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Adsorption of Chromium (VI) From Aqueous Solution Using Activated Carbon From the Pods of Wood Apple

N. Renugadevi, M. Sreeja and P. Lalitha
Avinashilingam University for Women, Department of Chemistry, Coimbatore - 641 043

In this study activated carbon from pods of wood apple, an agro waste has been used as an adsorbent for removal of Cr (VI) from aqueous solutions. Parameters, such as adsorbent dosage, concentration of the adsorbate, contact time, and pH were optimized with regard to Cr (VI) removal using the selected adsorbent. To analyze the efficiency of the activated carbon from wood apple (ACW) the experiments were also conducted with commercial activated carbon (ACC) and the result compared. The adsorption of Cr (VI) was found to be concentration and pH dependent. Percentage removal of Cr (VI) increased with decrease in pH and increase in adsorbent dosage for both ACC and ACW. On applying the adsorption data to Langmuir equation, linear plots of 1/Ce vs x/m obtained shows that the adsorption of Cr (VI) using activated carbon prepared from the pod of wood apple and commercially activated carbon followed Langmuir adsorption isotherm. Thus adsorption technique using activated carbon from agro wastes, like pods of wood apple is found to be an efficient method for the removal of heavy metals, like Cr (VI) from aqueous solutions.

KEYWORD

Adsorption, Chromium (VI), Adsorbent, Activated carbon, Isotherm.

INTRODUCTION

Activated carbon is the most widely used substance for the removal of heavy metals and other impurities from wastewater. It is used for adsorption of organic substances and non-polar adsorptive and it is also usually used for waste gas and wastewater treatment. Commercial activated carbon is effective for the removal of various pollutants. However, due to its high cost it is affordable (Gupta *et al.,* 2003). So there is a need for low cost and readily available materials for the removal of toxic pollutants from water. Therefore, researches are focused on the production of low cost adsorbents. Several adsorbents, like activated carbons from almond shells (Solano *et al.,* 1980), bagasse and coconut jute (Shrichand *et al.,* 1994), almond shell (Reinose *et al.,* 1982), apricot and peach stones (Razvigoroava *et al.,* 1993) have been used as adsorbents. The present study is focused on use of activated carbon from the pod of wood apple *(Limonia Acidissia)* in the removal of chromium from aqueous solution.

MATERIAL AND METHOD

Collection of wood apple pod

Wood apple pod was collected from a local juice manufacturing industry, Comibatore. The pod was cut into small pieces, dried in sunlight for 5 day and further dried in a hot air oven at 60°C for 24 hr. The completely dried material was chipped, powdered well and carbonized by chemical activation with sulphuric acid.

Preparation of chromium (VI) ion solution

All chemicals used were of analytical grade. In order to assess the performance of the adsorbent and to avoid interference by other contaminants in wastewater, the experiments were conducted with aqueous solution of heaxavalent chromium (adsorbate) prepared by dissolving 28 mg of potassium dichromate in 1L of double distilled water.

1 mL of stock solution = 100 mg of Cr (VI)

Estimation of Cr (VI) ion in the aqueous solu-

Table 1. *Characteristics of the adsorbents used*

Parameter	Adsorbent	
	ACC	ACW
Ash content, %	0.3871	0.0354
Moisture content, %	17.89	9.97
pH	6.87	2.41
Surface area, m^2/g	714.0	336.0
Bulk density, g/cc	0.2520	0.660
Specific gravity	0.9162	0.9019
Porosity, %	72.49	26.15

tion before and after adsorption

The complexing reagent was prepared by dissolving 250 mg of diphenyl carbazide in 50 mL of acetone. The reagent (0.05% in acetone) was kept in an amber bottle refrigerated and used for study. Heaxvalent chromium was determined spectrophotometrically by diphenyl carbazide method.

Equipment

Elico-110 pH meter was used to measure pH. Digital Systronics colorimeter-112 was used for spectrophotometric work. Neolab electrical horizontal bench shaker (120 rpm-200 rpm) with temperature control was used for agitation of solution containing adsorbent and adsorbate.

