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Leached compounds from the extracts of pomegranate peel, green coconut shell, and karuvelam wood for the removal of hexavalent chromium

https://doi.org/10.1515/gps-2018-0085
Received April 23, 2018; accepted August 2, 2018; previously published online September 27, 2018

Abstract: During biosorption, the biosorbent releases many organic compounds to the medium. In the present study, extracts of pomegranate peel (PP), green coconut shell (GCS), and karuvelam wood (KW) were prepared at three different conditions, namely 12 h, 3 h, and 3 h at pH 2, for the removal of hexavalent chromium [Cr(VI)]. The amount of organic compounds, mainly the leached organic compounds in the extract before and after treatment with Cr(VI) solution, was determined by chemical oxygen demand analysis. The total phenolic content, antioxidant activity, and total flavonoid content were used to estimate the chromium reduction potential of the extracts. The PP extract is the richest in all the three factors, followed by GCS and KW. The disappearance rate of Cr(VI) in the presence of PP extract reached 99.63% for the 50 mg/l concentration within 3 min, while it was 12% and 10% for GCS and KW, respectively, for the same concentration and time. Reaction mechanisms were formulated with the help of Fourier transform infrared spectroscopy to confirm the role of leached compounds from natural materials for the removal of heavy metal.

Keywords: antioxidant activity; biosorption; chromium reduction potential; total flavonoid content; total phenolic content.

Abbreviations

COD	chemical oxygen demand
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
DDW	double-distilled water
DPPH	2,2-diphenyl-1-picrylhydrazyl
GAE	gallic acid equivalent
GCS	green coconut shell
KW	karuvelam wood
PP	pomegranate peel
TPC	total phenolic content
TFC	total flavonoid content

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1 Introduction

The emission of toxic heavy metals to the biosphere increases due to rapid industrialization and urbanization, producing adverse effects on the ecosystem [1]. Pollution caused by heavy metals like chromium, arsenic, lead, etc., is one of the most significant issues faced by environmentalists [2]. Chromium is a widely used heavy metal in tanneries, electrochemical industries, and other chemical industries. In nature, chromium mainly exists in two oxidation states: hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] [3]. Cr(VI) causes many health issues, such as breathing problems, allergy, cancer, etc. [3, 4]. As per the guidelines of the World Health Organization and the Central Pollution Control Board of India, the total chromium content of drinking water is restricted to 0.05 mg/l [5–8]. Thus, the removal of Cr(VI) is highly essential to overcome the toxic effects.

With respect to the variations in pH of the medium, the ionic forms of chromium also differ. Cr(III) on hydrolysis results in compounds like neutral species $Cr(OH)_3^0$, mononuclear species $Cr(OH)_2^+$, $CrOH^{2+}$, $Cr(OH)_4^-$, polynuclear species $Cr_3(OH)_4^{5+}$, and $Cr_2(OH)_2$. Hydrolysis of Cr(VI) at low pH and higher concentration produces $Cr_2O_7^{2-}$ and CrO_4^{2-} at pH >6.5 [3]. The redox potential-pH and speciation diagrams show that Cr(VI) exists primarily as a salt of chromic acid (H_2CrO_4) at pH <1, hydrogen chromate ion ($HCrO_4^-$) at pH between 1 and 6, and chromate ion (CrO_4^{2-}) at pH >6 [4].

In recent times, the research community is searching for cheap and eco-friendly technology for heavy metal removal, and it has been found that biosorption is a better option. Biosorption is a sorption process where naturally occurring living and non-living things act as a biosorbent. During biosorption, many colored organic compounds are released into the medium. The literature reports that these released compounds have significant roles in the removal of heavy metals. The amount of released pigments during biosorption

can be quantified in terms of chemical oxygen demand (COD) representing the Cr(VI) reduction potential [9, 10]. Various plant parts are natural materials releasing compounds such as flavonoids, polyphenols, terpenoids, aldehydes, ketones, carboxylic acids, ether groups, and tannins, which have the ability to chelate metal catalysts [11–13].

