Biosorption of Cr (III) from Aqueous Solution Using Banana Peel Powder

Renieidy F. C. Dias, Regina Felisberto, Adriana F. Ramos, Roberto R. Faria, Francisco M. F. Dias & Derli R. C. Dantzger

O uso de cascas de banana moídas foi avaliado como biossorvente para a remoção de resíduos de Cr (III) em efluentes aquosos. O efluente aquoso utilizado foi gerado em aulas experimentais de química analítica quantitativa no Instituto Federal do Rio Grande do Sul (IFRS). Técnicas alternativas foram empregadas no presente trabalho, os ensaios combinaram duas metodologias para o tratamento deste resíduo. O primeiro explora a capacidade de cascas de banana como biossorvente na remoção de Cr (III), enquanto o segundo emprega a complexação de Cr (III) usando EDTA, sob irradiação de microondas, para fins de quantificação. A remoção máxima de 60% do conteúdo de Cr (III) foi alcançada em 40 minutos de tratamento, em escala de batelada.

Palavras-chave: *casca de banana; remoção de íons cr (III); irradiação por micro-ondas.*

The use of milled banana peels was evaluated such as biosorbent for the removal of Cr(III) residues in aqueous effluents. The aqueous effluent used was generated in experimental classes of quantitative analytical chemistry at the Federal Institute of Rio Grande do Sul (IFRS). Alternative techniques were employed in the present work, the assays combined two methodologies for the treatment of this residue. The first, explores the capability of banana peels as biosorbent in the removal of Cr(III), while the second employs the complexation of Cr(III) using EDTA, under microwave irradiation, for quantification purposes. A maximum removal of 60% of the content of Cr(III) was reached in 40 minutes of treatment, in batch scale.

Keywords: *banana peel; removal of cr (III) ions; microwave irradiation.*

Introdution

Heavy metals pollution is of great concern due to the severe consequences it imposes to human health and to the environment integrity.[1] Industrial effluents from many industrial processes contain toxic metals such as chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), lead (Pb), among others. Once accumulated in the human body, such metals cause irreparable damage to organisms due to their non-biodegradable nature.[2] Chromium exists in trivalent and hexavalent forms in aqueous systems, but the hexavalent form is mutagenic and carcinogenic to animals and humans. When the contamination by such metal goes over safe limits, it becomes an environmental problem.[3] The permissible concentration of hexavalent chromium according to CONAMA's resolution Nº.397/2008 in effluents must be at most 0.1 mg L^{-1}, and the maximum amount of allowed trivalent chromium is 1.0 mg L^{-1} Therefore, there is a large number of strategies investigated for removal of heavy metals from wastewaters (Table 1). [4]

According to (FAO, 2004) banana is the fourth most important fruit for consumption in the world. The banana peel, which constitutes 30–40% of the fruit, can be used for diverse purposes such as biomethane production, 6in animal food additives, and also as adsorbent for removal of metals (Fig.1). However, a good biosorbent material should meet several requirements like high adsorption capacity, high selectivity, low cost, easy desorption, and regeneration. [5-7]

Table 1. Commom methods to remove heavy metals from wastewater

Methods	Advantages	Disadvantages
Chemical Precipitation	Easy operation, Inexpensive	Large amounts of sludge Extra operational cost for sludge disposal
Chemical coagulation	Sludge settling, dewatering	Costly, High consumption of chemicals
Ion-exchange	Selective for metal ions, regeneration of materials	Costly, number of metal ions removed is lower
Electrochemical methods	Selective for metal ions, No consumption of chemicals	High capital and running cost, current density
Photo catalysis	Removal of metals and organic pollutant, simultaneously, less harmful by-products	Long duration time, limited applications
Adsorption using activated carbon	High efficiency (>99%)	Costly, no regeneration, Performance depends upon adsorbent
Membrane filtration	Low space requirement, low pressure, high separation selectivity	High operation cost