Analytical procedure

Characterization of the adsorbents : Physical characteristics, namely; ash content (%), moisture content (%), pH, surface area, bulk density, specific gravity, porosity (%) of the adsorbents used in this study were determined according to standard procedures, to identify the applicability of these adsorbents to remove Cr (VI) from aqueous solution by adsorption.

Batch experiment

Batch mode experiments were carried out to study the adsorption capacities of the adsorbents. Though industrial operations are not carried out batchwise, these are simple and effective in evaluating the basic parameters affecting adsorption process. In batch mode adsorption study, there is good contact between the Cr (VI) species and carbon by shaking at 150 rpm. Experiments were performed in duplicate. To analyze the efficiency of the activated carbon from wood apple (ACW) the experiments were also conducted with commercial activated carbon (ACC) and the results compared.

Study of the effect of initial concentration of Cr (VI) solution on Cr (VI) removal

Batch mode experiments were performed with a fixed amount of adsorbent by varying the initial concentration of Cr (VI) solution at pH 6.0±0.02. 100 mL of Cr (VI) solutions containing 0.1, 0.12, 0.14, 0.16, 0.18 and 0.2 mg of Cr (VI) were prepared from Cr (VI) stock solution. The solutions were taken in pyrex bottles containing 100 mg of the adsorbent ACW each and were agitated at 150 rpm thoroughly on a horizontal electrical bench shaker at 30°C for various time intervals (10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 min). Then the solutions were filtered through a Whatman 42 filter paper to separate the Cr (VI) laden adsorbent and the filtrate. The filtrates were analyzed spectrophotometrically using filter number 5 (540 nm) by complexing with diphenyl carbazide for residual Cr (VI) concentration. Similar procedure was repeated with 50 mg of ACC.

Study of the effect of pH on Cr (VI) removal

The effect of pH was studied by varying the pH from 2 to 5 (2, 2.5, 3, 3.5, 4, 4.5 and 5). 100mL of Cr (VI) solutions containing 0.2 mg of Cr (VI) were prepared from Cr (VI) stock solution. The pH of the solutions was adjusted to a desired pH using dilute sulphuric acid and the solutions were taken in pyrex bottles containing 50 mg of the adsorbent ACW and equilibrated thoroughly on a horizontal electrical bench shaker at 30°C for various time intervals (10 to 180 min). Then the solutions were filtered using Whatman 42 filter paper and the filtrates were analyzed for residual Cr (VI) concentration spectrophotometrically. Similar pro-

Table 2. *Effect of agitation time and initial concentration of Cr (VI) solution for adsorption of Cr (VI) onto ACW and ACC*

Conditions
Adsorbents dosage : ACW : 100mg; ACC:50 mg
pH:6.00 ± 0.02; Temperature : 30°C

Time, min	Percentage of Cr (VI) removed											
	Initial concentration of Cr (VI) solution, mg/L											
	ACW	ACC	ACW	ACC	ACW	ACC	ACW	ACC	ACW	ACC	ACW	ACC
	Conc 0.1		0.12		0.14		0.16		0.18		0.2	
10	36.92	53.06	31.76	45	30.58	39.60	27.1	35.0	25.6	33.33	25.65	31.0
20	41.52	57.14	40.0	48.5	35.29	42.85	34.44	38.35	31.0	36.0	30.0	33.6
30	43.07	61.22	42.35	52.6	37.64	45.71	36.66	41.09	33.3	40.0	30.6	37.11
40	47.69	65.38	47.05	55.6	40.0	48.58	37.77	45.66	35.55	42.66	33.2	39.20
50	50.16	69.38	49.41	59	44.9	51.42	41.11	47.94	40.0	46.66	34.6	42.6
60	53.84	71.42	52.94	60	48.23	52.85	45.55	49.31	43.33	49.33	35.1	45.0
90	58.46	73.46	57.64	62	58.82	54.4	51.0	53.42	46.0	52.0	35.5	47.82
120	61.53	75.51	60.4	64	60.0	55.6	53.4	54.42	51.11	54.00	45.9	49.0
150	69.23	77.55	67.05	66.0	63.52	58.57	63.33	57.53	61.11	57.33	54.3	51.82
180	70.76	79.59	70.58	68.0	67.77	64.28	64.4	64.24	63.55	60.00	55.55	53.60

cedure was repeated with 30 mg ACC.