Aquatic weeds [10], palm flower [9], rice husk [14], lemon shell [15], mangosteen peel [16], and many other biomaterials have been experimented on for the removal of chromium. In the present study, the Cr(VI) removal efficiency of the released compounds from pomegranate peel (PP), green coconut shell (GCS), and karuvelam wood (KW) were estimated based on COD, total phenolic content (TPC), antioxidant activity, and total flavonoid content (TFC). A review of the literature indicates that chromium removal based on the aforementioned properties has not yet been reported previously.

2 Materials and methods

2.1 Plant materials

The three biomaterials chosen for the preparation of extracts were peel of *Punica granatum* L. (pomegranate), shell of *Cocos nucifera* (coconut), and wood of *Prosopis juliflora* (karuvelam), which are all cheaply and abundantly available in the southern part of India. The main selection criterion for their choice was effective waste utilization. Raw materials for extract preparation were collected from the National Institute of Technology, Tiruchirappalli Campus. The biomaterials were initially washed with tap water to remove dust and dirt, and then washed three times with double-distilled water (DDW). Subsequently, they were dried under the sun for 3 days and in an oven for 24 h at 318 K. All the dried materials were powdered and sieved, and a particle size of 125 μm was chosen.

2.2 Chemicals

Potassium dichromate, sodium nitrite, sodium nitrate, sodium hydroxide, aluminum chloride, ferric chloride, 1,5-diphenylcarbazide, hydrochloric acid, sulfuric acid, a sodium carbonate and COD solution A and B of Spectroquant were purchased from Merck (Mumbai, Maharashtra, India). 2,2-Diphenyl-1-picrylhydrazyl (DPPH) (Sigma Aldrich CHEMIE, GmbH, Steinheim, Germany), gallic acid, and Folin-Ciocalteu reagent were procured from Nice Chemicals, Pvt. Ltd. (Cochin, Kerala, India). All the chemicals used were of analytical grade.

2.3 Extract preparation

Extracts were prepared for each material (PP, GCS, and KW) at three different conditions: (i) 12 h soaking – soaking of material for 12 h in DDW for maximum extraction of water-soluble compounds from the biosorbent for maximum Cr(VI) removal, (ii) 3 h soaking – soaking of material in DDW for 3 h, and (iii) 3 h soaking of material in DDW at a pH of 2 (adjusted using HCl). The conditions were selected based on preliminary studies, as pH 2 displayed better reduction of chromium for a given specified time than other pH values. For all the three extraction conditions and biomaterials, 1 g of sample was soaked in Erlenmeyer flasks containing 100 ml DDW and placed in an orbital shaker at 150 rpm at 303 K. After soaking, the extract was vacuum filtered and stored at 4°C.

2.4 Characterization of extracts

2.4.1 COD analysis: The amount of water-soluble compounds released during biosorption and the compounds that remained in solution after interaction with Cr(VI) solution were measured by COD analysis using a closed reflux method as per American Public Health Association [17].

For COD analysis, 2.2 ml of COD solution A and 1.8 ml of COD solution B were added to 1 ml distilled water in sample bottles and digested at 150°C for 120 min. Samples were cooled to room temperature and analyzed in Spectroquant colorimeter. The same procedure was repeated with extracts instead of distilled water. All the experiments were done in triplicate.

2.4.2 TPC: In the test to ascertain the presence of TPC as per Madaan et al. [18], 1 ml $FeCl_3$ was added to 1 ml extract. A dark blue color developed with the PP extract and a lighter blue color in the GCS and KW extracts, which indicated the presence of phenolic content. Quantitative determination of TPC before and after biosorption of Cr(VI) was determined and expressed as gallic acid equivalents (mg/g) [18]. Gallic acid stock solution was prepared by dissolving 5 mg gallic acid in 10 ml ethanol, and then made to 100 ml with DDW. For preparing a calibration curve, solutions of various concentrations of gallic acid were prepared from the stock solution. Aliquots (1 ml) of each dilution were then added with 10 ml DDW and 1.5 ml Folin-Ciocalteu reagent. The solution was mixed well and incubated for 5 min at room temperature. A 4 ml volume of 20% Na_2CO_3 (w/w) was added to each test tube, and it was made to 25 ml with DDW. This mixture was agitated and left aside for 30 min. The absorbance was determined at a wavelength of 765 nm. The calibration curve was plotted using absorbance against gallic acid concentration. Gallic acid was replaced with the sample extract for finding the TPC present in the extract. TPC was then calculated from Eq. (1), as given in the literature [19]. All experiments were done in triplicate.