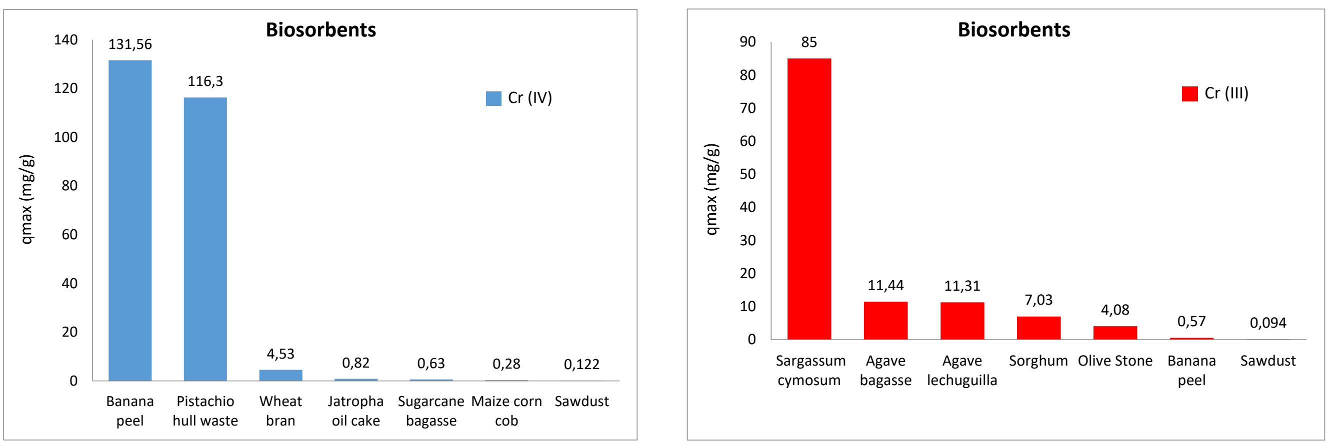

Figure 1. Various adsorbents used for removal of Cr(III) and Cr(VI)

Fig. 1 lists several of the studies carried out to quantify adsorption capacity. Some of these work pieces in the literature emphasize only the effectiveness of removal of metal ions by biosorbents, while others highlight the adsorption capacity of biosorbent materials for heavy metal ions. For instance, (Memon, Bhanger and Khuhawar, 2005) reported that sawdust from *Cedrus deodera* removed more than 99% of chromium ions from 100 mL environmental and industrial water samples, but the reported maximum adsorption capacity of Cr (VI) and Cr (III) are 0.122 mg g^{-1} and 0.094 mg g^{-1}, respectively, which is insignificant.[14] Also, a report by (Sumathi, Mahimairaja and Naidu, 2005) shows that sawdust from *Teclona grandis Linn. f* exhibited a higher adsorption capacity (1.5 mg g^{-1}) for adsorbing Cr (VI). This means that different species of sawdust may influence the adsorption capacity.[19]

Another important result is reported by Souza et *al.* 2016 — besides showing highly adsorption capacity (85 mg g^{-1}), it can also reduce metals, which is a great advantage because no reduction reagent is necessary.[9] Although their sorption capacity is usually significant, banana peels exhibited higher capacity than sargassum cymosum, and this is an interesting evidence to study.[17] Furthermore, different factors affecting biosorption such as temperature, pH, sorbent particle size, biosorbent dose, contact time, concentration, ionic strength, among others, influence the sorption process. [20-21].

The aim of the present work is to fix some parameters, as in the methodology described in reference (20), not to perform batch sorption tests on different conditions (pH, biosorbent dose or contact time). We used banana peels for adsorbing trivalent chromium in argentometric residue because its biomass is plentiful, easily obtained, and there is a broad interest in their use due to their sorption capabilities.

Materials and Methods

EQUIPMENT AND APPARATUS

A Walita Food Processor was used for the first trituration of the samples. A Herzog disk mill was used for reducing the particles size. A Gehaka Model 380G UV-Visible spectrophotometer was used in the quantifications). A microwave oven model Consul 700W was used in the formation of the chromium-EDTA complex under microwave irradiation. A Drying oven (Model SL 100/40, Solab) was used to dry the banana peels. A medium porosity filter paper (C40 Unifil) was used in the filtrations

REAGENTS

All reagents were of analytical grade and obtained from Synth PA (sodium acetate hydrate, glacial acetic acid, L-ascorbic acid, ethylenediaminetetracetic acid disodium salt and potassium chromate). All laboratory glassware were previously washed in a HNO_3 solution (30% m/m) for decontamination.

ADSORBENT PREPARATION

Samples of banana peel were collected from the daily consumption of the fruit. The powder used as biosorbent was obtained from the banana peels oven-dried at 44 (± 2) °C for 48 hours. The dryed peels were then milled in a food processor and stored in a desiccator until the second milling, using an oscillating disk mill, was performed. Residual moisture in the milled material was removed by oven-drying the fine powder.

Fig. 2 shows the different stages of the preparation of the powder from the banana peels.