Study of the effect of adsorbent dosage on Cr (VI) removal

The effect of adsorbent dosage was studied by preparing 100 mL of Cr (VI) solutions containing 0.2 mg of Cr (VI) from Cr (VI) stock solution, adjusted to pH 2.0 using dilute sulphuric acid. The solutions were taken in pyrex bottles containing 20, 40, 60, 80 and 100 mg of the adsorbent ACW. The pyrex bottles with Cr (VI) solution and the adsorbents were equilibrated thoroughly on a horizontal electrical bench shaker at 30°C for various time intervals (10 to 180 min) and the solutions were filtered using Whatman 42 filter paper and the filtrates were analyzed for residual Cr (VI) concentration spectrophotometrically. Similar procedure was repeated with 20, 30 and 40 mg of the adsorbent ACC.

Study of the effect of agitation time (contact time) on Cr (VI) removal

From Cr (VI) stock solution, 100 mL of solutions containing 0.2 mg of Cr (VI) were prepared, pH adjusted to 2.0 with dilute sulphuric acid and taken in pyrex bottles containing 100 mg of the adsorbent ACW. These pyrex bottles were taken on a horizontal electrical bench shaker and agitated well at 30°C for predetermined time of 10 to 180 min. The adsorbate and the adsorbents of the solutions in pyrex bottles were separated by filtration using Whatman 42 filter paper for predetermined time intervals of 10 to 180 min. The filtrates obtained were analyzed spectrophotometrically for residual Cr (VI) concentration. Similar procedure was repeated with 50 mg of ACC.

RESULT AND DISCUSSION

Characteristics of the adsorbent

The results of the physical characteristics, namely ash content, moisture content, pH, surface area, bulk density, specific gravity, and porosity of the adsorbents used in this

Table 3. *Effect of agitation time and pH for the adsorption of Cr (VI) onto ACW and ACC*

Conditions
Initial concentration of Cr (VI) solution : 0.2 mg/100 mL
Adsorbent dosage : 100 mg for ACW and 50 mg for ACC; Temperature : 30°C

Time, min	Percentage of Cr (VI) removed, pH 2.0		2.5		3.0		3.5		4.0		4.5		5.0	
	ACW	ACC	ACW	ACC	ACW	ACC	ACW	ACC	ACW	ACC	ACW	ACC	ACW	ACC
10	73.11	75.0	65.21	56.04	47.05	34.06	40.21	12.5	35.10	8.60	20.93	5.26	17.04	4.08
20	78.49	77.41	69.56	58.24	49.41	37.36	45.65	17.5	39.36	10.75	25.58	8.42	21.59	5.10
30	80.64	78.26	72.82	61.53	52.94	40.65	48.91	23.75	42.55	12.90	30.23	9.47	22.72	6.12
40	89.24	81.52	75.0	63.76	55.29	46.15	53.26	31.25	46.50	15.05	40.69	11.57	26.13	7.14
50	91.39	85.86	75.17	65.93	57.64	49.45	56.52	37.50	50.0	16.12	43.02	13.68	32.95	8.16
60	94.62	98.91	78.26	68.13	60.86	53.84	60.0	41.25	59.30	19.35	54.25	14.73	44.31	10.20
90	95.69	98.91	81.52	69.29	65.86	51.84	64.70	47.50	61.62	21.50	56.38	15.78	48.86	11.22
120	96.77	98.91	82.6	72.91	68.23	61.53	65.21	52.5	63.95	22.58	60.63	16.84	54.54	13.26
150	96.77	98.91	83.69	73.62	71.76	62.63	69.56	56.25	67.44	23.65	62.76	17.89	56.81	15.30
180	96.77	98.91	85.86	74.72	75.29	64.83	75.0	58.75	70.93	29.73	64.89	18.94	60.22	16.32

Table 4. *Effect of agitation time and adsorbent dosage for the adsorption of Cr (VI) onto ACW and ACC*

Conditions
Initial concentration of Cr (VI) solution : 0.2 mg/L; pH:2.0±0.02; Temperature : 30°C