$$\mathrm{TPC} = \mathrm{GAE} \times V \times \frac{D}{m} \tag{1}$$

where GAE is the gallic acid equivalent (mg/l), V is the volume of extract (l), D is dilution factor, and m is the weight (g) of the plant extract.

2.4.3 Antioxidant activity: Colorimetry using DPPH was followed for the determination of antioxidant activity or percentage inhibition, as it is reported as a fast, easy, and reliable method [20]. DPPH is a stable synthetic radical that can easily accept H^+ ions from the phenolic compounds present in the extract by the following reaction:

$$\mathrm{DPPH}^* + \mathrm{A\text{-}H} \rightarrow \mathrm{DPPH\text{-}H} + \mathrm{A}^*. \tag{2}$$

For this, 0.02 g DPPH was dissolved in 50 ml ethanol to produce a solution of a concentration of 0.4 mg/ml. A volume of 5 ml of each extract (1 mg/ml) was added to 1 ml DPPH and made to 10 ml with

ethanol. Absorbance was measured at 517 nm. Antioxidant activity was calculated using Eq. (3), as given by Kalita et al. [21] and Sahu and Saxena [22]. All the experiments were done in triplicate.

$$\text{Percentage inhibition} = \left(1 - \frac{\text{Absorbance of test}}{\text{Absorbance of control}}\right) * 100. \quad (3)$$

2.4.4 TFC: The presence of TFC in the extract was identified as described by the American Public Health Association [17] and Madaan et al. [18]. A few drops of dilute NaOH (0.1 M) was added to 1 ml extract, which was initially yellow in color and then the color disappeared upon adding dilute HCl (0.1 M). This confirmed the presence of flavonoids. The TFC was estimated using the aluminum chloride method, and the results were expressed as quercetin equivalents [22, 23]. For plotting the calibration curve, various concentrations of standard quercetin solutions were prepared from the stock solution of 100 mg/l by serial dilution. A 1 ml volume of the standard solution was taken in a test tube containing 4 ml DDW, and to this 0.3 ml of 5% $NaNO_2$ was added. After 5 min, 0.3 ml of 10% Al_2Cl_3 was added to the mixture. After 6 min, 2 ml of 1 M NaOH was added and it was made up to 10 ml with DDW. The procedure was repeated with the extracts instead of standard quercetin for estimating the TFC in the extract. Absorbance was measured at 475 nm. All the experiments were done in triplicate.

2.4.5 Quantification of Cr(VI): The 1,5-diphenyl carbazide method was used for evaluating Cr(VI). Absorbance was measured at 540 nm using a Shimadzu ultraviolet-visible spectrophotometer. For this analysis, a stock solution of concentration 1000 mg/l was prepared by dissolving the required quantity of potassium dichromate in DDW. Cr(VI) solution (50 mg/l) was prepared by serial dilution of the stock solution. A 100 ml volume of each of these solutions was taken in three separate 250 ml Erlenmeyer flasks. The pH of the solution was adjusted to 2. A 10 ml volume of each extract prepared at three different conditions (12 h, 3 h, and 3 h at pH 2) was added. It was kept in the incubator shaker for 3 h for attaining equilibrium at 303 K. For the kinetic study of Cr(VI) removal, samples were drawn at different time intervals. All experiments were done in triplicate.

The Cr(VI) quantification was also confirmed with the total chromium results in atomic absorption spectroscopy (AAS) to account for any Cr(III) present.

2.4.6 Fourier transform infrared spectroscopy (FTIR) analysis of extracts: The FTIR spectra of the extracts prepared at different conditions were taken. Differences in peak intensity and disappearance of various peaks were observed with extracts before and after treatment with Cr(VI) solution.

