Biosorption of Hg (II) and Cd (II) from Waste Water by using Zea Mays Waste

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Summary: Corn straws and corn cobs (Zea Mays waste) have been successfully utilized as bio-sorbents for the removal of mercury (II) and cadmium (II) from aqueous solutions, respectively. The maximum removal efficiency of mercury (II) and cadmium (II) was found to be 86.9 % and 92 % respectively at optimum conditions. Effects of pH, contact time, shaking speed, initial concentration of metal ion and amount of adsorbent were studied for both the metal ions. Kinetic studies were performed to measure the time for attaining equilibrium and adsorption data were employed to different adsorption models.

Introduction

For the survival of most living things, particularly human beings, water is indispensable component. Adequate supply of fresh and clean water is a basic need for all human beings on the earth, but millions of people from destitute section of society are deprived of fresh and clean water and are forced to intake contaminated water. Fresh water resources all over the world are threatened due to poor management, ecological degradation and over exploitation.

Trace amounts of some metals like calcium, magnesium, sodium and iron are present in drinking water and are essential for human health. But drinking water sometimes contains heavy metals which are hazardous to our health. These metals include mercury, cadmium, arsenic, antimony and lead etc. Heavy metals in drinking water may occur naturally or may be the result of some anthropogenic activities. Industry is the major source to contribute heavy metals in air, water, soil and food. Today even in the developed countries, thousands of tons of toxic industrial wastes including heavy metals are dumped into the soil and water bodies every year. These heavy metals are not biodegradable and their presence in water bodies leads to bioaccumulation in humans and other living organisms. Excessive intake of cadmium causes adverse effects on renal system [1] and it affects the kidney cytochrome [2]. It has been also reported that high-level exposure to cadmium increases the risk factor of breast cancer [3-5]. Cadmium has been considered by International Agency for Research on Cancer as category-I carcinogen [6]. Similarly mercury in acute dose can produce damage to central nervous system [7] but chronic dose cause damage with the passage of time [8-10]. A commonly known organic pollutant, methyl mercury is a neurotoxin that in high exposure can cause mental retardation and cerebral palsy [11]. The developing embryos are more sensitive to methyl mercury because it crosses the blood brain barrier and damages the central nervous system [12]. It is also reported that neural stem cells are potential target for methyl mercury in the developing nervous system [13]. Keeping in view the adverse effects, the removal of heavy metals from water supply is essential to protect human beings as well as aquatic life.

In the last few years a lot of work has been done regarding the removal of heavy metals from waste and drinking water. This includes oxidation, reduction, precipitation and co-precipitation, electro deposition, electro coagulation, membrane filtration, solvent extraction, adsorption and biosorption. Among these, adsorption process is simple, efficient, selective, cost effective, environmental friendly and reversible to some extent. It has been reported that materials like sea weeds [14], clays and sands [15], fungi [16] and agro wastes [17-19] have adequate potential to adsorb these heavy metals up to 90 %.

Corn (Zea Mays) is one of the most popular crops of agricultural countries. It is used in different forms like corn oil, corn flour, and corn cobs. In present study we have used corn cobs and corn straws as adsorbent for the removal of cadmium and mercury, respectively.

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Results and Discussion

The process of adsorption is a surface phenomenon. The nature (physical and chemical properties) of the adsorbent and adsorbate, both affect the adsorption phenomenon. Adsorption studies of Cd (II) and Hg (II) on corn waste were carried out by optimizing different parameters like pH, amount of adsorbent, concentration of metal ions and shaking speed.

Effect of Shaking Speed

It is a known fact that shaking consumes energy and it affects the adsorption rate or efficiency, so for the study of adsorption it is necessary to find out the optimal rpm (revolutions per minute). The maximum removal efficiency for cadmium was obtained at 150 rpm 89.23% adsorption, while for mercury the optimal shaking speed was 100 rpm obtaining 87.19 % adsorption (Fig. 1). Which indicates the adsorption values for both metals were lowest at 50 rpm and increased as the shaking speed increased up to their optimal level then after a slight decline both metals attain equilibrium.

