WATER REMEDIATION OF CHROMIUM (VI) BASED ON SULPHURIC ACID GENERATED BIO-CHAR FROM STEMS OF *Averrhoa carambola* PLANT AS ADSORBENT

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ABSTRACT

Sulphuric acid generated bio-char from stems of *Averrhoa carambola* plant (SBCSAC) is investigated for its Cr (VI) adsorption. At pH:2, complete removal of Cr(VI) from 25 ppm Cr(VI) solution is achieved with one hour equilibration with 0.1g/100 ml of SBCSAC at room temperature. The adsorption capacity of SBCSAC is 40 mg/g. It is higher than many sorbents reported. The interference of co-cations and co-anions is limited. SBCSAC can be regenerated and reused for four cycles with little loss of capacity. Cr(VI) in sewage samples of industries are removed completely using SBCSAC.

Key Words: *Averrhoa carambola*, Adsorbent, Cr(VI), Applications.

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INTRODUCTION

The contamination of water bodies with the Chromium species is one of the major environmental issues.¹⁻⁴ Chromium exists in trivalent and hexavalent states in stable waters.¹ Of the two oxidation states, the hexavalent state is more toxic.^{1,3} As per EPA, the maximum permissible limit of Cr species is 0.05 ppm in potable water; 0.1 ppm for surface or groundwater; and 0.25 ppm for industrial water.^{1,3} The harmful effects of these Chromium species include gastric problems, malfunctioning of liver and kidney and it leads to lung cancer.⁴

The main sources of Chromium contamination are the untreated or ill-treated discharges from industries.¹⁻⁶ The effluents from leather tanning, textile-printing works, ink manufacturing, chrome plating industries, nuclear energy plants and leaches of fly ashes from thermal power stations, are some of the many sources of Cr-contamination.¹⁻⁷ Chromium species get accumulated in water bodies due to their non-biodegradable nature and further, their involvement in the process of bio-amplification. This endangers aquatic life. Hence, the removal of Chromium from water is a major concern.

Chemical reduction and precipitation⁸⁻¹¹, flocculation⁹, electroplating-electrolysis^{12,13}, ion exchange¹⁴ and nano-filtration¹⁵, are some of the conventional methods employed for Cr-removal. The methods based on precipitation are not effective at low Cr-concentrations while the other methods are non-economical and need more technical support and are not adoptable in large-scale treatments. In this context, adsorption methods based on bio-adsorbents obtained from plant materials are attracting the researchers.¹⁶⁻³⁰ These sorbents are proving to be effective and the methodology involved is simple and the sorbents are derived from plant materials that are abundantly available and renewable.

Bioaccumulation¹⁶, activated carbons¹⁷⁻²⁰, coconut fiber²¹, eucalyptus bark²², maple sawdust²³, *Hevea brasiliensis* sawdust activated carbon²⁴, waste tea leaves and rice husk silica²⁵ are investigated for their effectiveness in Cr-removal. Further, barks of *Nerium odorum*²⁶, stems of *Calotropis zygantia*²⁶, barks of *Ziziphus Mauritiana* Plant²⁷, Spent coffee grounds³, *Phoenix sylvestris* seed powder²⁸, leaves of *Salvadora persica* and *Caesalpinia bonduc* plants²⁹ and *Chenopodium album* and *Eclipta prostrata* plant materials³⁰, are investigated for their Cr-sorption nature.

These bio-methods based on plant materials are simple and effective. They depend upon materials that are renewable, eco-friendly and cheap. The main problem in this aspect of research is the identification of bio-materials that have an affinity towards pollutants.

Our initial investigations reveal the bio-char obtained from *Averrhoa carambola* plant stems by digesting in Conc. Sulphuric acid, is effective as an adsorbent in the removal of hexavalent chromium from water. In the present work, the absorptivity of this 'H₂SO₄ –generated bio-char' towards Chromium (VI), has been investigated concerning different physicochemical characteristics for optimizing the extraction conditions for the maximum Cr-removal. The developed method has been applied to real polluted waters.

EXPERIMENTAL

Adsorbent Synthesis

Different plant materials and their bio-chars produced by different methods were investigated for their affinity towards Chromium (VI). Sulphuric acid generated bio-char of stems of *Averrhoa corambola* plant was identified to be effective.

