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Hexavalent Chromium Removal Using A Low-Cost Activated Carbon Adsorbent From *Areca catechu*

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Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms. In recent years various heavy metals are removed from solution using natural low cost adsorbents which are economically viable. The present study is aimed at removing hexavalent chromium from aqueous solution using activated carbon from *Areca catechu*. The effect of variation of initial concentration of Cr (VI) solution, variation of pH and dosage of adsorbent on the adsorption potential of Cr(VI) have been studied. The results of the study have been interpreted in terms of Langmuir adsorption isotherm and Freundlich adsorption isotherm. The adsorption of Cr (VI) onto activated carbon from *Areca catechu* was found to be concentration dependent. The maximum removal of Cr (VI) was observed at pH 2. The adsorption Cr(VI) using activated carbon prepared from the *Areca catechu* shell followed Langmuir and Freundlich adsorption isotherms.

KEYWORD

Areca catechu, Adsorption, Chromium(VI), Langmuir isotherm, Freundlich isotherm.

INTRODUCTION

Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms (Sheela *et al.,* 2004). According to World Health Organization (WHO) the metals of most immediate concern are mercury, lead, chromium, copper zinc and iron(Muhammad *et al.,* 2001).

The extensive use of chromium and its compounds in leather tanning, ferrochrome, pigments, electroplating and photography has led to increase in chromium content of wastewaters (Shiny *et al.,* 2004).The harmful effects of chromium are documented (Raj and Kumar, 1999; Wittbrodt and Palmer, 1995). Hence removal of Cr(VI) is essential and important. There are various methods to remove Cr(VI), like chemical participation, membrane process, ion exchange, liquid extraction and electro dialysis. These methods are non-economical and have many disadvantages, such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost (Nameni *et al.,* 2008). In recent years various heavy metals are removed from solution using natural low cost adsorbents which are economically viable, such as agricultural wastes including sunflower stalks, waste tea, rice straw, tree leaves, peanut and walnut husks (Karthikeyan *et al.,* 2008).

The present study is aimed at removing hexavalent chromium from aqueous solution using activated carbon from *Areca catechu*. The effect of variation of initial concentration of Cr (VI) solution, the variation pH and dosage of adsorbent on the adsorption of Cr(VI) has been studied. The results of the study have been interpreted in terms of Langmuir adsorption isotherm and Freundlich

Table 1. *Adsorption potential of cr (vi) with variation of initial concentration of cr (vi) solution*

Conditions

Adsorbent dosage : 100 mg ; pH : 4.00 ± 0.02 ; Temperature : 32°C ; Contact time : 10-180 min

Time,	Removal of Cr (VI) in percentage, mg/L			
min	0.06	0.08	0.1	0.12
10	17. 16	13.12	10.6	10.5
20	20	15.25	12.3	12
30	23	17.5	14.1	13.5
40	25.83	21.75	17.6	15
50	28.66	26.12	21.1	17.91
60	31.5	28.37	24.6	20.91
90	34.33	30.5	26.4	23.91
120	37.16	32.62	29.9	26.91
150	43	37	34.4	29.91
180	45	39.25	36.9	32.91

Table 2. *Adsorption potential of Cr (vi) with pH variation*

Conditions

Adsorbent dosage : 100 mg; Temperature : 32°C; Contact time : 10-180 min; Concentration of Cr (VI) solution : 0.12 mg/L

Time,	Removal of Cr (VI) in percentage				
min	pH 2	pH 2.5	pH 3	pH 3.5	pH 4
10	24.58	20	16.16	12.33	10.5
20	32.08	21.83	17.75	13.91	12
30	39.66	23.66	21	15.41	13.5
40	45.33	25.5	24.25	18.5	15
50	51	27.33	25.83	20	17.91
60	56.66	30.91	29.08	23.08	20.91
90	60.41	38.25	35.5	26.16	23.91
120	64.16	41.83	40.33	29.25	26.91
150	68	47.33	42	33.91	29.91
180	69.83	52.75	43.58	35.41	32.91

adsorption isotherm.

MATERIAL AND METHOD

The low-cost carbon was prepared from the shells of *Areca catechu* using concentrated H_2SO_4. The shells of *Areca catechu* were collected from Thondamuthur village in Coimbatore district.