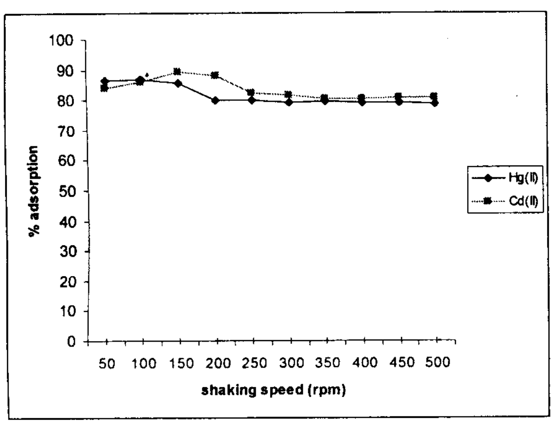

Fig. 1: Effect of shaking speed on biosorption of Hg (II) and Cd (II).

This variation may be attributed to the change in the concentration of metal ions around the surface of adsorbent which changes the adsorption equilibrium. In start gentle shaking causes the agitation, metal ions and adsorbent particles move rapidly around each other and their relative concentration increase which results more adsorption. However, when shaking speed crosses a certain limit, the kinetic energy of metal ions as well as that of the adsorbent particles increases, the resultant adsorption decreases. This is understandable because at high shaking speed the kinetic energy of the particles may overcome the weak adsorption bonds between the adsorbent and the metal ion hence the overall adsorption decreases.

Effect of Adsorbent Mass

As shown in Fig. 2, the rate of adsorption has been increased by increasing the amount of adsorbent to a maximum of 2.5 g/100 mL (using 50 ppm metal solution) for Cd (II) and 0.5 g/100 mL (10 ppm metal solution) for Hg (II). By increasing the quantity of adsorbent beyond the optimal mass, there is no significant change in removal efficiency. These results indicate that removal efficiency is directly related to the number of available adsorption sites. Once equilibrium is attained there is no effect on adsorption efficiency.

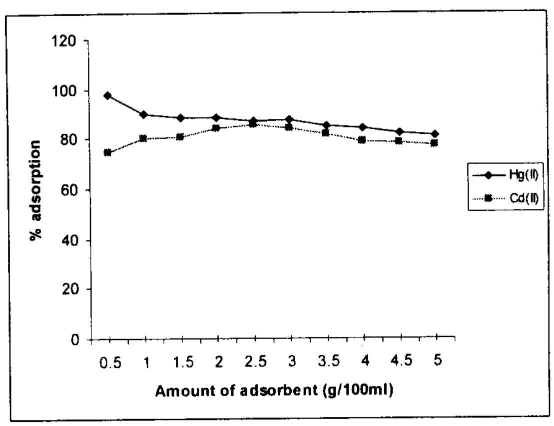

Fig. 2: Effect of Amount of adsorbent on biosorption of Hg (II) and Cd (II).

Effect of Contact Time

It has been observed that at a constant concentration of metal ions and fixed amount of adsorbent, the adsorption efficiency increases with the increasing the contact time up to a certain level. Fig. 3 shows that the adsorption rate first increased rapidly but after reaching to optimal time value the removal efficiencies slightly decreased with increasing the contact time. The effect may be due to the saturation of adsorption sites with metal ions on the solid particle. The optimal contact time for

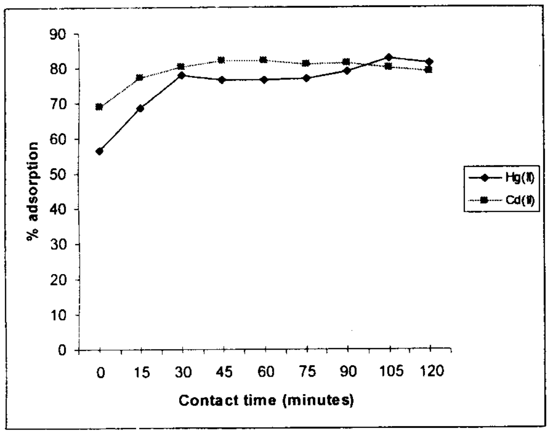

Fig. 3: Effect of contact time of adsorbent and metal ion solution on biosorption of Hg (II) and Cd (II).

