Coconut coir as biosorbent for Cr(VI) removal from laboratory wastewater

Mário H. Gonzalez[a,c], Geórgia C.L. Araújo[b], Claudia B. Pelizaro[a,c], Eveline A. Menezes[a,c], Sherlan G. Lemos[c], Gilberto Batista de Sousa[a], Ana Rita A. Nogueira[a,*]

[a] *Grupo de Análise Instrumental Aplicada, Embrapa Pecuária Sudeste, P.O. Box 339, 13560-970 São Carlos, SP, Brazil*
[b] *Escola de Artes, Ciências e Humanidades da Universidade de São Paulo, Av. Arlindo Bettio, 1000, Ermelino Matarazzo, 03828-000 São Paulo, SP, Brazil*
[c] *Departamento de Química, Universidade Federal de São Carlos, Rodovia Washington Luis, P.O. Box 245, 13565-905 São Carlos, SP, Brazil*

ARTICLE INFO

ABSTRACT

A high cost-effective treatment of sulphochromic waste is proposed employing a raw coconut coir as biosorbent for Cr(VI) removal. The ideal pH and sorption kinetic, sorption capacities, and sorption sites were the studied biosorbent parameters. After testing five different isotherm models with standard solutions, Redlich–Peterson and Toth best fitted the experimental data, obtaining a theoretical Cr(VI) sorption capacity (SC) of $6.3\,mg\,g^{-1}$. Acid–base potentiometric titration indicated around of 73% of sorption sites were from phenolic compounds, probably lignin. Differences between sorption sites in the coconut coir before and after Cr adsorption identified from Fourier transform infrared spectra suggested a modification of sorption sites after sulphochromic waste treatment, indicating that the sorption mechanism involves organic matter oxidation and chromium uptake. For sulphocromic waste treatment, the SC was improved to $26.8 \pm 0.2\,mg\,g^{-1}$, and no adsorbed Cr(VI) was reduced, remaining only Cr(III) in the final solution. The adsorbed material was calcinated to obtain Cr_2O_3, with a reduction of more than 60% of the original mass.

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1. Introduction

The use of biological materials as biosorbent has been interesting due to the diversity of sorption sites available for metallic ions uptake; high selectivity for metallic ions and their different chemical forms; the possible use of biosorbent non-living; sorption capacity (SC) similar to the synthetic materials; lower susceptibility to interference of alkaline and earth alkaline metals than ionic change of resins, facility of using in a row or in flow systems, and due to its relative abundance [1]. Different materials have been evaluated to the Cr(VI) biosorption as an alternative for treatment of laboratorial and industrials waste [2–9]. The Cr(VI) presents known carcinogenic and mutagenic activity and the conventional procedure to its neutralization is constituted by four steps which presents shortcomings such as the need for toxic sludge allocation, the high cost of chemical compounds used in reduction of Cr(VI) and its incomplete reduction [10,11].

Sulphochromic solutions are used as reductor reagent for soil organic matter. The analysis of 2500 soil samples produces about 150 L of extremely acid waste (pH ≤ 1) solution, containing around $10,000\,mg\,L^{-1}$ of Cr(VI). In the present work, coconut coir, an agricultural waste previously used to biosorption of As, Cu, Cr, Hg, Ni and U in aqueous and organic solution [12–14] was evaluated to sorption of Cr(VI) remained in laboratorial waste produced from soil organic matter determination. The ideal pH sorption and the sorption kinetics and sorption isotherm related to this process were investigated.

2. Materials and methods

2.1. Materials

A cutting Mill TE 048 (Marconi) was used to grind the naturally dried coconut coir. An inductively coupled plasma optical emission spectrometer (ICP OES, Varian, Vista-RD) was employed for total Cr analysis. A digital potentiometer (Model 355, Mettler) and a glass combined electrode were used for pH adjust and for potentiometric titrations. The filtration in the kinetics studies was performed using $0.45\,\mu m$ porosity membranes (Millipore® Corporation). Fourier transform infrared (FT-IR) spectra of non-adsorbed and adsorbed coconut coir were obtained employing MB-Series (Bomem) and used as auxiliary to elucidate the biosorbent sorption sites. In the flow analysis an acrylic column with $50\,cm^3$ was used.

* Corresponding author. Tel.: +55 1633615611; fax: +55 1633615754.
E-mail addresses: anarita@cppse.embrapa.br, anarita_nog@hotmail.com (A.R.A. Nogueira).