Plant Description

Averrhoa carambola is a small shrub that belongs to *Oxalidaceae* family of the plant kingdom. It grows to a height of about 10 meters. It is well grown in tropical conditions, especially in Southeast Asia. It yields fruits that are edible and possess medicinal values.

Fig.-1: *Averrhoa carambola* Plant showing Affinity for Cr(VI)

Preparation of Sulphuric Acid Activated Carbon

Stems of *Averrhoa carambola* plant were cut into small pieces and half-dried under the Sun-light. The pieces were submerged in Conc.H₂SO₄ for 2 days. It was further digested in a round-bottomed flask using a condenser for 1 hour. Then the material was carbonized.

Thus synthesized bio-char was filtered. It was washed thoroughly with distilled water until the washings were neutral. Then the bio-char was dried at 110°C for 2 hours. It was ground in mortar and pestle for reducing the particle size. It was sieved through a 75µm ASTM mesh. This Sulphuric acid generated Bio-char from Stems of *Averrhoa carambola* plant was named as SBCSAC. It is investigated for its sorption characteristics. This is employed as an adsorbent in the present investigation.

Reagents and Chemicals

Chemicals used were of Analytical Grade. 500 ppm Chromate stock solution was prepared. It was diluted as per need. 0.25% of Diphenyl carbazide in 50% of acetone and 6 N H₂SO₄ were used.

Method

Investigations were made through Batch Modes.^{9,10,31} Synthetic simulated waters of different concentrations of Cr were prepared for the present investigation to evaluate different parameters.

General Procedure

100 ml of Chromium (VI) solutions of different concentrations were taken into 250 ml Iodine Flasks. To each flask, weighed quantities of SBCSAC were added. Initial pHs were adjusted using dil HCl or NaOH.

The flasks were shaken in a Mechanical shaker at 300 rpm for the required time. Then the contents in the flask were filtered. The filtrates were assayed for residual Chromium (VI). Diphenyl Carbazide Spectrophotometric method was used to estimate the residual Chromium as described by Arthur I. Vogle.³² The influence of pH (initial), time of equilibration, concentration of SBCSAC, initial Cr(VI) concentration and temperature on the sorption of Cr(VI) were investigated. For this, the general procedure described above was adopted by varying the targeted parameter while maintaining others at constant (optimum) values. Further, after establishing the optimum conditions of extraction, the possible interference of co-ions (five folds) was investigated. Regeneration and applications were also made. The results are presented in Figs.-2 to 8; Tables-1 and 2.

RESULTS AND DISCUSSION

Optimization of Extraction Conditions

Factors affecting the extraction were optimized for the maximum possible Chromium (VI) removal. The investigation results are presented hereunder.

Initial pH

By varying the initial pH, the extraction was studied using Chromium (VI) solution of concentration 25 ppm. The other conditions were kept constant: SBCSAC: 0.1 g/100 ml; equilibrium time: 60 min; rpm: 300 and temp. 303 K. The observations are depicted in Fig.-2. There is a spectacular dependence of extraction on the pH of the solution. With the increase in pH, extraction of Chromium (VI) falls.

Fig.-2: pH Vs % Cr(VI) Removal

Fig.-3: pH_{ZPC} Evaluation for SBCSAC

100.0% removal of Cr is noticed at pH: 2. At pH 4, % removal is 98.5; at pH:6 : 75.5%; at pH:8: 45.0%; at pH:10 :23.0%; and at pH:12 : 15.0%.

These findings can be explained from the viewpoint of pH_{ZPC} of SBCSAC. pH_{ZPC} was evaluated for the adsorbent, Fig.-3. The value is 5.5. Above this pH_{ZPC}, the surface has a negative charge. It is due to the dissociation of functional groups on the surface of SBCSAC. Below this value, the dissociation is less favored. At low pHs, the surface of SBCSAC possesses a positive charge. So, Chromium (VI) being anion is attracted towards the surface of SBCSAC only at low pHs. At pHs above pH_{zero}, the negative charge on SBCSAC repels negatively charged Chromium (VI) species. So adsorption is less favored. The optimum pH is 2. At this pH, complete removal of Chromium (VI) was noticed.