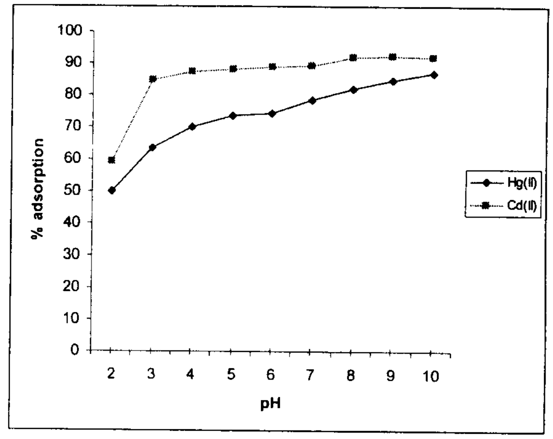

Fig. 4: Effect of pH of the solution on biosorption of Hg (II) and Cd (II).

cadmium (II) was 60 min. with 82.2 % adsorption and 105 min. for mercury (II) with 82.9 % adsorption. The slight decrease in adsorption after optimum contact time may be due to the breakage of newly formed weak adsorption bonds due to constant shaking.

Effect of pH

The adsorption process is strongly affected by pH of the solution. The effect of pH change on adsorption was studied for both metals by changing the pH of the contents from 2-10 using dilute solutions of HCl and NaOH.

It has been observed from Fig. 4 that maximum adsorption of both metals took place in basic media. Maximum adsorption for Hg (II) was observed at pH 10 and cadmium at pH 9. Published literature [20] shows that at very high and very low pH values the surface of the adsorbent is surrounded mainly by H^+ and OH^- ions. These positively and negatively charged ions may compete with metal ions and as the result adsorption decreases. That's why metal ions show low adsorption at very high and low pH values [20]. On the other hand sometimes precipitation of metal ions as hydroxide also occurs at high basic pH values, which is not feasible for good adsorption.

Influence of pH on adsorption phenomenon also related with the functional groups present on bioadsorbent. The potential binding sites on bioadsorbents may be carbohydrates, amino groups, hydroxyl groups and carboxylic groups. These functional groups may dissociate or ionize at different pH values. So the surface chemistry of functional groups also plays an important role in the adsorption process.

Adsorption Isotherms

The adsorption of both metal ions was investigated as the function of their own concentration at optimum conditions. The adsorption data obtained (for both metals) were subjected to different adsorption isotherm *i.e.* Langmuir, Fruendlich and Dubnin-Radushkevich (D-R).

Langmuir Adsorption Isotherm

Figs. 5 and 6 show Langmuir isotherms of adsorption data for Hg (II) on corn straws and Cd (II) on corn cobs, respectively.

The adsorption in data for metals is also applied to the given linearized form of Langmuir model;

$$C_{eq} / q = 1/Qb + C_{eq}/Q \quad (1)$$

where

q = adsorbed concentration of adsorbate on per gram of adsorbent

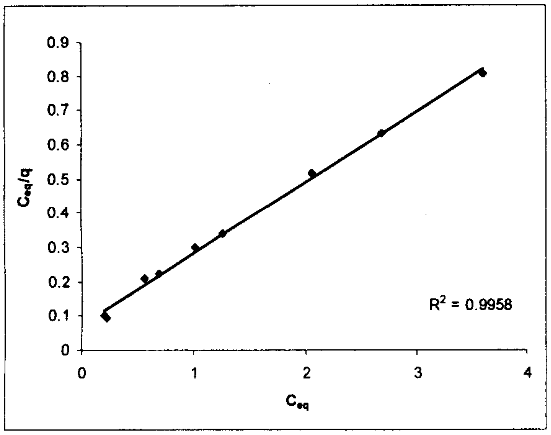

Fig. 5: Langmuir adsorption isotherm for Hg (II) biosorption by corn straws at optimum conditions.

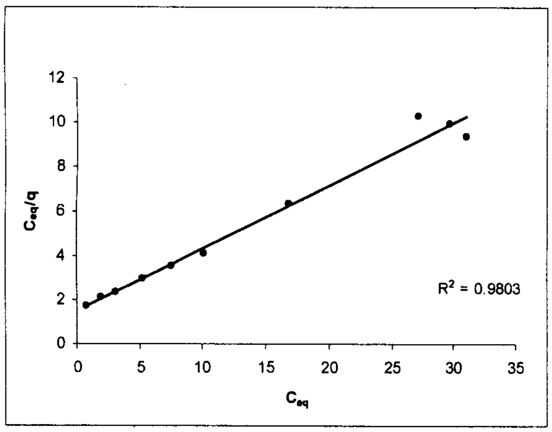

Fig. 6: Langmuir adsorption isotherm for Cd (II) biosorption by corn cobs at optimum conditions.

