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Removal of Chromium (VI) by Biosorption Using Different Agricultural Byproducts of Some Important Cereal Cropsas Biosorbents

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Abstract: Corn cob powder (*Zea maize*) waste of very popular food cropin Asia, Bagasse of Sugar Cane (*Saccharum Officinarum*), Rice husk (*Oryza sativa husk*) were used as biosorbent. The efficiency of these biosorbents for the removal of Cr (VI) from aqueous solution was studied by varying the parameters: pH, temperature, contact time and biosorbent concentration. A strong dependence of absorption capacity on parameters was observed.In case of corn cob powder the biosorbent size did not affect chromium biosorption rate and capacity. Analysis of variance was applied to know the significance of these variables. Values <0.05 are significant. The maximum %age reduction for corncobs, Sugar Cane and Rice husk was 98.7%, 98.64% & 100% respectively.

Key words: Heavy metals · Chromium (VI) · Biosorption · Corncobs · Sugar Cane Bagasse · Rice husk.

INTRODUCTION

Toxic heavy metals are a growing threat to the environment. Heavy metals are harmful for life when present above the permissible limit [1]. One of the major problems that heavy metals cause with respect to their effects on aquatic organisms is their long biological half-life. Therefore, they are among the most frequently monitored micro pollutants [2]. The contact of industrial pollutants with aquatic ecosystems leads to a risk directly related to the existence of hazardous substances which could have potential negative effects on the biological balance of natural environments [3]. Lead, cadmium and mercury are examples of heavy metals that have been classified as priority pollutants by the U.S Environmental protection Agency [4]. Chromium (VI) is a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from the textile dyeing, leather tanning, electroplating and metal finishing industries.The hexavalent form of chromium is considered to be in a group "A" human carcinogen because of its mutagenic and carcinogenic properties [5].

Biosorbents are prepared from naturally abundant waste biomass. A corncob is the central core of maize. Maize is the member of class family *Poaceae*. Maize is a major staple cereal and therefore, produces large volume of waste (corncobs) [6]. Corncobs are, recyclable, organic and natural, virtually dust free and non-sparking [7]. Corncobs are rich in cellulose and hemicellulose, which comprise about 80% of the dry matter which are converted into metal ion adsorbents for wastewater treatment [8]. Sugar cane is also a member of the grass family. Bagasse is a byproduct of sugar mills which is found to be effective in removing chromium from aqueous solution by ion exchange and adsorption mechanisms. The rice hulls, one of the major residues after rice production is inedible. All these are used as biosorbent for the removal of toxic heavy metal like chromium (IV) from the aqueous solution by biosorption method [9].

Biosorption can be defined as the removal of metallic ions by means of passive adsorption or complexation by living biomass or organic waste [10]. Biosorption is a process in which solids of natural origin are employed for binding heavy metals. It is the physico-chemical binding of metal/radionucleide species in biomass [11]. More specifically, the metal binding in biosorption may be due to a combination of several sequestering mechanisms such as complexing, co-ordination, chelation, adsorption, ion exchange or micro-precipitation (as metal or metal salts) [12]. This process is characterized as less disruptive and can be often carried out on site, eliminating the need to transport the toxic, materials to treatment sites [13]. Biosorption is proven to be quite effective for removing metal ions from contaminated solution in a low-cost and

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environment-friendly manner [14]. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, biosorbent regeneration and metal recovery potentiality, minimization of chemical and/or biological sludge, no additional nutrient requirement and regeneration of biosorbent and the possibility of metal recovery [15].

Present work is aimed at the removal of chromium from aqueous solutions using different agricultural by products as biosorbents which will lead to the reduction of chromium toxicity in specific and environmental pollution in general from the aqueous ecosystems.

MATERIALS AND METHODS

Chemicals: Potassium Dichromate ($K_2Cr_2O_7$) (Merck), Sulphuric acid (H_2SO_4) (Merck), 1,5-Diphenyl carabazide ($C_{14}H_{13}N_4O$ (BDH),Hexamine (Winlab),Sodium Hydroxide pellets (NaOH) (Merck),Distilled water and Acetone (Merck) were of analytical grade.

Preparation of Adsorbents: Corncobs, Sugar cane Bagasse and Rice husk were used as biosorbents. Corn was collected from field. The corn on the cobs was removed. The corn cobs were dried in sunlight for 3 days. Bagasse was collected from Shoukat Sugar Mills situated on Majra road Sialkot, Punjab (Pakistan) and oven-dried at 105°C for 3 minutes.Rice husk (RH) was collected from Cheema Rice Mills situated on Sambrial road Sialkot, Punjab (Pakistan) and oven-dried at 105°C for 3 minutes.The dried matters were milled and sieved and particles of 200 mesheswere selected for investigation.

Preparation of Chromium Solution: A stock solution of Cr (VI) (1000 mg /dm^3) was obtained by dissolving 2.8289 g of $K_2Cr_2O_7$ salt in 1000 ml of distilled water. Estimation of chromium (vi) Cr (VI) was estimated spectrophotometrically using 1, 5-Diphenyl carbazide as a complexing agent, 1,5-Diphenyl carbazide is an organic reagent which forms red-violet complex with Cr (VI). The absorbance of this complex was noted at 540nm.