Equilibration Time

With sorbent dosage at 0.1g/200 ml, 25 ppm Chromium(VI) solution was equilibrated at different times; the rpm is 300 and temperature is: 303 K. The findings are plotted in Fig.-4.

Fig.-4: Time Vs % Cr(VI) Removal

With the increase of time of equilibration, % removal is linearly (nearly) increased up to 60 minutes. After that, a study state is reached. At 15 minutes, 58.0% of removal is noticed; at 30 minutes: 75.0% ; at 45 minutes : 92.0%; and 100.0% at 60 min or above. The minimum time needed for complete removal of Chromium (VI) is 60 minutes.

SBCSAC Concentration

To assess the optimum SBCSAC concentration, definite amounts of SBCSAC ranging from 25 mg to 250 mg were added to 100 ml of 25 ppm Chromium (VI) solution. The resulting mixture's pH was adjusted to 2. Then the solutions were agitated for 60 minutes at 300 rpm and 303 K.

The solutions were filtered and the residual Chromium (VI) was assessed. The findings are plotted in Fig.-5. It is seen from the figure, % removal is almost linearly increased with the rise in SBCSAC concentration up to 100 mg/100 ml. After that, steady state results. With SBCSAC concentration of 25 mg/100 ml, the % removal is: 51.0%; with 50 mg/100ml: 68.0%; with 75 mg/100 ml: 85.6% and with 100 mg/100ml or above: 100%. So at optimum 100 mg/100 ml, complete removal of Chromium (VI) is noticed. SBCSAC adsorption capacity is: 40 mg/g. This is highest than many reported adsorbents.

Fig.-5: Dosage Vs Cr(VI) Removal

Initial Cr-concentration

0.1 g of SBCSAC was added to 100 ml of different Chromium (VI) concentrations ranging from 20 ppm to 100 ppm. The initial pH of these solutions was adjusted to 2. Then the solutions were equilibrated for 60 minutes at 300 rpm and at 303 K. The solutions were filtered. Residual Chromium (VI) was assessed. The results were plotted in Fig.-6.

With the raise in initial concentration, % removal is decreased; below 25 ppm : 100% ; 30 ppm: 90.0% ; 40 ppm : 73.0% ; 50 ppm : 61.0% ; 60 ppm: 51.0% ; 70 ppm : 40.0% ; 80 ppm: 35.0% and 90 ppm : 30.0%.

All these investigations were made using 0.1 g/100 ml of SBCSAC. So, for a fixed adsorbent, the active sites are fixed. When the concentration of Chromium (VI) is low, active sites available per molecule of Chromium(VI) are more. With the rise in concentration, many of the active sites are blocked or engaged and hence, the effective availability of free sites is less. So, the % removal is decreased with the enhancement in the Chromium (VI) concentration.

Interferences of Co-ions

The effect of fivefold excess of Co-ions on % removal is investigated and the results are presented in Fig.-7(a) and 7(b).

Fig.-6: Initial Concentration Vs % Cr(VI) Removal

Fig.-7a: Co- anions Interference

Fig.-7b: Co- cations Interference

Interference caused by generally co-existing ions in the water on the percentage removal of Chromium (VI) was assessed. For this, simulated solutions having fivefold excess of co-ions were prepared. They were treated with the 0.1 g/100 ml of SBCSAC at pH:2 for 60 minutes at 300 rpm and 303K. The solutions were filtered and the filtrate was estimated for residual Chromium (VI). The results were plotted in Fig 7 a and b. Nitrates, Bicarbonates and Chlorides show no interference. Phosphate and Sulphate interfere to a less extent. Co-cations investigated show marginal interference.

Regenerating and Reusing of SBCSAC

One of the important features to be assessed in using these bio-adsorbents is their reuse after regeneration. Regeneration is a treatment to be given to spent adsorbents to regain their adsorption ability. So spent SBCSAC was treated with various solutions of acids, bases and salts. A definite quantity of spent SBCSAC

was treated with these diverse solutions and agitated for one hour. Then the solutions were filtered. SBCSAC was washed repeatedly with distilled water until the washings were neutral to the litmus. Then SBCSAC was dried at 105°C, cooled and reused as adsorbent. It was found that the 0.1N NaOH solution was an effective solvent for regeneration. These regeneration steps are repeated. The number of recycles Vs % removal of Cr is plotted in Fig 8. Percentage of Cr-removal is found to be: 100 for first regeneration; 98.5 for a second; 97.8 for third; 92.1 for fourth; 89.5 for fifth; 70.1 for sixth and 60.0 for seventh. Hence, SBCSAC is retaining its capacity until the fourth regeneration with marginal loss.