3 Results and discussion

Performance evaluation of the extracts prepared from PP, GCS, and KW for the removal of Cr(VI) is presented on the basis of COD, TPC, TFC, and antioxidant activity. Initial investigations showed the effect of pH in the process along with time influencing the potential of the three extracts in the study. The extraction conditions were 12 h, 3 h, and 3 h at pH 2 for performance assessment of all the three extracts. The contents of the natural materials (PP, GCS, and KW) were found to be responsible for the efficient removal of the metal. The main functional groups were from polyphenolic compounds, flavonoids, carboxylic acids, and other contents, which could account for the possible reaction mechanisms with Cr(VI), with FTIR analysis supporting the findings.

3.1 COD analysis

COD analysis was performed to quantify the organic compounds released into the medium. The presence of various types of leached compounds have been reported earlier, as polyphenols, condensed tannins, hydrolyzable tannins, and gallotannins in PP extract [13, 23, 24]; phenolic compounds in GCS [25]; and alkaloids, flavonoids, and tannins in KW [26].

The organic compounds extracted from PP, GCS, and KW were calculated in terms of COD. The higher amount of initial COD value is an indication of the amount of reducing compounds present in the extract. The COD values estimated before and after treatment of extract with 50 mg/l Cr(VI) solution are listed in Table 1. The difference in COD values show the amount of reduction or amount of proton (H^+) transferred during biosorption. In the reduction process, the PP extract had the higher initial COD values of 4580, 4620, and 5830 for the extracts obtained after 12 h, 3 h, and 3 h at pH 2, respectively, due to higher organic contents. About $90 \pm 2\%$ COD reduction was achieved in all the three conditions by the PP extract, exhibiting the highest reduction compared with the other two extracts. The initial COD value of the GCS extract was higher than that of the KW extract; however, the reduction observed was much less in GCS than in KW. In KW, about 84–86% of COD reduction was obtained for the initial COD values of 2220 and 1850 for the extracts obtained after 12 and 3 h of extraction time, respectively, demonstrating lesser chromium reduction owing to a reduced amount of organics released from it. This indicates that the compounds leached from GCS were more stable as the leachate contains phenolic compounds with fewer multiple hydroxyl groups. Mathew et al. had inferred the higher reduction potential of phenolic compounds with multiple hydroxyl groups [27]. It was noticed that 3 h at pH 2 is the most favorable condition for the extraction of organic compounds from raw materials. Hence, the pH of the solution plays a more important role than contact time for leaching organic compounds from all extracts.

Table 1: Change in COD before and after adsorption of Cr(VI) from 50 mg/l solution.

Condition for extraction	PP			GCS			KW		
	Initial COD (mg/l)	Final COD (mg/l)	% Reduction of COD	Initial COD (mg/l)	Final COD (mg/l)	% Reduction of COD	Initial COD (mg/l)	Final COD (mg/l)	% Reduction of COD
12 h	4580	390	91.5	2670	1770	33.7	2220	320	85.6
3 h	4620	520	88.7	2680	1290	51.9	1850	300	83.78
3 h at pH 2	5830	630	89.2	2810	2380	15.3	3620	310	91.4

3.2 TPC

The color intensity during the initial experiments depicted the presence of large amounts of TPC in PP extract compared to the other two extracts. After mixing with Cr(VI) solution, the intensity of color was reduced for PP and no color change was observed in the case of GCS and KW extracts due to the complete utilization of phenolic compounds from GCS and KW. The calibration curve for gallic acid given in Figure 1 was used for calculating TPC. Table 2 gives the amount of TPC present in the extracts before and after the removal of Cr(VI) from a 50 mg/l solution. Although the initial TPC of PP extract is higher, a significant drop in TPC was seen. However, with GCS and KW, the initial TPC was less, and after the removal of chromium, no TPC was observed in them for all the conditions.