The sorption isotherms evaluation was performed employing the Sigma Plot 8.0 software (Statistical Solutions). A stock 1000 mg L^{-1} Cr(VI) stock solution was prepared from dilution of K$_2$Cr$_2$O$_7$ (Merck) in water. The analytical work solutions of 50 and 200 mg L^{-1} Cr(VI) were prepared from appropriated dilution of the stock solution. A 5 mol L^{-1} H$_2$SO$_4$ (Merck) solution was used to pH adjust.

The used Cr(VI) laboratory waste—sulphochromic solutions, was obtained from a soil fertility laboratory and the coconut coir was provided by a local industry.

2.2. Methods

2.2.1. pH sorption and sorption kinetics evaluation

A mass of around 6.25 g of the biosorbent coconut coir was previously hydrated and preconditioned at pH 1.0; 2.0; 3.0; 4.0; and 5.0 using 1 mol L^{-1} H$_2$SO$_4$ or KOH solution. Following, the biosorbent were suspended in aliquots of 100 mL of 200 mg L^{-1} Cr(VI) solutions which were on the same pH of the coconut coir. The suspensions were shaken during 5, 10, 15, 20 and 30 min at 200 rpm, filtered and the chromium amounts were determined by ICP OES, in order to evaluate the ideal pH and the kinetics of sorption.

2.2.2. Adsorption isotherms

Around of 6.25 g of the coconut coir biosorbent were suspended in water and trapped in an acrylic column with 50 cm^3. Afterward, 200 mg L^{-1} Cr(VI) solution at pH 2.0 was percolated through the column and aliquots of 3 mL were colleted, in a total of 21 different aliquots. The solutions were then analyzed by ICP OES to remaining Cr determination. The obtained results were used to isotherms constructions. Mathematical treatments were performed and five theoretical isotherms models: Langmuir, Freundlich, Toth, Redlich–Peterson and SIPS were tested in order to define the one that best fitted with the experimental data [15].

2.2.3. Sorption sites studies

In the potentiometric titration of acid sites, around 25 mg of air dried and ground coconut coir were suspended in 50 mL of KNO$_3$ 0.5 mol L^{-1}, shaken and the initial pH was recorded. The acid sites were titrated up to pH 2.0 with standardized HNO$_3$ solutions. After that, a similar suspension was titrated up to pH 12.0 with standardized KOH solutions. In order to obtain consistent data, the pH change must be lower than 0.3 units for each added acid or base aliquot. The intervals among additions were 5 min. These procedures were important to reach the equilibrium before pH measurement. Afterwards, a mathematical method based on non-linear regression of the titration curves was used for determination of materials acid–base characteristics sorption sites. Potentiometric acid–base titrations have been widely used to illustrate the nature of the acidic equilibrium constant (K_a). By investigating the pH variations caused by known volumes of titrant, it is possible to infer qualitatively about the number of acid constants and their characteristics. Nevertheless, the chemical heterogeneity of biosorbents surfaces difficult the pK_a interpretation from the titration curves analysis [16]. The determination of well defined pK_a's is not a limitation and dissociation regions associated to functional groups can be differentiated (*e.g.* phenolic and carboxylic). Such acidic regions can provide important information about the extent, preference and complexation affinity of the sorption sites related to hydrogen and metal ions [17]. In the literature, the constants found in data treatments can be considered as the averaged of acidic constants, representing functional group classes. The use of models in the study of the interaction of hydrogen ions with natural organic complexants is previously proposed [17,18]. The simplest and less satisfactory model is that one which assumes the biosor-

bent as a mixture of ligands. Despite the variety of models, the majority represents the sorption process by unique experimental conditions. Usually, the consideration of occurrence of multiple discrete monoprotic sites in the complexation process is acceptable [17]. In this work, the titration data are obtained and then carried out their fitting to the equation previously described [15], with consequent determination of the acidity constants and acid sites concentration. It was established that the biosorbent initially could present up to six discrete monoprotic sorption sites to perform the data treatment. A non-linear regression of the titration curves was used to find the acid–base sorption sites characteristics. To perform the non-linear regressions, the Sigma Plot 8.0 software (Statistical Solutions) was used. This software uses the Marquardt–Levenberg algorithm to find the coefficients (parameters) of the independent variables that give the best data fit to equation. This algorithm looks for the values of the parameters that minimize the squared sum of differences between observed values and predicted ones of the dependent variable. This condition is known as convergence.