Q = monolayer adsorption capacity (mg /g)
b = affinity of adsorbent and adsorbate rates

In Fig. 5 and 6, C_{eq} / q are plotted against C_{eq} and getting straight lines with the squared value of correlation factor obtained in the case of Hg (II) is 0.9958 and 0.9803 for Cd (II). Q and b were determined from the slope and intercept of the plots. The values of Q were found to be 4.83 mg/g for Hg (II) and 3.61 mg/g for Cd (II), similarly the values of b for Hg (II) was 2.75 L / g and 0.183 L /g for Cd (II).

Another essential characteristics of this isotherm is a dimensionless constant separation factor R_L [21] which is equal to;

$$R_L = 1/\ 1+bC_0 \quad (2)$$

where
C_0 = initial concentration of metal ions

The R_L values are found to be 0.0347 to 0.0137 for concentrations 10-26 mg / L of Hg (II) and 0.3534 to 0.0518 for concentrations 10-100 mg / L for Cd (II).

If the values of R_L lie between 0 to 1, it indicates a favorable adsorption [22].

Fruendlich Isotherm

Fig. 7 and 8 show Fruendlich adsorption isotherm of Hg (II) and Cd (II) on corn straws and corn cobs, respectively.

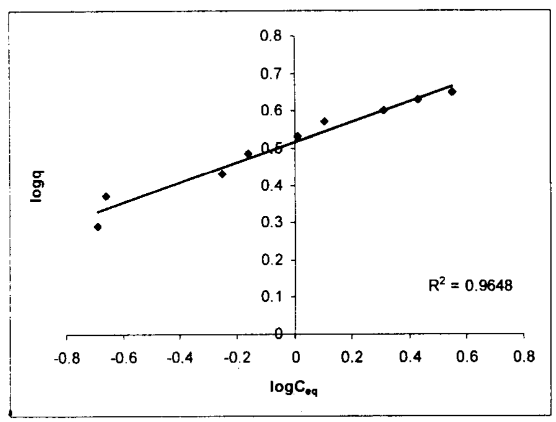

Fig. 7: Fruendlich adsorption isotherm for Hg (II) biosorption by corn straws at optimum conditions.

The linearised form of Fruendlich equation is [23];

$$\log q = \log K + 1/n \log C_{eq} \quad (3)$$

where
K = mutilayer adsorption capacity
n = Fruendlich constant related to the energy or intensity.

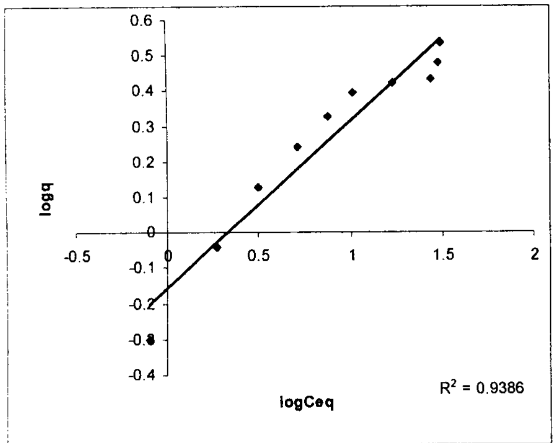

Fig. 8: Fruendlich adsorption isotherm for Cd (II) biosorption by corn cobs at optimum conditions.

The values of K and n are determined from the slope by intercept of the plot and was found to be K = 3.25 and n = 3.709 for Hg (II) and K = 0.67 and n = 2.08 for Cd (II). Values of n indicate steepness or flatness of the slopes. 1/n close to 1 indicates steep slope and high adsorption capacity at equilibrium concentrations. On other hand 1/n << 1 indicates flat slope and reduced adsorption capacity at low equilibrium conditions [24]. In Fruendlich isotherm the squared values of correlation factor are 0.9648 for Hg (II) and 0.9386 for Cd (II).