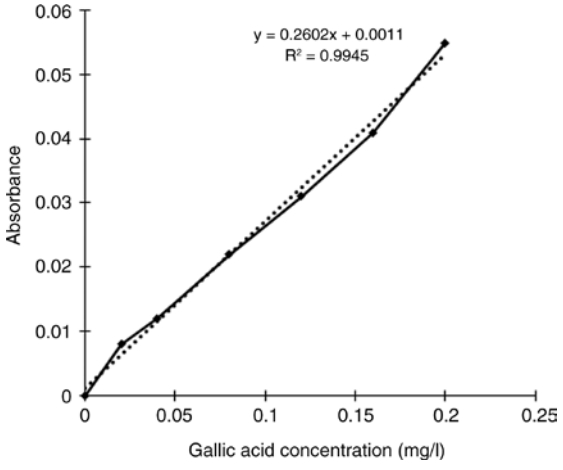

Figure 1: Calibration curve for gallic acid.

3.3 Antioxidant activity

The antioxidant activity of plant extracts is mainly due to the presence of phenolic and polyphenolic compounds in them. This is an indirect measurement of their free radical scavenging activity, which depends on the ability of the compounds to lose hydrogen [20]. It also helps in understanding the main structure, the structure of the side chains, and the substitutions on aromatic rings [28]. The radical scavenging potential is determined by the number and position of the hydroxyl group and the methoxy group in the phenolic ring [27]. The majority of naturally occurring antioxidants are in the form of phenolic and flavonoid structures, which mostly account for properties like dismutation of radicals and chelate formation [13].

The PP extract showed the highest antioxidant activity, 68.5% more than GCS and 74.57% more than KW. The antioxidant activity of the PP extract, presented in Figure 2, is almost equal in all the three extraction conditions. The intense color change from deep purple to yellow observed while adding DPPH to the PP extract means that its proton-releasing ability is very high for free radicals [29]. One of the reasons for the highest antioxidant activity of PP extract was the presence of polyphenols with highly reactive multiple hydroxyl groups [25, 29]. As far as

Table 2: Change in TPC before and after adsorption of Cr(VI) from 50 mg/l solution.

Condition for extraction	PP			GCS			KW		
	Initial TPC	Final TPC	% Change in TPC	Initial TPC	Final TPC	% Change in TPC	Initial TPC	Final TPC	% Change in TPC
12 h	134.42	17.20	87.21	15.28	0.00	100.00	7.59	0.00	100.00
3 h	150.75	12.39	91.78	11.43	0.00	100.00	4.71	0.00	100.00
3 h and pH 2	140.18	10.47	92.53	12.39	0.00	100.00	3.75	0.00	100.00

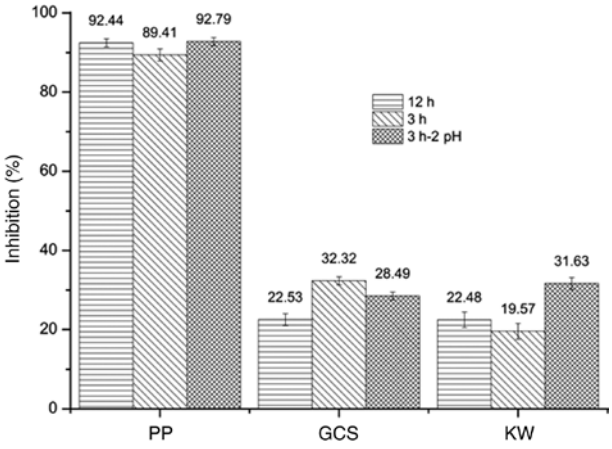

Figure 2: Percentage inhibition or antioxidant activity of extracts at different extraction conditions.