ADSORPTION EXPERIMENTS

Batch experiments of biosorption were performed at constant temperature 25.5 (± 2.1)°C in beaker flaks. In all sets of experiments, it was added 30.00 (± 0.05) mL of the argentometric Cr(VI) residue, 2 mL of an ascorbic acid solution (0.6 mol L^{-1}) , and 1.26 g of the banana peel powder. The mixture was stirred for 40 minutes. After shaking the flasks, the solids filtered by simple filtration. The filtrates (CR solution) were analyzed by an UV-Vis spectrophotometer, for determinate the concentration of chromium (III) species, using methodology (22).

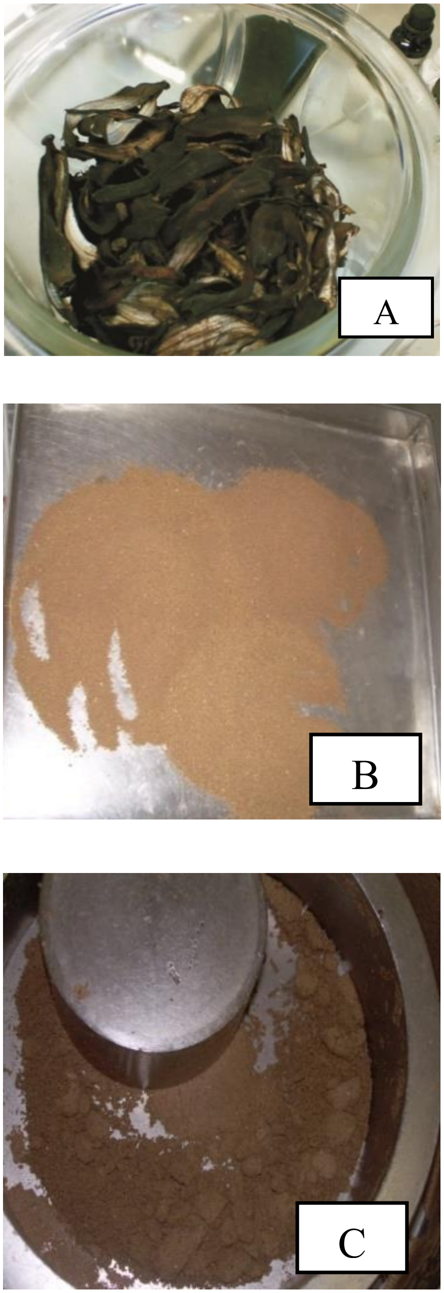

Figure 2. Dehydrated banana peels before the first milling (a); Dehydrated banana peels after first milling in a food processor (b); Dehydrated banana peels after second milling in an oscillating disk mill (c)

STANDARDS, STOCK SOLUTIONS AND DETERMINATION OF CR(III) CALIBRATION CURVE

A stock solution containing 1000 mg L^{-1} of Cr(VI) was prepared using potassium chromate. In order to prepare the calibration curve, aliquots of the stock solution were transferred to 250 mL erlenmeyers flaks, using volumetric pipettes, in order to prepare solutions at different concentrations (10 to 150 mg L^{-1}) of Cr (VI). Additionally, were added 2 mL ascorbic acid (0.6 mol L^{-1}), 5 mL acetate buffer (acetic acid/sodium acetate/1 mol L^{-1}; pH = 4.75) and 20 mL EDTA (0.1 mol L^{-1}) to erlenmeyers. Also, after filtration, CR solution was placed in a 250 mL erlenmmeyer and treated with the same reagents which stock solutions.

All the erlenmeyers was then capped with a short stem glass funnel, to avoid the projection of the solution during its heating, and the system was transferred to the microwave oven for 3 minutes, at approximately 700W to accelerate the formation of the extremely stable Cr(III)-EDTA colored complex. After exposition to the microwave irradiation, the solution was cooled to the ambient temperature and transferred to a 100.00 mL volumetric flask, being the volume completed with deionized water. In Fig. 3c the chromium (III) samples already complexed with EDTA are shown.

A blank test was prepared to monitor each repetition of the biosorption process. The readings were performed using the UV-Vis spectrophotometer and a previous wavelength scan was performed in the range of 400 to 550 nm to define the maximum wavelenght related to the absorption.

Results and Discussion

Fig. 4 presents the graph with the results of the scan performed with the standard concentration of 150 mg.L^{-1}, from which was determined the wavelength to do the readings. In Fig. 5 the experimental values for the calibration curve are shown as well as the equation of the line obtained. The chromium contents are presented in Table 2. The calculation of the amount of metal bound by the biosorbent, in terms of percentage of the Cr(III) removed, was obtained from the mass balance for the biosorbent in the system, using Eq. (1).

