linear regression and slope analyses for the statistical data were carried out. The correlation coefficients for all the regression analyses were in the range of 0.9675-0.9961.

RESULTS AND DISCUSSION

The sorption of cadmium(II) ions onto coconut husk was optimized by studying various parameters such as nature of electrolyte, shaking time, amount of sorbent and sorbate concentration, to get maximum sorption. The effect of temperature and foreign ions on the sorption and selectivity of sorbent was also studied.

Effect of Electrolyte

The composition and nature of electrolyte affect the sorption of metal ions by influencing the surface properties of sorbent and the chemical behaviour of sorbate. Therefore, selection of appropriate electrolyte for the sorption is of prime importance. The sorption of cadmium(II) ions onto coconut husk was investigated in deionized water, HCl and HNO₃ in the concentration range of 0.0001-0.1 M and buffer solutions of pH 1-10. The concentration of cadmium, amount of coconut husk and agitation time was chosen arbitrarily as 2.29 × 10⁻⁵ M, 100 mg and 20 min respectively. The results are shown in Table 1 and Fig. 1. It is clear from the results of Table 1 that sorption increased with the decrease in acid concentration in both the mineral acids. The results are in conformity with the sorption of Cd(II) ions onto rice husk /7/ and Haro river sand /9/. Comparatively the sorption in deionized water is greater. The percent sorption of Cd(II) ions increased with

the increase in pH of buffer solutions up to 7; subsequently it decreased with an increase in pH. The lower sorption at higher acidic concentration and lower pH values may be due to the competition between the positively charged Cd^{++} ions and H^+ . The maximum sorption around pH 7 buffer solution may be attributed to the cellulosic part of the coconut husk, where site binding sorption occurs. It might be due to the surface complexation phenomenon, which is facilitated by the dissociation of surface functional groups ($-\text{COOH}$ and $-\text{OH}$). At higher pH the lower sorption may be attributed to the above mentioned reason. The findings of our work are in conformity with cadmium sorption onto peanut /6/ and onion /12/ skin, and rice husk /7/. The deionized water was selected as an appropriate medium for the sorption of Cd(II) ions onto coconut husk.

Fig. 1: Effect of pH on the sorption of Cd(II) ions (2.29×10^{-5} M) onto coconut husk (100 mg)

Table 1

Sorption of Cd(II) (2.29×10^{-5} M) ions onto coconut husk (100 mg) after 20 min agitation time.

Electrolyte	$K_d (\text{cm}^3 \text{g}^{-1})$	%Sorption
Deionized water	192	80.9
0.1M HNO_3	4	7.6
0.01M HNO_3	20	30.5
0.001M HNO_3	69	60.4
0.1M HCl	1.5	3.2
0.01M HCl	4	8.8
0.001M HCl	103	69.6

Influence of the amount of sorbent

The amount of sorbent affects the sorption, therefore, sorption of cadmium (2.29×10^{-5} M) ions was investigated as a function of solid/solution ratio in the range of 10-300 mg of coconut husk/4.5 cm^3 , using 20 min. shaking time. The results are presented in Fig.2. It is clear from this figure that the % sorption increased

up to 100 mg of coconut husk and remained almost constant. Therefore, 100 mg of coconut husk was considered to be an optimum quantity for the removal of cadmium ions from aqueous solution and this amount was used in further experiments.

Fig. 2: Influence of the amount of sorbent on the sorption of Cd(II) ions (2.29×10^{-5} M) onto coconut husk.