Table 3. *Adsorption potential of Cr (VI) with dosage variation*

Conditions

pH : 2±0.02; Temperature : 32°C; Contact time :10-180 min ; Concentration of Cr (VI) solution : 0.12mg/L

Time,	Removal of Cr (VI) in percentage, mg/L			
min	50	100	150	200
10	21.5	24.58	35.41	43.55
20	22.91	32.08	43.08	48.41
30	24.33	39.66	47.75	54.91
40	27.16	45.33	55.41	61.33
50	30	51	60	64.58
60	32.91	56.66	67.75	69.41
90	37.16	60.41	75.41	75.83
120	41.5	64.16	83.08	85.5
150	42.91	68	87.75	92
180	44.33	69.83	90.83	98.41

Preparation of activated carbon

The shells of *Areca catechu* were cut into small pieces, dried for 5 day and further dried in a hot air oven at 60°C for 24 hr. The completely dried material was powdered well and chemically activated by treating with concentrated sulphuric acid with constant stirring and kept for 24 hr. The carbonized material obtained washed well with plen of water several times to remove excess acid and dried at 105-110°C in a hot air oven for 24 hr. The adsorbent thus obtained was ground well and sieved through a 250 mesh and kept in an airtight container for further use.

Preparation of Cr (VI) metal ion solution

All chemicals used were of analytical grade. In order to assess the performance of the low-cost adsorbent prepared and to avoid interference by other contaminants in wastewater, the experiments were conducted with an aqueous solution of Cr (VI) prepared by dissolving 283 mg of potassium dichromate in 1L of double distilled water.

Table 4. *Interpretation of results of adsorption of cr (vi) in terms of Langumir adsorption isotherm for variation of concentration of Cr (VI) solution*

Time, min	Initial concentration, mg/L	$1/C_e$	m/x	Separation factor R_L	Intercept k_1/k_1^1	Slope $1/k_1^1$
10	0.06	0.0201	0.9708	0.9572	0.7443	12.4567
	0.08	0.0143	0.9523	0.9438		
	0.1	0.0111	0.9433	0.9307		
	0.12	0.0093	0.7936	0.9180		
20	0.06	0.0208	0.8333	0.9619	0.6589	9.8314
	0.08	0.0147	0.8196	0.9499		
	0.1	0.0114	0.8130	0.9381		
	0.12	0.0094	0.6944	0.9267		
30	0.06	0.0216	0.7246	0.9656	0.5936	6.7480
	0.08	0.0151	0.7142	0.9546		
	0.1	0.0116	0.7092	0.9439		
	0.12	0.0096	0.6172	0.9335		
40	0.06	0.0224	0.6451	0.9719	0.4803	7.0070
	0.08	0.0159	0.5747	0.9629		
	0.1	0.0121	0.5681	0.9541		
	0.12	0.0098	0.5555	0.9455		
50	0.06	0.0233	0.5813	0.9786	0.3633	8.6668S
	0.08	0.0169	0.4784	0.9717		
	0.1	0.0126	0.4739	0.9649		
	0.12	0.0101	0.4651	0.9582		
60	0.06	0.0243	0.5291	0.9832	0.2841	9.7533
	0.08	0.0174	0.4405	0.9777		
	0.1	0.0132	0.4065	0.9723		
	0.12	0.0105	0.3984	0.9670		
90	0.06	0.0253	0.4854	0.9853	0.2482	9.3144
	0.08	0.0179	0.4098	0.9805		
	0.1	0.0135	0.3787	0.9757		
	0.12	0.0109	0.3484	0.9716		
120	0.06	0.0265	0.4484	0.9878	0.2051	9.2755
	0.08	0.0185	0.3831	0.9838		
	0.1	0.0142	0.3344	0.9799		
	0.12	0.0114	0.3095	0.9759		
150	0.06	0.0292	0.3875	0.9881	0.1998	6.5118
	0.08	0.0198	0.3378	0.9842		
	0.1	0.0152	0.2906	0.9804		
	0.12	0.0118	0.2785	0.9765		
180	0.06	0.0307	0.3636	0.9893	0.1794	6.1503
	0.08	0.0205	0.3184	0.9858		
	0.1	0.0158	0.2710	0.9823		
	0.12	0.0124	0.2531	0.9789		

Table 5. *Interpretation of results of adsorption of Cr (VI) in terms of Freundlich adsorption isotherm for variation of concentration of Cr (VI) solution*

