

Chemically Modified Banana Peel as a Potential Bioadsorbent to Remove Chromium (VI) from Effluent

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Abstract: Heavy metal contaminants are present in wastewater from almost every industry. Due to the higher treatment costs, small scale tannery industries, which are located in many parts of Ethiopia are one of the main contributors to the release of heavy metal contaminated wastewater into the environment without proper treatment. Hence, this study focuses on the removal of one of the such pollutants, hexavalent chromium (VI) by using chemically treated banana peel as a metal adsorbent. There were also studies on removal of Chromium (VI), Cr (VI) by modified banana peels. Banana peels were modified by the prescribed methodology and modified into perfect bio-absorbents. The stock solution (synthetic Cr (VI) solution) was treated by powdered bio-adsorbent at different dosage of adsorbent, 1g, 3g & 5g/50mL and at different pH environment, pH 2, pH 7 & pH 10.7 and at different contact times, 30 minutes, 60 minutes & 90 minutes. Treated samples were analyzed by UV-Visible spectrophotometer and respective concentrations of treated samples were determined. The most suitable conditions for the removal of Cr (VI) in this study are: pH 2 (90% removal, at 1g/50mL and 30 min), adsorbent dose 1 g/50 mL (94% removal, at pH 2.0 and 30 min), and contact time of 60 min. (93% removal, at 1 g/50mL and pH 2.0). Data produced in this study also checked with Langmuir isotherm and it followed model perfectly. Based on the studies and cheap availability of banana peels made them an efficient bio-adsorbent for Cr (VI) from effluent.

Keywords: Adsorbent dosage, Adsorption, Banana peels, Hexavalent chromium, Langmuir isotherm, pH

I. INTRODUCTION

Heavy metal contaminants present in effluent reach our bodies by tissue through food chain [1]. There are abundant sources of toxic metals such as Cd, Zn, Cr, Pb, and Cu from various industries [2]. Developing nations like Ethiopia, due to rapid industrialization, receiving huge amounts of toxic metal pollutants into environment. Some of the heavy metals act as essential metal ions required in key biochemical functions but in a very low concentrations ppb to less than 10 ppm [3], [4]. However, very small amounts of heavy metals are required for the vital biochemical reactions in the body against fatal impacts as a marginal increase in their concentrations [5, 6]. There are deaths reported by heavy metal contamination from the various parts of the world. Production of reactive oxygen species (ROS) and stress caused due to oxidation are the main culprits of the toxicity or carcinogenic effects [7], [8], [9].

Chromium occur in nature in various oxidation states from Cr (II) to Cr (VI) [10]. Cr (III) being the most stable oxidation state followed by Cr (VI) [9]. Oxidation state of chromium plays an important role in deciding the toxicity level, lowest being the metallic form and highest is the hexavalent form. Cr (VI) has been regarded as carcinogenic by several regulatory organizations including World Health Organization (WHO) [11], [12, [13]. As per the WHO, drinking water limit for Cr (VI) is 50 µg per liter [14]. Every year there are hundreds of thousands of people especially industrial workers are suffering of Cr (VI) toxicity [15]. Every year environment is receiving more than 30 tons of chromium contaminants [16]. As per United States of America's Occupational Safety and Health Administration (OSHA) the maximum permissible limit for Cr (VI) is $5\mu g/m^3$ for an 8-hr time-weighted average shift [17] and in normal residential areas it is from 1 to 100 ng/cm³ [18].

There are a number of Cr (VI) and other heavy metal removal techniques available in literature. However, there are intricacies in removal of heavy metals from environment and effluent as they are present in very minute quantities which is a challenging task. Most common technologies include precipitation, coagulation, complexation, adsorption by activated carbon, solvent extraction, ion exchange, electro-deposition, foam floating, cementation and membrane operations [19].

Construction of waste water treatment plant is an additional cost for any industry which do not give any direct profits to the organization and are considered as un-economical, and have disposal problems.



Bio-adsorption is a unit operation in which liquid (effluent) - solid (adsorbent) transfer process. These processes can be defined by adsorption and precipitation reactions. Adsorption by cheaply and readily available biomass is an efficient and most cost effective methods to treat effluent and wastewaters [20].

There are many low-cost adsorbents from various sources such as industrial by-products, modified polymers and biopolymers, agricultural wastes were developed and used successfully to remove heavy metal contamination from effluent. Though activated carbon removes organic contaminants effectively but it has limitations and expensive in removing inorganic pollutants like Cr (VI) [21].

Selective adsorption of Cr (VI) were carried out by various researchers: red-mud [22], photo-catalytic magnetic beads [23] inorganic nano-particle polymers [24] fertilizer industrial waste material [25], dried activated sludge biomass [26] and hydrous titanium oxide (HTO) [27].

Recent studies on agricultural waste materials such as rice husk, rice straw, activated carbon from coconut shells, fruit peels etc. have demonstrated the ability of these materials as potential bio-adsorbents for heavy metals present in effluent [20], [28].