Effect of shaking time

For the maximum sorption the effective distribution of sorbate between the sorbent and electrolyte is necessary. The influence of shaking time on the sorption of cadmium(II) ions (2.29×10^{-5} M) onto coconut husk has been studied from 1-60 minutes (Fig. 3). It is clear from the figure that sorption increased up to 20 minutes shaking time and beyond 20 minutes no further increase in sorption was observed. For further experiments 20 minutes shaking time was used. The kinetic data of sorption were subjected to the Morris-Weber /13/ equation:

$$q_t = R_d \sqrt{t} \quad (4)$$

where q_t is the sorbed amount of Cd(II) ions onto coconut husk (mole g^{-1}) at time interval t , and R_d is the rate of intraparticle diffusion. When q_t was plotted against $\sqrt{t}$ a linear plot with a correlation factor of 0.9675 was obtained (Fig. 3). The computed value of intraparticle diffusion rate R_d was 6.6 nmole g^{-1} which is in agreement with 5 nmole g^{-1} estimated for the sorption of Hg(II) ions onto coconut husk /5/. It is concluded from the value of R_d that the sorption is much faster than the surface diffusion and the equilibrium could be established inside the particle.

Influence of the amount of sorbate

Another important parameter, the initial concentration of Cd(II) ions, that influences its sorption, has been studied in the range of 2.3×10^{-6} - 9.2×10^{-4} M, using 20 min shaking time and 100 mg of coconut husk. The results are presented in Fig. 4. It is clear that sorption (~84%) increased up to Cd(II) ions concentration of 2.3×10^{-5} M and then decreased with a further increase in the concentration of Cd(II) ions. The decrease of Cd(II) ions at its higher concentration may be due to the availability of a lesser number of active sites.

Fig. 3: Sorbed concentration of Cd(II) (2.29×10^{-5} M) onto coconut husk (100 mg) as a function of shaking time.

Fig. 4: Effect of concentration of Cd(II) ions on its sorption onto coconut husk (100 mg).

The sorption data were further analyzed by fitting them to the Freundlich /14/ and Dubinin-Radushkevich (D-R) /15/ models. The Freundlich isotherm is the most widely used mathematical description for the sorption of metal ions from solutions. This isotherm suggests that sorption is not restricted to one specific class of sites and assumes surface heterogeneity. It does not predict saturation of the surface of sorbent by sorbate and thus infinite surface coverage is predicted mathematically. The Freundlich isotherm was tested in the following linear form:

$$\log C_{\text{ads}} = \log C_m + \frac{1}{n} C_e \quad (5)$$

where C_{ads} and C_e are the concentration of mercury ions sorbed at equilibrium onto coconut husk (mole g^{-1}) and in aqueous solution (mole L^{-1}) and C_m and $1/n$ are Freundlich constants. When $\log C_{\text{ads}}$ was plotted against $\log C_e$, a linear plot with a correlation factor of 0.9948 was obtained (Fig. 5). The value of Freundlich constant $1/n = 0.92 \pm 0.4$ was computed from the slope of the plot. It indicates the sorption intensity. The fractional value ($0 < 1/n < 1$) shows the heterogeneous nature of sorbent surface, the higher the fractional value the higher is the heterogeneity of the surface /16/. The $C_m = 52.6 \pm 22.2 \text{ mmole g}^{-1}$, the sorption

capacity, has been computed from the intercept of the linear plot. The values of $1/n=0.81\pm0.05$ and $C_m = 2.84\pm0.07$ mmole g^{-1} have been reported for Cd(II) ions sorption onto rice husk [7].

Fig. 5: Freundlich sorption isotherm of Cd(II) ions onto coconut husk.

Fig. 6: D-R sorption isotherm of Cd(II) ions onto coconut husk.

The Dubinin-Radushkevich isotherm assumes that there are very small subregions of the sorption surface that are uniform in structure and energetically homogeneous. The linearized form of the D-R isotherm is

$$\ln C_{ads} = \ln X_m - \beta \epsilon^2 \quad (6)$$

where C_{ads} is the amount of Cd(II) ions sorbed per unit mass of sorbent (mole g^{-1}), X_m is the maximum sorption capacity of sorbent (mole g^{-1}), β is a constant ($\text{kJ}^2 \text{mole}^{-2}$) and ϵ is Polanyi potential which is equal to