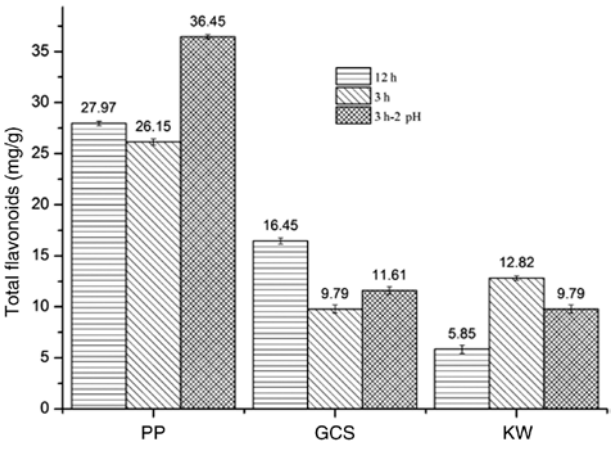

Figure 4: TFC in PP, GCS, and KW extracts for 12 h, 3 h, and 3 h at pH 2 extraction.

the extracts of GCS and KW are concerned, the antioxidant activity is nearly the same, as the amount of organic compounds released was very low and have been consumed completely.

3.4 TFC

Quercetin, a higher electron donor among the investigated flavonoids, was used in the quantification of TFC in the extracts. Moreover, the presence of quercetin has been already reported in the contents of PP extract [13].

Figure 3 shows the quercetin calibration curve for the TFC, and the variation in the level of flavonoids is shown in Figure 4. Figure 4 indicates that the TFC is higher in PP compared to the other two extracts. It is evident that the TFC of the extracts are lesser than the TPC but still present a higher level in PP compared to GCS and KW.

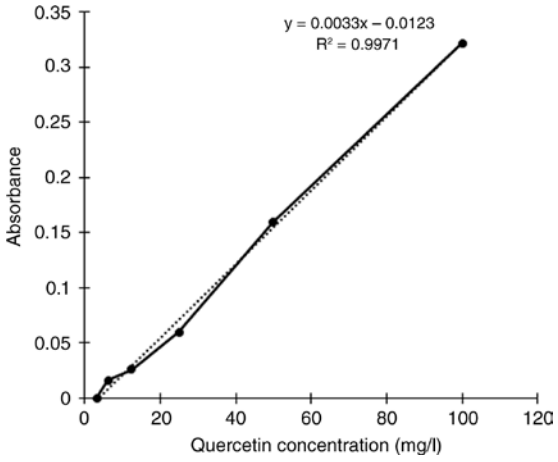

Figure 3: Quercetin calibration curve for flavonoid quantification.

3.5 Cr(VI) removal

For all extracts, the maximum removal of Cr(VI) with 50 mg/l occurred for the 12 h extract compared to the removal with the 3 h and 3 h at pH 2 extracts. The Cr(VI) disappearance reached 100% within 6 min for the PP extract; however, in the case of the other two, the maximum removal was <25% after 3 h. In the case of the GCS extract after 120 min, the removal became almost saturated to about 20% for the 12 h extract and to about 10% for the 3 h and 3 h at pH 2 extracts. The removal efficiency with the KW extract started decreasing after 120 min for the 12 h condition and after 60 min for the other two conditions. PP maintained its efficiency at >90% from the third minute onwards for all the three extracts. GCS acquired equilibrium but KW did not stabilize even after 3 h due to redox reactions. Figure 5A–C confirm the percentage removal of Cr(VI) using the PP, GCS, and KW extracts at 303 K and pH 2 for 50 mg/l chromium solution.

Cr(VI) removal studies at 20 and 100 mg/l concentrations were also performed for the PP extract, which show its high removal efficiency. It was observed that for 20 mg/l Cr(VI) solution, 100% removal was attained at the third minute for all three conditions (12 h, 3 h, and 3 h at pH 2). For 100 mg/l, at equilibrium, the removal rate was 99.80%, 98.78%, and 96.33% for 12 h, 3 h, and 3 h at pH 2, respectively. The difference between total chromium (from AAS) and Cr(VI) reflected the negligible presence of Cr(III) due to shift reactions in all three extracts.