Dubinin-Radushkevich (D-R) Isotherm

Fig. 9 and 10 show D-R adsorption isotherm of Hg (II) and Cd (II) on corn straws and corn cobs respectively. The Dubinin-Radushkevich (D-R) isotherm [25] assumes about heteroginity of the surface, the D-R isotherm can be expressed in linear form as follows;

$$\ln q = \ln X_m - \beta \varepsilon^2 \quad (4)$$

where

X_m = maximum adsorption capacity

β = activity coefficient

ε = Polanyi potential

$$\varepsilon = RT \ln (1+1/C_{eq}) \quad (5)$$

R = ideal gas constant

T = temperature in Kelvin and

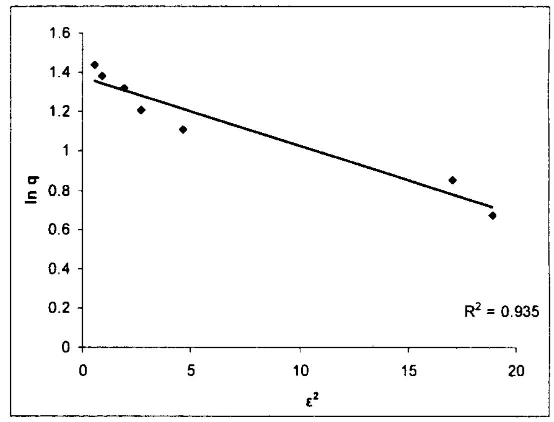

Fig. 9: D-R adsorption isotherm for Hg (II) biosorption by corn straws at optimum conditions.

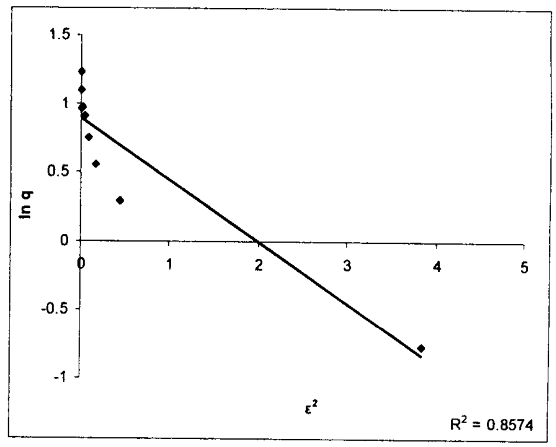

Fig. 10: D-R adsorption isotherm for Cd (II) biosorption by corn cobs at optimum conditions.

The values of X_m for Hg (II) is 3.98 mg g^{-1} and 2.34 mg g^{-1} for Cd (II), while the values of β for Hg (II) and Cd (II) are found to be 0.037 and 0.46 $mol^2 k J^{-2}$, respectively.

The comparison of parameters of all three isotherms is given in Table-2.

Desorption Studies

Desorption studies were performed by using doubly distilled deionized water and 0.1 M solutions of ethylene diamine tetraacetic acid (EDTA), HNO_3, NaOH and KCl as desorbing agents. For this purpose 50 ml of both solutions (50 ppm for cadmium and 10 ppm for mercury) were contacted with 5g of respective adsorbents for 1 hour. Then these solutions were filtered off and 1g of each adsorbate loaded adsorbents was then transferred to 10ml of each desorbing agent solution. These test solutions were shaken at speed 100 rpm for 1 hour. These experiments were done at room temperature (30°C). Fig. 11 shows that highest recovery of both metal ions was found with EDTA solution *i.e.* about 76 % for Hg (II) and 81 % for Cd (II).

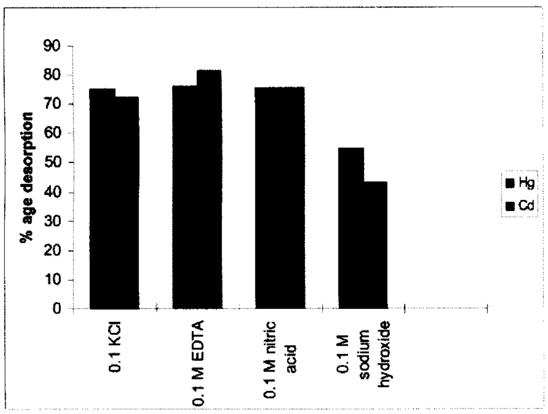

Fig. 11: Metal ion recovery from respective adsorbents by using different desorbing agents.