Time, min	Initial concentration, mg/L	logCe	log x/m	Intercept	Slope N	1/n
10	0.06	1.6963	0.0128	-0.3706	0.2183	4.5797
	0.08	1.8419	0.0211			
	0.1	1.9513	0.0253			
	0.12	2.0301	0.1003			
20	0.06	1.6812	0.0791	-0.2560	0.1922	5.2014
	0.08	1.8312	0.0863			
	0.1	1.9429	0.0899			
	0.12	2.0236	0.1583			
30	0.06	1.6646	0.1398	-0.1443	0.1643	6.0845
	0.08	1.8195	0.1461			
	0.1	1.9339	0.1492			
	0.12	2.0161	0.2095			
40	0.06	1.6483	0.1903	-0.0847	0.1724	5.8002
	0.08	1.7965	0.2405			
	0.1	1.9159	0.2455			
	0.12	2.0086	0.2552			
50	0.06	1.6314	0.2355	-0.1567	0.2521	3.9651
	0.08	1.7715	0.3201			
	0.1	1.8970	0.3242			
	0.12	1.9934	0.3324			
60	0.06	1.6138	0.2764	-0.2639	0.3429	2.9183
	0.08	1.7581	0.3560			
	0.1	1.8773	0.3909			
	0.12	1.9772	0.3996			
90	0.06	1.5954	0.3138	-0.2968	0.3861	2.5895
	0.08	1.7450	0.3873			
	0.1	1.8668	0.4216			
	0.12	1.9604	0.4578			
150	0.06	1.5340	0.4116	-0.1790	0.3852	2.5960
	0.08	1.7024	0.4712			
	0.1	1.8234	0.5365			
	0.12	1.9243	0.5550			
180	0.06	1.5118	0.4393	-0.1926	0.4157	2.4054
	0.08	1.6860	0.4969			
	0.1	1.8000	0.5670			
	0.12	1.9057	0.5965			

Preparation of complexing reagent

The complexing reagent was prepared by dissolving 250 mg of diphenyl carbazide in 50 mL of acetone.

Equipment

Elico pH meter was used to measure pH. Elico CL157 colourimeter was used for spectrophotometric work. Genuine Equipment Manufacturers mechanical shaker was used for the shaking of solution containing adsorbent and adsorbate.

Effect of variation of initial concentration of Cr (VI) solution on the adsorption of Cr (VI)

Standard solutions [100 mL of Cr (VI)] containing 0.06, 0.08, 0.1 and 0.12 μg of chromium (VI)] were taken in Pyrex bottles. To it was added 100 mg of adsorbent and shaken in an electrical horizontal bench shaker for various time intervals (10 to 180 min) at room temperature and at constant pH 4+ 0.02. The solutions were filtered and Cr (VI) concentrations in the filtrate were estimated calorimetrically by complexing with diphenyl carbazide.

Effect of variation of pH on the adsorption of Cr (VI)

The optimum pH for the maximum Cr (VI) adsorption was found by varying the pH from 2.0 to 4.0.The pH of the solution was adjusted using dilute sulphuric acid and it was measured using Elico pH meter. 100 mL samples containing 0.12 μg of Cr (VI) were contacted with 100 mg of adsorbent by altering the pH of the solution. These solutions were shaken for various time intervals (10 to 180 min) in an electrical horizontal bench shaker. The solutions were filtered and analyzed calorimetrically to find the adsorption potential of Cr (VI) from aqueous solution for the variation of pH from 2 to 4.

Effect of variation of adsorbent dosage on the adsorption of Cr (VI)

Standard chromium solution (100 mL) containing 0.12 mg/L of Cr (VI) were taken in Pyrex bottles containing 50, 100, 150 and 200 mg of the adsorbent at pH 2±0.02. The system was equilibrated thoroughly on a horizontal bench shaker at room temperature for 180 min. Then the solutions were filtered and analyzed colorimetrically, to find the amount of Cr (VI) adsorbed.

RESULT AND DISCUSSION

Effect of variation of initial concentration of Cr (VI) solution on adsorption of Cr (VI) from aqueous solution

The adsorbate concentrations were varied form 0.06 to 0.12 mg/L and batch studies were performed to optimize the initial concentration of the adsorbate. The results (Table 1) show an increasing percentage removal Cr (VI) when the adsorbate concentration was varied from 0.12 to 0.06 mg/L. This may be probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of Cr (VI) causing a decrease in percentage removal of Cr (VI) corresponding to an increased initial adsorbate concentration.