Fig.-8: Regenerations Vs % Removal

Applications

SBCSAC was evaluated to control the Chromium pollution in effluents from industries. Samples were collected from various industries. For 100 ml of each sample, 0.1 g of SBCSAC was added. pH was adjusted to 2. The solution was agitated for 60 minutes at 300 rpm and 303 K. The solution was filtered and assayed for residual Chromium (VI) content. Experiments were repeated thrice. The average values were noted in Table-1.

Table-1: Chromium (VI) Removal from Industry Effluents Samples
(pH:2, SBCSAC : 0.1gm/100 mL, time: 60 min, rpm:300, temperature: 303 K)

Samples	Ci*	Ce*	% Removal
Tannery Industries			
1	8.5 ppm	Zero	100%
2	11.5 ppm	Zero	100%
3	15.0 ppm	Zero	100%
Chromate Plating Industries			
1	12.0 ppm	Zero	100%
2	14.0 ppm	Zero	100%
3	18.0 ppm	Zero	100%

Ci* and Ce* are initial and final concentration of Cr(VI);

The values are average of 3 samples: Standard Deviation: 0.05%

Comparative Study with the Previous Works

The Chromium-sorption capacity of SBCSAC is compared with the good bio-adsorbents reported. Table-2 is the comparison table. It may be concluded that SBCSAC has sorption capacity more than many reported. Further, SBCSAC is derived from a plant that is grown well in South East Asian Countries.

Table-2: Adsorption Capacities Comparison

S. No.	Adsorbent	pH	Ci. Of Cr(VI) (in ppm)	Adsorption Capacity for Cr (VI)	References
1	Barks Of <i>Ziziphus mauritiana</i> plant	2	20.0	18.8 mg/g	26

2	Active carbon derived from Lantana camara plant	2	50.0	26.25 mg/g	17
3	Saw dust of Coconut tree	3	20.0	3.6 mg/g	33
4	Leaves of <i>Salvadora persica</i> plant	2	50.0	16.2 mg/g (leaves) 22.9 mg/g (ashes)	29
5	Leaves of Caesalpinia bonduc plant	2	50.0	12.7 mg/g (leaves) and 19.6 mg/g (ash)	29
6	Spent coffee grounds		50.0	22.75 mg/g	3
7	Active carbon of Coconut shell	4	25.0	20.0 mg/g	34
8	Saw dust of beech tree	1	200.0	16.0 mg/g	36
9	bagasse of Sugar cane	2	500.0	13.4 mg/g	35
10.	Phoenix sylvestris seeds powder (PSSP)	2	20	22.5 mg/g	28
11.	Sulphuric acid generated bio-char from stems of <i>Averrhoa carambola</i> plant (SBCSAC)	2	25.0	40 mg/g	Present work

C_i = initial concentration of Chromium (VI)

CONCLUSION

- Stems of *Averrhoa carambola* plant are used as a precursor for generating bio-char.
- Sulphuric acid generated bio-char of stems of *Averrhoa carambola* plant (SBCSAC) is effective for the removal of Chromium (VI) from water.
- Complete removal of Chromium (VI) is observed in the pH range: 2 to 4 from 25 ppm Chromium (VI) solution. The optimum equilibration time is one hour and sorbent dosage is 0.1g/100 ml of SBCSAC. 300 rpm is used at room temperature of 303 K.
- The adsorption capacity of SBCSAC is 40 mg/g. It is higher than many sorbents reported.
- The interference of co-ions is marginal.
- Spent SBCSAC can be claimed back by treating with 0.1 N NaOH. Thus regenerated SBCSAC can be reused. Until four cycles of regenerations, only a marginal loss of adsorption capacity for Chromium (VI) is observed.
- SBCSAC is effectively applied to remove completely Chromium (VI) from samples collected from industrial effluents.

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