In an effort to find a low cost environmentally friendly bioadsorbent to remove Cr (VI) from effluent, particularly from tannery waste, has landed us in using chemically modified banana peels comprising nearly 40% of the total weight of banana. This technique also helped in the solid waste management of banana peels in and around DebreZeit, Ethiopia [29], [30]. Bio-adsorbents derived from banana peels are efficient in removing Cr (VI) from effluent due to their large surface area, good mechanical properties and high swelling capacities.

II. EXPERIMENTAL

As the batch operation helps every process in separate and controlled manner, all the experiments were carried out in batch mode.

A. Biomass preparation

Fresh banana peels were collected from DebreZeit and its surrounding places, as it is easy for transport and available in huge amounts. The peels were then dried in shade for several hours. Hydrolysis of dried peels NaOH (10%) for three hours at temperature 105°C. Lignin and pectin were removed by washing and drying for 24 hours at 105 °C.

B. NaOH (10%) – Alkaline Hydrolysis

500 g of banana peels were hydrolyzed with 500 mL of NaOH (10%). This treatment was followed by washing with distilled water to make the biomass neutral. This process breaks polymeric chains into simple monomers to increase the surface area of the adsorbent.

C. Hydrolysis of banana peels by HCl (10%) - Acid hydrolysis

500 g of banana peels were hydrolyzed with 1500 mL of HCl (10%) while heating for three hours. This treatment was followed by washing with distilled water to make the biomass neutral. This process also breaks glycoside linkages of polymeric chains into simple monomers to increase the surface area of the adsorbent.

E. Chemically treated banana peels as bio-adsorbent for Cr (VI)

A test solution containing 1g/50 mL K₂Cr₂O₇ at a pH of 2.0 was used on chemically modified banana peels as bioadsorbent of an amount of 1g/50 mL in a 250 mL standard flask at normal temperature. The concentration of unabsorbed Cr (VI) was determined by UV-Visible spectrometer using 1 g of 1, 5-diphenylcarbazide in 100 mL acetone in a 0.2 N sulfuric acid. The process was carried at a wave length of 544 nm. Prior to this calibration of pH was done by using 2, 7, and 10.7 pH buffers.

0.1 g of $K_2Cr_2O_7$ was dissolved in 1000 mL of distilled water which make a standard stock solution of Cr (VI) of 100 mg/L. Working standard Cr (VI) concentrations of 62.5, 125, 187.5, 250, 375 and 500 µg were prepared from the stock solution. Dilute sulfuric acid is used to adjust the pH of all working solutions to approximately to 2.

Analytical procedure

The construction of the calibration curve is achieved by measuring the absorption of six standard solutions against blank using Cary-50 UV-VIS spectrophotometer. Briefly, standard solutions containing 2.5 to 20.0 μ g L⁻¹chromium (VI) were prepared as consequently 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 mL of chromium standard solutions which were pipetted out into 100 mL volumetric flasks. The solutions were diluted with approximately 40 mL of distilled water. Then to each flask, 2 mL of hydrochloric acid and 2 mL of the DPC indicator solutions were added and diluted to the corresponding volume. The reagents were mixed thoroughly by swirling and the flasks were mixed once again and left for 15 minutes to allow color development. The pH of the solutions was adjusted to 2. The absorbance of the solution was measured after 15 - 30 minutes. The absorbance of the colored solutions has a linear relationship to the chromium (VI) concentration and it is measured at wavelength 544 nm against the blank.

In order to check pH dependence, adsorbent dosage response and contact time response, experiments were carried out at pH-2.0, 7.0 and 10.7; adsorbent dosage-1, 3 and 5 g/50 mL; and response time- 30, 60 and 90 minutes.



pH dependence of adsorption

To study the effect of pH on adsorption capacity of the adsorbent, the study was carried at three different pH values - 2.0, 7.0 and 10.7. The respective values are presented in Table-1 and in Fig.1.

Table-1: Effect of	pH on adsorption	capability of adsorbent
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Table-1: Effect of pH on adsorption capability of adsorbent							
S. No.	pH of the medium	Original Conc. of Cr (VI) - μg/mL	Conc. of Cr (VI) after treatment - µg/mL	% Removal			
1	2.0	5.0	0.505	90			
2	7.0	5.0	0.589	88			
3	10.7	5.0	0.676	86			



Fig. 2: Cr (VI) removal by adsorbent removal at different pH values



There is a gradual decrease in adsorption capacity of adsorbent as pH increases from acidic to basic through neutral indicating acidic conditions are ideal for the adsorption. These results are also in good agreement with the previous researcher's results.

Adsorption metal ions such as Cr (VI) is highly dependent on the pH of medium [31]. It is the medium's pH which decides whether the metal is in ionic form and also the functional groups attached to it [32]. As reported by Fiol and Villaescusa [33], metal ions binding capacity to ligands either by chelation or hydrolysis is highly depends on the pH of the medium. But as pH increases chelation reduces and hydrolysis increases which results in reduced metal ion adsorption due to precipitation [34]. Similar study [35] also shows on copper precipitation as cupric hydroxide which drastically reduces copper adsorption. Same phenomenon happens when pH of the medium reduces beyond 2 as observed by Hossain et al. [32] on cupric ions adsorption by modified banana peels. The optimum pH, however, was observed between pH 2 and 6.