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where R is the universal gas constant in kJ mole^{-1} , T is the absolute temperature in Kelvin and C_e is the equilibrium concentration of sorbate in solution (mole L^{-1}). The plot $\ln C_{ads}$ against ϵ^2 is depicted in Fig. 6, which is a straight line with a correlation factor of 0.9961. It can be concluded that D-R isotherm is obeyed

over the entire range of Cd(II) ions concentration investigated. The values of D-R constants $\beta = -0.0068 \pm 0.0002 \text{ kJ}^2 \text{ mole}^{-2}$ and of $X_m = 35.1 \pm 6.8 \text{ mmole g}^{-1}$ were computed from the slope and intercept of the plot. If the surface of the sorbent is heterogeneous in nature and an approximation to Langmuir isotherm is chosen as a local isotherm for all the sites that are energetically equivalent, then the quantity β can be related to the mean sorption energy (E) as

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

The value of E calculated from Eq.8, comes out to be $8.5 \pm 0.1 \text{ kJ mole}^{-1}$.

Effect of foreign ions on the sorption

Sorption of Cd(II) ions onto coconut husk may be influenced by the common anions, cations and complexing agents due to their competition for the sorption sites, association, dissociation and complex formation. The electrical charge on the sorbent surface is also determined by surface coordination with sorbing or other complexing agents. Therefore, the effect of common anions and cations on the sorption of Cd(II) ions ($2.29 \times 10^{-5} \text{ M}$) onto coconut husk from deionized water was assessed. The anions were added as their sodium salts and the cations were in the form of nitrates or chlorides. Their concentration was kept at $2.29 \times 10^{-4} \text{ M}$, about 10 fold the Cd(II) ions concentration used in the optimized conditions. The results are presented in Tables 2 and 3. It is clear from the results that the EDTA, borate, oxalate, thiosulphate, carbonate and Eu(III) enhanced the sorption. Ascorbate, Sb(III), Ce(III), Fe(III), Pb(II), Al(III), Cr(III) and Y(III) suppressed the sorption (69-35%). In other words the ions which reduced the sorption must be removed from the sorptive medium otherwise sorption of cadmium(II) ions will be drastically curtailed. The reduction in the sorption of Cd(II) ions onto coconut husk may be due to the formation of strong complexes with ascorbate and their lower sorption affinity towards the sorbent. The effect of metal ions which reduce the sorption of Cd(II) ions may be due to their competition with these ions for the same sorption sites on the sorbent surface.

Influence of temperature on sorption

Temperature is one of the major factors that affects the sorption. Therefore, the influence of temperature on the sorption of Cd(II) ions ($2.29 \times 10^{-5} \text{ M}$) onto sawdust (100 mg) from deionized water was studied from 278-323K. It was observed that sorption increased (~90%) with an increase in temperature. Similar results have been reported for the sorption of Cd(II) ions onto rice husk /7/ and various oxides surfaces /17, 18/. The increase in sorption may be due to the acceleration of sorption steps, or may be the creation of some new active sites /19/ or may be due to transport against a concentration gradient, and/or diffusion across the energy barrier /20/.

Table 2

Effect of anions on the sorption of Cd(II) (2.29×10^{-5} M) ions onto coconut husk (100 mg)
after 20 min agitation time from deionized water.

Anions	$K_d(\text{cm}^3 \text{g}^{-1})$	% Sorption
Nil	224	83.2
EDTA	390	89.6
Borate	296	86.8
Oxalate	280	86.2
Thiosulphate	246	84.5
Carbonate	245	84.5
Sulfate	241	84.3
Cyanate	236	83.9
Chloride	231	83.7
Chromate	221	83.1
Tartarate	202	81.7
Citrate	146	76.4
Ascorbate	25	35.5

Table 3

Influence of cations on the sorption of Cd(II) (2.29×10^{-5} M) ions onto coconut husk (100 mg)
after 20 min agitation time from deionized water (b = added as chlorides)