The efficiency of the biosorbents for the removal of Cr (VI) from aqueous solution was studied by varying the parameters: pH, temperature, contact time and biosorbent concentration. A strong dependence of absorption capacity on parameters was observed.

RESULTS

This study was carried out to examine the %age reduction of chromium (VI) from sample solutions. Corncob biosorption capability was checked out by optimizing conditions of various parameters i.e. temperature, pH, biosorbent concentration and contact time.

It has been also reported that biosorption capacities for heavy metals are strongly pH sensitive and that adsorption increases as pH of the solution increases.In the experiments performed, it was observed that the %age reduction of metal increase with increase in pH.

Time contact also affected the biosorption efficiency. By changing the contact time at various conditions, a considerable change in biosorption rate was observed.

Temperature also greatly affected the rate of metal removal. This study was carried out at four different temperatures (30, 50, 70and 90°C). The maximum %age reduction was obtained by increasing the temperature upto 70°C.

The concentration of both the metal ions and the biosorbent is a significant factor to be considered for effective biosorption. With increase in biosorbent concentration from 2.55 to 5 g/100ml an increase in %age removal of metal was observed.

The Model F-value of 2132.22 implies the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AB, AC, AD, BC, BD, CD, A^2, B^2, C^2, $D^2$are significant model terms. And it greatly effected the %age reductin by biosorbent. Values greater than 0.1000 indicated the model terms are not significant. And they don't adversly effect the %age reduction. "the lack of fit F-value" of 3.64 implies there is a 6.50% chance that the lack of fit F-value this large could occur due to noise. Lack of fit is bad.we want the model to fit.This relatively low probability (<10%) is troubling.

From the normal plot of residual which is plottes between normal %age probability on y-axis and internally studentized residuals on x-axis, it is depicted from the graph that all values lies almost on the calibration line. Therefore it is according to normality standard and aur results followed it.

Table 1: %age reduction of Chromium by using corn cobs in the given set of parameters

Run	pH	Temperature (°C)	Concentration (gm/1)	Contact time (min)	% age reduction (Corncobs)	% age reduction (Bagasse)	% age reduction (Rice husk)
1	7	50	2.55	55	85.8	65.79	86.28
2	7	50	2.55	55	86.1	88.04	94.48
3	12	30	0.10	10	91.61	97.8	19.84
4	2	70	0.10	10	12.87	95.3	99.75
5	7	50	2.55	55	85.5	31.54	99
6	7	50	7.45	55	85.6	87.33	48.08
7	3	50	2.55	55	69.45	91.3	29.72
8	7	50	2.55	55	85.8	97.28	10
9	12	70	0.10	100	97.59	25.02	89.75
10	12	70	0.10	10	90.43	*46.2*	99.16
11	2	70	5.00	100	98.7	*96.13*	97.66
12	2	30	5.00	10	58.03	65.02	98.70
13	7	50	2.35	55	85.91	86.11	98.96
14	12	30	5.00	10	74.56	97.64	99.12
15	7	90	2.55	55	93.6	61.05	100.00
16	12	30	0.10	100	87.4	84.05	83.74
17	12	30	5.00	100	29.71	88.26	98.72
18	12	70	5.00	100	55.24	76.3	98.20
19	7	50	2.55	55	86.09	92	96.08
20	70	5	10.00	85.19	85.19	90.2	96.09
21	7	50	2.55	55	86.5	90.2	99.90
22	2	70	0.10	100	77.59	24.3	96.45
23	2	30	5.00	100	68.19	59.25	31.25
24	2	30	0.10	100	57.56	59.23	99.55
25	7	50	2.55	145	81.19	89.26	98.85
26	2	30	0.10	10	8.35	90.02	97.65
27	2	70	5.00	10	77.15	94.2	98.80
28	7	10	2.55	55	62.37	86.3	89.64
29	7	50	2.55	55	85.15	80.02	99.00
30	7	50	2.55	35	82.7	24.9	99.33

Table 2: Analysis of variance for response surface Quadratic model *Zea mays*

Source	Sum of squares	df	Mean square	F-value	p-value prob>F
Model	14909.51	14	1064.96	2132.22	< 0.0001
A-pH	338.12	1	338.12	676.96	< 0.0001
B-Temperature	1620.19	1	1620.19	3243.86	< 0.0001
C-Concentration	188.19	1	188.19	376.78	< 0.0001
D-Time	149.07	1	149.07	298.46	< 0.0001
AB	52.60	1	52.60	105.31	<0.0001
AC	4490.01	1	4490.01	8989.66	< 0.0001
AD	2956.37	1	2956.37	5919.09	< 0.0001
BC	170.50	1	170.50	341.36	< 0.0001
BD	176.69	1	176.69	353.76	< 0.0001
CD	1599.40	1	1599.40	3202.24	< 0.0001
A2	683.66	1	683.66	1368.79	< 0.0001
B2	102.53	1	102.53	205.28	< 0.0001
C2	6.99	1	6.99	13.99	0.0020
D2	145.80	1	145.80	291.92	< 0.0001
Residual	7.49	15	0.50		
Lack of Fit	6.33	9	0.70	3.64	0.0650
Pure Error	1.16	6	0.19		
Cor Total	14917	29			