Time, min	Percentage of Cr (VI) removed, Activated carbon dosage, mg: ACW 20	ACC 20	ACW 40	ACC 40
10	5.95	38.88	8.33	68.88
20	8.33	44.44	11.90	72.22
30	11.90	47.77	16.66	78.33
40	16.66	52.22	19.04	74.44
50	17.85	55.55	21.42	77.77
60	19.04	58.58	25.0	80.00
90	26.19	62.22	26.19	81.11
120	27.38	65.55	28.38	82.22
150	30.95	67.77	34.52	84.44
180	34.52	70.00	38.09	88.55

study are given in table 1. It is quite obvious from the table that all the characteristics of ACW are comparatively less than that of commercially available activated carbon and hence one can anticipate a considerable difference in their adsorption behaviour.

Table 5. *Langmuir and Freundlich adsorption isotherms for Cr (VI) adsorption onto ACW and ACC*

Conditions
Adsorbent dosage : 50 mg; pH : 6.0 ± 0.02; Temperature : 30°C; Time : 60 min

Initial	Langmuir Isotherm				Freundlich Isotherm			
concentration	ACW		ACC		ACW	ACC	ACW	ACC
f Cr (VI),mg/L	1/Ce	m/x	1/Ce	m/x	log Ce	log x/m	log Ce	log x/m
0.1	0.021660	0.01886	0.03498	0.06849	1.45618	1.16435	1.6643	1.7245
0.12	0.014910	0.01574	0.01666	0.06944	1.77832	1.15839	1.8265	1.8029
0.14	0.010890	0.01492	0.01147	0.06756	1.94043	1.17031	1.9629	1.8262
0.16	0.008737	0.01388	0.00903	0.05882	2.04411	1.23047	2.0586	1.8576
0.18	0.007316	0.01298	0.00765	0.05617	2.11622	1.25049	2.1357	1.8867
0.2	0.006064	0.00142	0.00645	0.05555	2.19037	1.25531	2.2172	2.8453
Intercept	0.001210		0.05662		log K_F	0.9377	-0.7545	
Slope	0.7552		0.4209		1/n	0.1391	1.3881	
r	0.7332		0.69402		r	0.8262	0.6737	

Effect of initial concentration of Cr (VI) solution on Cr (VI) removal

The result of the variation of initial concentration of Cr (VI) solution given in table 2 clearly depict the increase in the percentage removal of Cr (VI) from 55.55 to 70.76% with ACW and from 53.60 to 79.59% with ACC in 180 min of agitation time, when the initial concentration of Cr (VI) solution was varied from 0.1 to 0.2 mg/L. The results suggest that the Cr (VI) removal using adsorption technique is concentration dependent. It is noted that Cr (VI) adsorbed at any contact time increases for greater initial concentration of Cr (VI) solutions. This is predictable, since at higher initial concentration, a more efficient utilization of the adsorptive capacity of the adsorbent is expected due to higher driving force (Ho and Mckay, 2004). The decrease in percentage removal of Cr (VI) with increase in initial concentration indicates that there exists a reduction is solute [Cr (VI)] adsorption, owing to the lack of available active sites required for the high initial concentration of Cr (VI). Cr (VI) removal using ACC was found to be greater when compared to ACW. This may be attributed to the greater surface area of the absorbent ACC compared to ACW as shown in table 2.

Effect of pH on Cr (VI) removal

The percentage removal of Cr (VI) increased from 60.22 to 96.77% (Table 3), and 16.32 to 98.91% for the adsorbents ACW and ACC, respectively for a variation of pH from pH 5 to pH 2 in 180 min of agitation time. It is well evident from table 3 that nearly complete removal of Cr (VI) is noted at pH 2.0 in 60 min of agitation at 30°C with the adsorbent ACC depicting its maximum adsorption efficiency at lower pH. For ACW the complete removal is found to be at 120 min of agitation time at pH 2. At pH 2, the adsorption of Cr (VI) is maximum and saturation occurs as a result of non availability of Cr (VI) species for adsorption with respect to both the adsorbents used in the study. At lower pH, the large numbers of H^+ ions neutralize the negatively charged coal surface or convert a neutral group to a positively charged group and enhance the adsorption of Cr (VI) species. The enhancement of the adsorption of Cr (VI) species is also may be due to decrease in the forces of repulsion between the adsorbent and adsorbate.