Cations	$K_d(\text{cm}^3 \text{g}^{-1})$	% Sorption
Nil	224	83.2
Eu(III)	250	84.8
Mo ^b (V)	166	78.6
K ^b (I)	159	77.9
Ni(II)	141	75.8
Zr ^b (IV)	132	74.6
Ag(I)	120	72.6
Co(II)	116	71.9
Sr(II)	112	71.3
Y(III)	104	69.8
Cr(III)	101	69.1
Al(III)	99	68.7
Pb(II)	80	63.9
Fe(III)	75	62.4
Ce ^b (III)	58	56.5
Sb ^b (III)	25	35.6

The $\log K_c$ vs $1/T$ was plotted, where $K_c = F/(1-F)$ and T is absolute temperature in Kelvin and F represents the fraction sorbed at equilibrium; a straight line with a correlation factor of 0.9961 was obtained (Fig. 7). The values of ΔH , ΔS and ΔG were computed using the relations:

$$\log K_c = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (9)$$

$$\Delta G = -RT \ln K_c \quad (10)$$

Fig. 7: Variation of sorption equilibrium of Cd(II) ions onto coconut husk with temperature.

The slope and intercept of Fig.7 give $\Delta H = 18.1 \pm 0.6 \text{ kJ mole}^{-1}$ and $\Delta S = 74 \pm 2 \text{ J mole}^{-1} \text{ K}^{-1}$. The value of $\Delta G = -3.8 \pm 0.04 \text{ kJ mole}^{-1}$ at 298 K was computed using Equation 10. The values $\Delta H = 0.82 \text{ kJ mole}^{-1}$, $\Delta S = 22.4 \text{ J mole}^{-1} \text{ K}^{-1}$, $\Delta G = -5.75$ have been reported for Cd(II) ions sorption onto rice husk [7].

Sorbent selectivity

In order to check the sorbent selectivity, the sorption onto coconut husk of several radionuclides representing different oxidation states was measured under optimized conditions chosen for Cd(II) ions. The results along with their separation factors (α) with respect to Cd(II) ions are presented in Table 4. All the metal ions studied except Hg(II), Cr(III) and Eu(III) (84-91%) have lower sorption than Cd(II) ions. Zn(II), Se(IV), Tc(VII) and I(I) have shown lower sorption (<13%) which indicates that these can be separated from Cd(II) ions using coconut husk column.

CONCLUSIONS

1. Up to 90% Cd(II) ions can be removed by coconut husk from deionized water in 20 min.
2. The kinetics of sorption of Cd(II) ions onto coconut husk obey Reichenberg, Morris-Weber and Lagergren equations.
3. The sorption of Cd(II) ions onto coconut husk follows Freundlich and D-R isotherms.

Table 4

Sorption of other metals onto coconut husk (100 mg) after 20 min agitation time from deionized water.

Metal ions	K_d (cm ³ g ⁻¹)	% Sorption	$\alpha = K_d \text{ Cd(II)}/K_d \text{ M}$
Cd(II)	224	83.2	-
Hg(II)	915	90.9	0.2
Cr(III)	291	86.6	0.8
Eu(III)	239	84.1	0.9
Tm(II)	170	79.1	1.3
Ag(I)	89	66.2	2.5
Sb (III)	59	56.5	3.8
Co(II)	53	53.8	4.2
Cs(I)	14	24.1	16.0
I(I)	6	12.2	37.3
Tc(VII)	2	4.6	112
Se(IV)	1.4	2.9	160
Zn(II)	0	0	∞

- The positive value of ΔH and negative value of ΔG show the endothermic and spontaneous nature of sorption respectively.
- EDTA, borate, oxalate, thiosulphate, carbonate and Eu(III) have enhanced the sorption while ascorbate and Sb(III) have reduced it.
- The coconut husk column can be used to separate Cd(II) ions from Zn(II), Se(IV), Tc(VII) and I(I) ions.

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