Experimental

Adsorbents and Reagents

Corn cobs were collected from corn oil mill while corn straws were collected from fields near Faisalabad city, Pakistan. Dirt and particulate matter from both the adsorbents were removed by extensive washing in deionized water and later the adsorbents were dried at 105 °C for 24 hours. They were grinded in mechanical grinder and passed through set of sieves to obtain mesh size 50 to 80 and stored in desiccators.

All the chemicals used in this study were of AnalaR Grade (Merck). The standard solutions of both the metals (1000mg L^{-1}) were prepared by dissolving appropriate amounts of cadmium nitrate and mercury chloride in doubly distilled deionized water. All the dilutions were prepared from the stock solutions.

Instruments and Apparatus

Metal contents before and after adsorption were determined by atomic absorption spectroscopy. Atomic absorption spectrometer (Perkin Elmer Analyst 100) equipped with standard hollow cathode lamps was used in these studies. pH measurement were obtained by means of (HANNA pH211 with glass electrode) pH meter.

General Procedure

A known volume of standard metal solution was taken in 250 ml stoppered Pyrex glass flask. Weighed amount of adsorbent was added in the flask, and then flask was shaken on the mechanical shaker by using the experimental conditions as shown in Table-1. After shaking for certain time the contents were filtered through Whattmann-No 1 filter paper. Metal contents were determined in the filtrate by atomic absorption spectroscopy. In order to ensure

Table-1: Experimental conditions

Experimental conditions	Metal ions	Shaking speed (rpm)	Amount of adsorbent (gL^{-1})	Contact time (min)	pH	Temperature (K)
Shaking speed (rpm)	Hg(II)	5-200	5	60	7	293
	Cd(II)	5-200	20	60	7	293
Amount of adsorbent (gL^{-1})	Hg(II)	100	5-50	60	7	293
	Cd(II)	150	5-50	60	7	293
Contact time (min)	Hg(II)	100	5	0-120	7	293
	Cd(II)	150	25	0-120	7	293
pH	Hg(II)	100	5	105	2-10	293
	Cd(II)	150	25	60	2-10	293

Table-2: Langmuir, Fruendlich and D-R parameters of adsorption for Hg (II) and Cd (II) on corn straws and corn cobs respectively

Metal ions	Langmuir isotherm			Fruendlich isootherm			D-R isotherm		
	Q(mgg^{-1})	b(Lg^{-1})	R^2	K(mgg^{-1})	n	R^2	X_m(mgg^{-1})	β(mol^2kj^{-2})	R^2
Hg(II)	4.83	2.75	0.995	3.25	3.70	0.964	3.98	0.037	0.876
Cd(II)	3.61	0.183	0.971	0.67	2.08	0.927	2.34	0.46	0.80

precision every experiment was replicated thrice and mean values of these results were used for calculations.

The following expression was used to calculate the percentage adsorption of the metals;

$$\% \text{ age adsorption} = [(C_o - C_{eq}) / C_o] \times 100 \quad (6)$$

where

C_o = initial concentration of metal ion
C_{eq} = equilibrium concentration of metal ion

Biosorption Studies

For the determination of rate of metal sorption by adsorbent, the supernatant was analyzed at different intervals of time ranging from 0-120 min. To study the effect of different amounts of adsorbent on metal sorption, various doses of adsorbents ranging from 5-50g/L (for mercury) and 10-100g/L (for cadmium) were used. The effect of shaking speed was determined by shaking the mixtures at different rpm in a rotary shaker.

Adsorption isotherms studies were carried out with different initial concentrations for both metal ions. Langmuir, Fruendlich and Dubinin-Radushkevich (D-R) models were applied to the adsorption isotherms and different constants were calculated. Correlation coefficients were also determined from the adsorption isotherm data.

Conclusion

In this work biosorption process for the removal of Hg (II) and Cd (II) ions from the aqueous solution by using corn straws and corn cobs has been presented. The maximum removal efficiencies found were 86.9 % for Hg (II) at pH 10 and 92 % for Cd (II) at pH 9. The effect of other operational parameters like contact time, shaking speed, temperature, amount of adsorbent and initial metal ion concentration were also studied. It can be safely concluded that corn straws and corn cobs can be effectively used as biosorbent for the removal of Hg (II) and Cd (II) from aqeous effluents at optimal conditions.

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