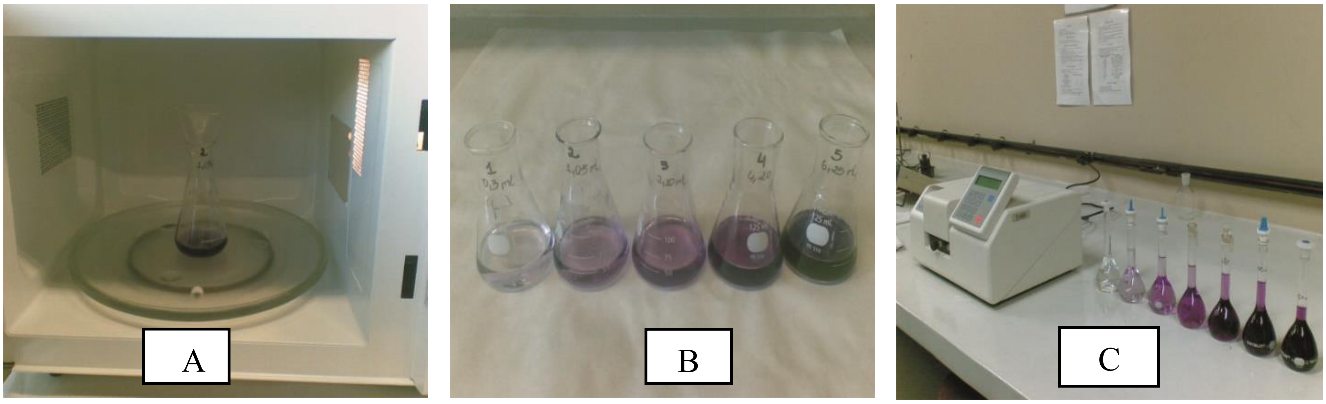

Figure 3. Cr (III) complexed inside the microwave oven (a); Cr (III) complexed after irradiation of microwave radiation (b); Solutions containing different concentrations of complexed Cr (III); ready for UV-vis reading (c)

$$R\,(\%) = (ci - cf)/ci \quad (1)$$

where ci is the concentration of Cr(III) in the CT solution sample, and cf is the concentration of chromium in the CR solution sample.

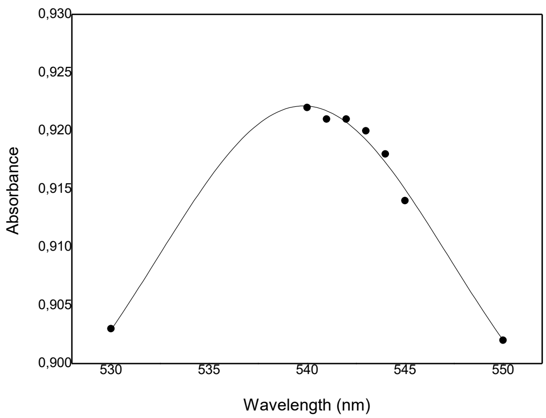

Figure 4. *Wavelength with maximum absorption in 540 nm.*

According to the data exhibited in Table 2, the Cr(VI) standard solution of known concentration was quantitatively reduced to Cr (III). The reference (22) was used for reducing Cr (VI) into Cr (III), accelerating the formation of the Cr (III)-EDTA complex by microwave radiation, and finally determine trivalent chromium using a UV-Vis spectrophotometer. Other works prove this methodology for obtaining of the product in a relatively short time.[23] The conversion of hexavalent chromium to trivalent chromium using ascorbic acid was very satisfactory with 99.8% yield.

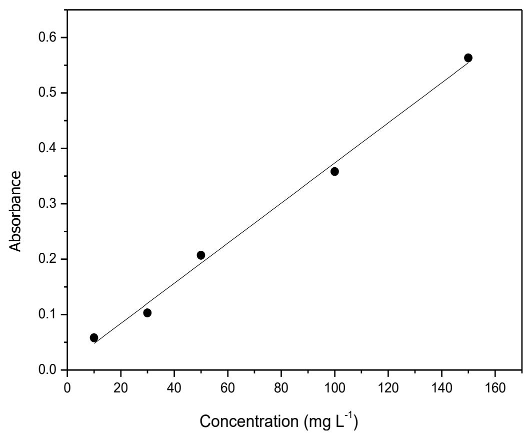

Figure 5. *Calibration curve for the chromium(III)-EDTA complex. Equation of the curve: $y = 0.01168 + 0.0036*x$; $R^2 = 0{,}9928$*

The use of the milled banana peels as biosorbent resulted in the decrease of the chromium concentration from 39.8 to 15.8 mg. L^{-1} (Table 2), corresponding to a removal of 60% of the Cr (III) present in the solution. The results described show that it is possible to use banana peels to remove trivalent chromium, but according to several pieces of work in the literature, the biomass may present low adsorption capacity due to other factors, for instance, pH levels.