In Figure 6, showing the FTIR spectra of all extracts, peaks were observed in the area of wavenumber ranging between 1500 and 400 cm^{-1}, representing the presence of carboxylic acids, aromatics, alkyl halides, and amides. The disappearance of all these groups and the increase in

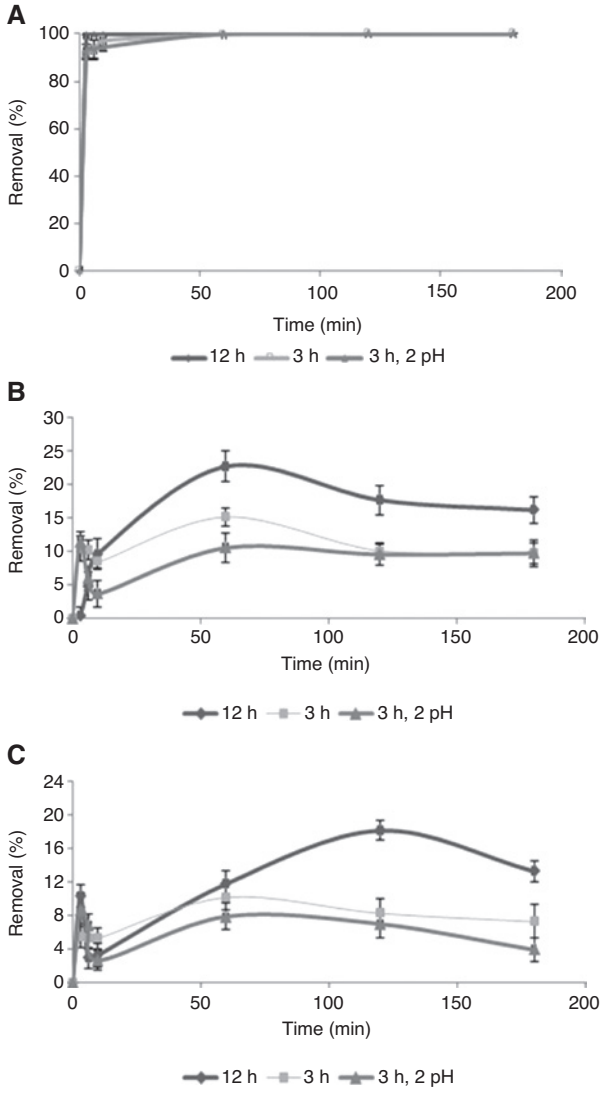

Figure 5: Percentage removal of Cr(VI) using (A) PP, (B) GCS, and (C) KW extracts at 303 K and pH 2.