Table 3: *Saccharum officinarum*

Sources	Sum of squares	df	Mean square	F-value	P-value Prob > F
Model	13288.76	14	949.20	4.84	0.0022
A-pH	1230.66	1	1230.66	6.28	0.0242
B-Temperature	855.64	1	855.64	4.37	0.0541
C-Concentration	395.91	1	395.91	2.02	0.1757
D-Time	208.25	1	208.25	1.06	0.3190
AB	125.55	1	125.55	0.64	0.4360
AC	373.46	1	373.46	1.91	0.1877
AD	1254.22	1	1254.22	6.4	0.0231
BC	54.46	1	54.46	0.28	0.6058
BD	555.54	1	555.54	2.83	0.1130
CD	13.91	1	13.91	0.071	0.7935
A2	3637.43	1	3637.43	18.56	0.0006
B2	0.12	1	0.12	6.32E-04	0.9803
C2	160.30	1	160.30	0.82	0.3801
D2	22.17	1	22.17	0.11	0.7413
Residual	2939.92	15	195.99		
Lack of Fit	2874.06	9	319.34	29.09	0.0003
Pure Error	65.87	6	10.98		
Cor Total	16228.68	29			

Table 4: *Oryza sativa*

Source	Sum of squares	df	Mean square	F-value	p-value
Model	20134.66	14	1438.19	52.07	< 0.0001
A-pH	309.49	1	309.49	11.20	0.0044
B-Temperature	5219.98	1	5219.98	188.99	< 0.0001
C- Concentration	645.79	1	645.79	23.38	0.0002
D-Contact Time	24.63	1	24.63	0.89	0.3599
AB	1396.52	1	1396.52	50.56	< 0.0001
AC	2186.50	1	2186.50	79.16	< 0.0001
AD	30.25	1	30.25	1.10	0.3119
BC	7568.13	1	7568.13	274.00	< 0.0001
BD	301.20	1	301.20	10.90	0.0048
CD	22.80	1	22.80	0.83	0.3780
A2	3479.05	1	3479.05	125.96	< 0.0001
B2	53.85	1	53.85	1.95	0.1830
C2	367.68	1	367.68	13.31	0.0024
D2	41.11	1	41.11	1.49	0.2413
Residual	414.32	15	27.62		
Lack of Fit	344.83	9	38.31	3.31	0.0795
Pure Error	69.48	6	11.58		
Cor Total	20548.98	29			

DISCUSSION

The study indicated that the biomass (corncob, sugar cane bagasse and rice husk) could be used as efficient biosorbent materials for the treatment of chromium (VI) ions bearing wastewater [16]. The results obtained in our study are in good agreement with previous reports showing that the chromium (VI) biosorption is very effective using these biosorbents. The ANOVAs (Analysis of Variance) model was used for the mathematical description of the biosorption of chromium (VI)by corncobs, sugar cane bagasse and rice husk [17].

A number of studies have been carried out on metal removal by biosorption, all of which showed considerable reduction, for instance 60-80% removal using agricultural by-product. Greater efficiency of about 90-98.7% of chromium(VI)removal was recorded using corncob, 98.64% by sugar cane bagasse and the maximum %age reduction was done by rice husk i.e 100%.

It has been also reported that biosorption capacities for heavy metals are strongly pH sensitive and that adsorption increases as the solution pH increases.In this experiment, it was observed that the %age reduction of metal increase with increase in pH.Time contact also affects the biosorption efficiency. By changing the contact time at various conditions, a considerable change in biosorption rate was observed [18].

Temperature greatly affects the rate of metal removal. This study was carried out at four different temperatures (30, 50, 70and 90°C). The maximum %age reduction was obtained by increasing the temperature upto 70°C.The concentration of both metal ions and the biosorbent is considered to be a significant factor for effective biosorption. With increase in biosorbent concentration from 2.55 to 5 g/100ml an increase in %age removal of metal was observed.

Since theecotoxicological risk of Cr (VI) has been well documented, removalof toxic Cr (VI) from wastewater using natural material such as RH will certainly have apositive effect on the ecosystems.

CONCLUSION

Pollution of the aquatic environment with toxic valuable metals is widespread. Consideration of the modes of purifying these contaminations must be given to strategies that are designed to high thorough put methods while keeping cost at minimum. Biosorption readily provides an efficient alternative to traditional physiochemical means for removing toxic metals. The results of the present study demonstrated that corn cobs were excellent biosorbentfor the removal of chromium ions. The study showed that pH, biomass dosage, agitation time and initial metal concentration highly affected the overall metal uptake capacity of the biosorbent. The results obtained were quite promising in terms of numerical strength of the percentage removal for the metal investigated.

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