Table 2. Experimental results obtained for standard, control, and residual solutions containing Cr(III).

Sample	Cr(III) concentration (mg. L^{-1})
Standard solution[a]	49.90
Control solution[b]	39.80
Residual solution[c]	15.80 (±0.01)

[a] Chromium(VI) standard solution of concentration 50 mg.L^{-1}, used for validation of the reduction process; [b] Model wastewater (argentometric chromium residue) not submitted to the biosorption process; [c] Argentometric chromium residue solution submitted to the biosorption process (average value exhibited)

In the present work, during the addition of an ascorbic acid solution, the pH value was 2.2 for ascorbic acid concentration at 0.6 mol/L (pKa = 4.25).[24] According to numerous authors, the removal efficiency of Cr (III) increases at the pH range between 3 and 5. Above a pH of 6 it starts precipitating as $Cr(OH)_3$, thus becoming less useful for adsorption. Upon decreasing pH to lower values, it is seen that H^+ ions compete with Cr^{3+} for binding sites in the adsorbent or the protonate.

Therefore, the pH is an important parameter to be monitored during biosorption process of heavy metal from liquid laboratory chemical waste. For instance, Rearte et al., 2013 revealed that the pH can influence metal biosorption in three ways: first, it affects the configuration of the active ion-exchange sites; second, it affects the ionic state of the sorbate in the solution; and third, extreme pH values may damage the structure of the biosorbent material.[25]

Also, another important factor that may have been crucial for causing the lower removal of chromium (III) was the competition of the silver ions in the solution for the binding sites in the adsorbent. Silver was present in the form Ag_2CrO_4 in the solution, and for a pH lower than 6.5, the silver chromate becomes excessively soluble (Eq. 2).[26] Consequently, because of balance, the silver ions are also soluble in the solution.

$$2Ag_2CrO_4\downarrow + 2H^+ \longleftrightarrow 4Ag^+ + Cr_2O_7^{2-} + H_2O \quad (2)$$

Therefore, we believe the following two factors were very important to reduce the removal of Cr (III) from the residue: very low acid pH and silver ions as interferers in the solution. The result was a low capacity for banana peels adsorption for these condition.

Conclusions

In conclusion, Costa et al. showed that formation of the Cr(III)-EDTA complex under microwave irradiation was possible be employed with successfully and satisfactory, because this method allows the determination of total chromium in a fast, practical, accurate, selective and with low cost, avoiding prolongated heating.

Moreover, from the examples in this paper, it is clear that the banana peel should will be more explored such as biosorbent. The results demonstrated are promising to treat wastewaters, because had a removal of 60% of Cr^{+3} ions from samples, and this result is better than others results described in the literature, which was unfavourable to obtain better adsorption capacity by banana peel was pH and silver ions present in the solution. Thus, more attention will be paid to improving the treatment methods and descontamination of the biosorbent in future.

Interesting possible applications of banana peel as biosorbent was discussed, but, of course, further studies in this field are recommended, thus such as study using microwave radiation with EDTA complex formation also it is necessary, already that is not fully explored.

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Renieidy F. C. Dias[b*], Regina Felisberto[a], Adriana F. Ramos[a], Roberto R. Faria[b], Francisco M. F. Dias[c] & Derli R. C. Dantzger[d].

[a] Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul, Campus Porto Alegre, Av. Coronel Vicente, 281 Sétimo Andar. Centro Histórico - Porto Alegre/RS.

[b*] Universidade Federal de Uberlândia, Instituto de Química, Campus Santa Mônica, Av. João Naves Avila 2121, Santa Mônica, 38408-100 Uberlândia-MG, Brasil.

[c] Universidade Estadual Vale do Acaraú - Campus Cidao, Endereço: Av. Dr. Guarani, nº 317, Bloco da Química, Bairro: Derby Club, Sobral- CE- Brasil CEP: 62010-305.

[d] Universidade do Oeste Paulista (UNOESTE), R. José Bongiovani, 700 - Cidade Universitária, Pres. Prudente - SP, Brasil CEP:19050-920.

[*] E-mail: flavia.clemente@ufrgs.br