Effect of pH variation on Cr (VI) removal from aqueous solution

In order to optimize the pH for maximum Cr (VI) removal, experiments were conducted with 100 mL of 0.12 mg/L of Cr (VI) solution with 100 mg adsorbent by varying the pH from 2 to 4 at various time intervals .The results indicated a maximum adsorption of (69. 83%) at pH 2 in 180 min of contact time (Table 2). The decrease in adsorption at higher pH may be due to the negative charges on the surface of the adsorbent repelling the negatively charged chromate ions in solution.

Effect of adsorbent dosage on Cr (VI) removal from aqueous solution

The effect of variation of adsorbent dosage was determined by varying the adsorbent dosage from 50 to 200 mg with 100 mL of 0.12 mg/L of Cr (VI) solution. It is evident from the results (Table 3) that the adsorption potential of the adsorbent increases with increase in dosage. The maximum adsorption of Cr (VI) was noted with 200 mg of adsorbent dosage. The increase in percentage adsorption of Cr (VI) with increase in the adsorbent dosage may be due to the availability of more surface area of the adsorbent for adsorption of Cr (VI) species.

Adsorption isotherms

The data obtained in the study by varying the concentration of Cr (VI) solution was interpreted in terms of Langmuir and Freundlich adsorption isotherms.

Langmuir adsorption isotherm : Langmuir adsorption isotherm is based on the assumption that points of valency exists on the surface of the adsorbent and that each of these site is capable of adsorbing only one molecule. Thus the adsorbed layer will be one molecule thick. The Langmuir adsorption isotherm is commonly given by :

$$X/m = (k_1^1\ C_e/1 + k_1C_e)$$

Where

x - Amount of Cr (VI) adsorbed (mg/L)

m - Weight of adsorbent (mg)

C_e - Concentration of Cr (VI) at equilibrium

k_1 and k^1 - Langmuir constants which are the measures of maximum energy of adsorption and adsorption capacity, respectively.

On rearranging

$$1/x/m = 1/k^1/k_1 + 1/k^1C_e$$

The plot of (1/x/m) versus 1/Ce is linear with slope equal to $1/k_1$ and intercepts ($1/k^1/k_1$). The slope, intercept and separation factors are calculated (Table 4). The linear plots of $1/C_e$ vs m/x shows the applicability of Langmuir adsorption isotherm for the present system indicating the formation of monolayer coverage of adsorbate on the surface of the adsorbent.

Separation factor-R_L : The essential characteristics of Langmuir adsorption isotherms can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter 'R_L' which is defined by :

$$R_L = 1/(1 + bC_i)$$

where, C_i is initial concentration of Cr(VI) in mg/L and b is Langmuir constant (k^1_1)

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L < 1$	Favourable

The R_L values obtained are less than unity for Cr(VI) adsorption onto a low -cost adsorbent used in this study. This showed the feasibility of the Cr (VI) adsorption process at all initial concentration of aqueous solution of Cr (VI) used in this study.

Freundlich adsorption isotherm : Attempts were made to fit the adsorption data obtained in this study into Freundlich adsorption isotherm. The linear form of Freundlich adsorption isotherm is given below :

$$\log x/m = \log k_f + 1/n \log C_e$$

where x is the amount of Cr(VI) adsorbed in mg, m is the weight of the adsorbent (g), C_e is the amount of Cr (VI) in the bulk solution in mg and K_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The linear form of Freundlich adsorption isotherms at room temperature is obtained by plotting log x/m versus log C_e for different concentrations of the aqueous solution of Cr (VI). K_f and 1/n are evaluated from the slope and intercept, respectively (Table 5). The results demonstrate the applicability of the Freundlich isotherm in explaining the process of adsorption of hexavalent chromium onto the adsorbent.

CONCLUSION

The adsorption of Cr (VI) onto activated carbon from *Areca catechu* was found to be concentration dependent. Removal of Cr (VI) increased with decrease in pH and it was found to increase from 32.91% to 69.83% for the variation of pH from 4 to 2. The maximum removal of Cr (VI) was observed at pH 2. Percentage removal of Cr (VI) increased from 44.33 to 98.41% with increasing adsorbent dosage from 50 to 200 mg. The adsorption Cr(VI) using activated carbon prepared from the *Areca catechu* shell followed Langmuir and Freundlich adsorption isotherms. The favourable value of R_L showed the feasibility of the process at all initial concentrations (0.06 to 0.12 mg/L) of Cr (VI) solution used in this study. Thus it can be concluded that the activated carbon prepared from the *Areca catechu* shell is inexpensive and use of the same provides an effective solution for treatment of effluents containing hexavalent chromium.

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