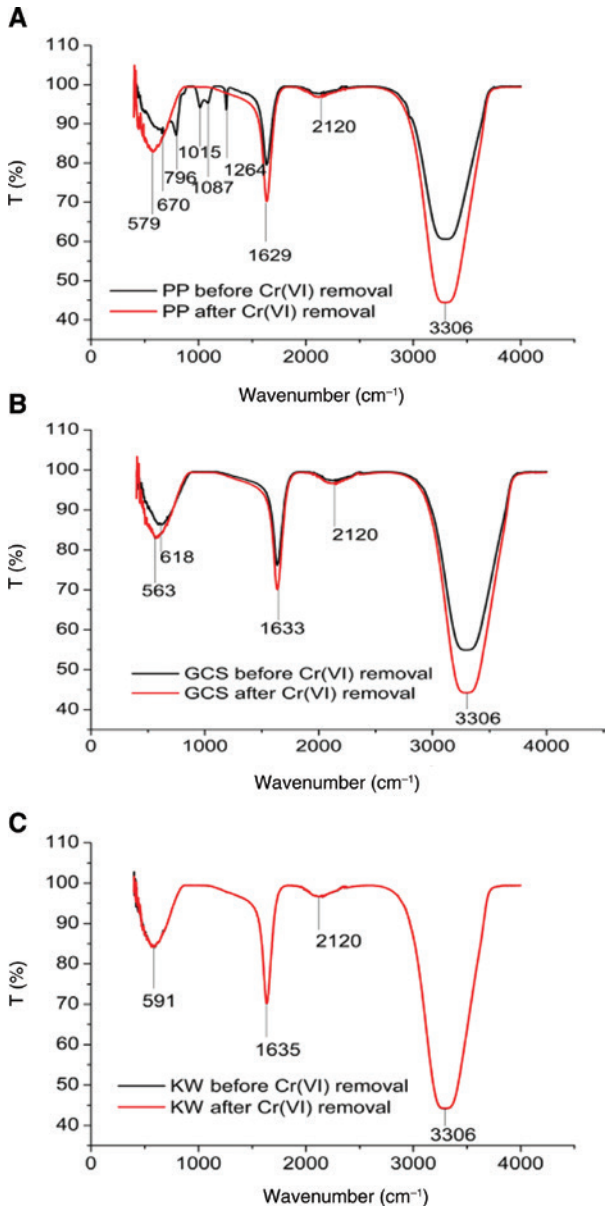

Figure 6: FTIR spectrum of (A) PP, (B) GCS, and (C) KW before and after treatment with Cr(VI) at 303 K and pH 2.

the intensity of peaks at wavenumbers 1629 and 3306 cm^{-1} showed the major role of these compounds in the removal of Cr(VI). Also, these results with the three extracts, in general, gave a clear depiction of the role of functional groups deriving the possible reaction mechanisms.

Cr(VI) on hydrolysis gives CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$ [3, 10]. The chromate anions react with the organic matter present in the peel extracts to produce Cr(III) as per the following reduction mechanism:

$$HCrO_4^- + \text{organic matter} + H^+ \rightarrow Cr^{3+} + H_2O. \quad (4)$$

Moreover, on further oxidation,

$$HCrO_4^- + \text{organic matter} + H^+ \rightarrow CrO_4^{2-} + CO_2. \quad (5)$$

The expected mechanisms due to the presence of phenolic and carboxylic groups are as follows:

$$\cdots COOH + M^{n+} \rightarrow \cdots COOM^{(n-1)+} + H^+, \quad (6)$$

$$\cdots C_6H_5 \cdots OH + M^{n+} \rightarrow \cdots C_6H_5 \cdots OM^{(n-1)+} + H^+, \quad (7)$$

$$\cdots COOH + M(OH)^{(n-1)+} \rightarrow \cdots COOM(OH)^{(n-2)+} + H^+, \quad (8)$$

$$\cdots C_6H_5\text{-}OH + M(OH)^{(n-1)+} \rightarrow \cdots C_6H_5 \cdots OM(OH)^{(n-2)+} + H^+, \quad (9)$$

where M is the metal ion.

From the experimentation, it was confirmed that the higher the antioxidant activity, phenolic content, and flavonoid content, the better is the removal of Cr(VI). Metal chelation reaction occurred due to the presence of a high amount of polyphenolic compounds. Phenolic compounds with three hydroxyl radicals release protons easily to form metal chelates. This chelation should have been the reason for not showing the peak at 540 nm in the ultraviolet spectrophotometer. The experimental results also complemented the reaction mechanism that the pigments released during biosorption have a major role in the removal of Cr(VI).

4 Conclusion

Organic compounds released during the biosorption of Cr(VI) using PP, GCS, and KW extracts were quantified using COD analysis. After treatment with 50 mg/l Cr(VI) solution, these extracts showed a heavy reduction of COD in PP compared to KW and GCS. TPC, antioxidant activity, and TFC were observed to be in the order of PP > GCS > KW, crediting the PP extract for better removal of the metal ion. A 100% removal of Cr(VI) solution with 20 and 50 mg/l and a >96% removal with 100 mg/l were attained with the PP extract. Metal chelation reaction occurred during the interaction between extract and chromium solution, which might be the reason for the non-detection of metal ion present in the medium. The higher efficiency of the PP extract establishes that it is a good, sustainable, eco-friendly solution for the removal of Cr(VI) from aqueous medium compared to GCS and KW.

Acknowledgments: The authors thank the director of NIT, Tiruchirappalli; Dr. S. Velmathi, Department of Chemistry, NIT, Tiruchirappalli; and head of Chemical Engineering Department and research scholars of the Chemical Engineering Department, NIT, Tiruchirappalli, especially Navamani Kartic D, Tamilmani J, Indulekha John, Bhuvaneswari G, and Selvakumar P for extending all facilities and support in completing this work.

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