Effect of adsorbent dosage on Cr (VI) removal

It is observed that the percentage of Cr (VI) removed increase 34.52 to 38.09% with ACW when it dosage is increased twice and 70% to 88.55 in the case of ACC (Table 4) at pH 2. This increase in adsorption may be due to the increase in total surface area with increase in total adsorbent doses at a fixed initial solute concentration (Ho Mckay, 1998). It is noted that there is no appreciable change in he percentage removal of Cr (VI) beyond a particular time and this was presumed to represent the equilibrium time. It is suggested that the adsorbed solute may either block the access to the internal pores or cause particles to aggregate thereby resulting in decrease in the availability of active sites for further adsorption.

Adsorption isotherm

Langmuir adsorption isotherm : The Langmuir equation correlates the amount of adsorbate adsorbed with the equilibrium aqueous concentration. The linear transformation of the Langmuir equation (Rao and Bhole, 2001) is given as :

$$1/(x/m) = 1/b + 1/ab\ C_e$$

where, x is the amount of Cr (VI) adsorbed in mg, m is the weight of adsorbent (g), C_e is the concentration of Cr (VI) at equilibrium in mg, 'a' and 'b' are the Langmuir constants which are the measure of maximum energy of adsorption and adsorption capacity, respectively. The Langmuir adsorption isotherm data for Cr (VI) adsorption on the adsorbents ACC and ACW are summarized in table 5. The values of correlation coefficient 'r'>0.6 show the applicability of the above equation to the adsorption process.

Freundlich adsorption isotherm : The Freundlich adsorption isotherm equation is used for determining the applicability of heterogeneous surface energy in the adsorption process. The linear form of Freundlich equation (Sumanjit and Prasad, 2001) is represented as :

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

where, x is the amount of Cr (VI) adsorbed in mg, m is the weight of adsorbent (g), C_e is the amount of Cr (VI) in the bulk solution in mg, K_F and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

The Freundlich adsorption isotherm data for Cr (VI) adsorption onto ACC and ACW are summarized in table 5. The value of 1/n (less than 1) indicates the favourability of Freundlich adsorption isotherm for Cr (VI) adsorption studies conducted at pH 6.0±0.02 at 30°C for the adsorbents used in this study. The constant 'n' in Freundlich adsorption isotherm is actually a correction factor for the mutual interaction among the adsorbed species. If the forces within the surface layers are attractive 'n' is greater than unity and if repulsive 'n' is less than unity (Ozer *et al.*, 2000). The experimental values of 'n' are greater than unity suggesting the attractive nature of the forces between the adsorbed species. If the values of Freundlich constant 'n' is in the range of 2-10 shows the best adsorption characteristics (Mckay *et al.*, 1980). The values of Frundlich constant (n) in the present study for adsorption of Cr (VI) species was found to be in the range of 2-10 with respect to both the adsorbents used in this study which indicate best adsorption characteristics.

CONCLUSION

The present study revealed the following :

The adsorption of Cr (VI) was found to be concentration and pH dependent in the case of the both the adsorbents used. Percentage removal of Cr (VI) increased with decrease in pH and increase in adsorbent dosage for both ACC and ACW. On applying the adsorption data to Langmuir equation, linear plots of 1/Ce vs x/m obtained shows that the adsorption of Cr (VI) using activated carbon prepared from the pod of wood apple and commercially activated carbon followed Langmuir adsorption isotherm.

Thus adsorption technique using activated carbon from agro wastes, like pods of wood apple is found to be an efficient method for the removal of heavy metals, like Cr (VI) from aqueous solutions.

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AUTHOR

1*. Dr. N. Renugadevi, Lecturer (SG), Department of Chemistry, Avinashilingam University for Women, Coimbatore - 641 043.

2. Ms. M. Sreeja, Research Scholar, Department of Chemistry, Avinashilingam University for Women, Coimbatore - 641 043.

3. Dr. P. Lalitha, Lecturer, Department of Chemistry, Avinashilingam University for Women, Coimbatore - 641 043.