Adsorbent dosage response

To study the dosage of adsorbent response on Cr (VI) removal, three doses of adsorbent, 1, 3 and 5 g/50 mL were chosen. The results obtained are presented in Table-2 and depicted in Fig. 3.

	Table-2:	Dosage	response	of	adsorbent
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S. No.	Amount of adsorbent (g/50mL)	Original Conc. of Cr (VI) - μg/mL	Conc. of Cr (VI) after treatment - µg/mL	% Removal
1	1.0	5.0	0.275	94
2	3.0	5.0	0.490	90
3	5.0	5.0	0.525	89



Fig. 3: Effect of dosage of adsorbent on Cr (VI) removal

The results obtained were clearly revealing that as the dosage of adsorbent increased from 1 g/L to 5 g/L, the adsorption capability of the adsorbent gradually decreases to a slight extent, if not appreciable due to the decreased binding sites as partial aggregation of them increases [36]. Similar decrease in adsorption can also be observed when adsorbents dosage reduces due to reduced binding sites [37].

The studies clearly show that metal ion concentration plays an important role in the chemisorption by biomass. In a similar study it was observed that removal of Cr (III) by wheat straw increases as Cr (III) concentration increases [38]. Along with metal ion concentration, adsorbent concentration also plays important role in the adsorption process where adsorption capacity reduces even metal ion concentration increases when biomass amount is constant [32].

Contact time response

To check the contact time response towards removal capacity of the adsorbent three time intervals, 30, 60 and 90 minutes were selected and results were presented in Table-3 and Fig. 4.

Table-3: Contact time response towards removal of Cr (VI)

S. No.	Contact time of adsorbent (Minutes)	Original Conc. of Cr (VI) - µg/mL	Conc. of Cr (VI) after treatment - µg/mL	% Removal
1	30	5.0	0.508	90
2	60	5.0	0.370	93
3	90	5.0	0.448	91







Results clearly shows that as the contact time increases as time increase to 60 min form 30 min to 60 min. An increase in removal capacity to 93 % from 90% and decrease in removal capacity was observed as time increases beyond 60 min. Initially adsorption rate is quite high due maximum number of active binding sites available on biomass [31] and there was only a gradual increase from 90 to 93% in adsorption rate was observed due to decrease in available binding sites on biomass. The slight decrease in adsorption at higher time intervals may also be due to overcrowding which increases repulsive forces among the species exist [31], [39], [40].

Absorption model

Used the following models to study the interaction of Cr (VI) with the bio-adsorbent (banana peel).

Langmuir isotherm model

Where





Ce $\frac{mg}{L}$	0.505	0.589	0.676	0.275	0.490	0.525	0.508	0.370	0.448
Qe	44.95	44.11	43.24	47.25	45.1	44.75	44.92	46.3	45.52
$\frac{Ce}{Qe}$	0.0112	0.01335	0.0156	0.00582	0.01086	0.01173	0.0113	0.00799	0.00985



Fig. 5: Linear relations between final concentration and Qe

y = 0.024x - 0.001 equation of straight line whith slope 0.024



$$\frac{Ce}{Qe} = \frac{1}{QmaxK} + \frac{Ce}{Qmax} \text{ and } \frac{1}{Qmax} = 0.024$$
$$Qmax = \frac{1}{0.024} = 41.66$$
$$\frac{1}{QmaxK} = -0.001$$

Thus

 $K = \frac{1}{41.66 * (-0.001)} = -0.04166$ $RL = \frac{1}{1 + KCo} = \frac{1}{1 - 0.04166 * 0.144} = 1.006$

The absorption isotherm model equation is

$$\frac{Ce}{Qe} = \frac{1}{174.4K} + \frac{Ce}{174.4}$$

IV. CONCLUSION

Adsorption of toxic metal ions present in industrial effluent by chemically modified banana peel in this research work clearly shows that the biomass used is very effective. In the present study a synthetic Cr (VI) solution is used to replicate effluent and this contaminant is removed by using chemically treated and modified banana peel. Nine different samples have been treated with powdered banana peel adsorbent. Un-adsorbed Cr (VI) concentration was determined with help of UV-visible spectrometer. Chemically treated banana peels acted as a good adsorbent for the removal of Cr (VI) from synthetic Cr (VI) water. Optimum pH for Cr (VI) adsorption was found to be 2.0 (90% removal), adsorbent dose 1g/50mL (94 % removal) and contact time of 60 min. (93%). Hence it is concluded that the adsorption process is pH, dosage amount of Eng biomass and contact time dependent phenomenon. The heterogeneity of biomass surface was confirmed by perfect fitting of data in Langmuir isotherm.

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