To confirm the functional groups involved in the Cr(VI) adsorption by coconut coir, FT-IR spectra using KBr disks were obtained for the biosorbent linked and non linked to Cr(VI).

2.2.4. Treatment of acid laboratory wastewater

Portions of 50 g of dried and hydrated coconut coir were suspended in 400 mL of 1:1 previously diluted sulphochromic wastewater solution. The dilution was needed since previous studies showed that the addition of non diluted sulphochromic wastes presented no Cr(VI) sorption. Probably, the high Cr(VI) concentration plus the high acidity promoted very fast oxidation of organic matter, destroying the sorption sites. This suspension was 30 min shaken at 200 rpm and the supernatant was recovered to ICP OES total chromium determination. The use of dried biosorbent was studied attempting to minimize the procedure steps. The diphenylcarbazide procedure was employed to evaluate the efficiency of Cr(VI) removal by the biosorbent [19].

3. Results and discussion

3.1. Ideal sorption pH and sorption kinetics evaluation

In Fig. 1 the sorption profile for the analyte investigated in different pH values is shown. The Cr(VI) adsorption increased with pH decrease, which is in accordance to previous published works which employed biosorbents for Cr(VI) adsorption
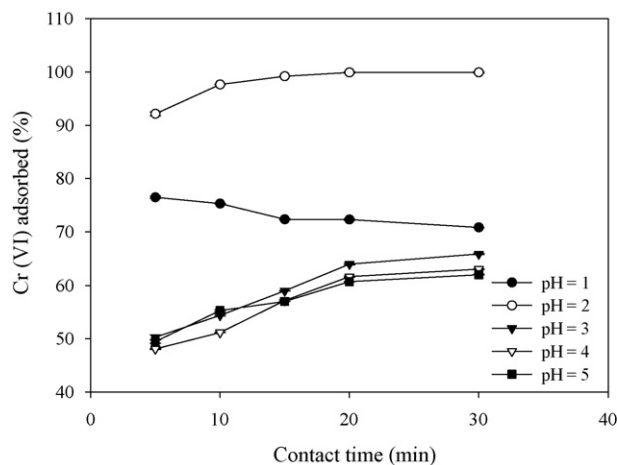

Fig. 1. Sorption and kinetic curves of Cr(VI) by coconut coir in different values of pH, employing 100 mL aliquots of 200 mg L^{-1} Cr(VI) analytical solution and 6.25 g of biosorbent, $n = 6$.

[6]. Some authors suggested that there are two possible mechanisms for Cr(VI) adsorption by biosorbents which involves oxidation–reduction reactions, and combined ionic extraction promoting the remaining of Cr(III) in solution [10]. In the first mechanism, the Cr(VI) would be firstly adsorbed on the biosorbent surface and thus oxidized to Cr(III) by a reaction with the organic carbon, one of the biomass components. On the other mechanism, the Cr(VI) would be firstly reduced to Cr(III) by biomass being subsequently adsorbed on the surface of biosorbent. The authors mentioned that both mechanisms could happen simultaneously and/or parallely, and the presence of protons in solution would be vital for acid sorption mechanism, being the improvement in Cr(VI) sorption directly proportional to the pH decreasing. In the present study, there is no a Cr(III) adsorption by coconut coir. This possibility was evaluated performing an experiment with a Cr(III) solution at pH 2 and posterior supernatant chromium determination, which showed that there was no one adsorption. Therefore, we believe that the Cr(VI) adsorption occurs in the same time of oxidation of organic matter.

The highest Cr(VI) adsorption was obtained at pH 2, which correspond to an adsorption higher than 95% of the available analyte present in the solution. According to Baes and Mesmer [20], Cr(VI) hydrolyzes extensively and the dimerization of $HCrO_4^-$ and $Cr_2O_7^{2-}$ occurs at concentrations higher than 0.01 mol/L in pHs lower than 6. This species would be adsorbed at pH 2. The sorption kinetics study is important to predict the minimum contact time necessary to a maximum removal of analytes by the biosorbent. As can be observed in the Fig. 1, the removal of ions was reached before the first 10 min when the experiment was carried out at pHs 2 and 1. This fact is in accordance with previous studies employing plant material as biosorbent, which presented rapid metallic ions sorption and reached the equilibrium in less than 10 min [21,22].

3.2. Adsorption isotherms

The Cr(VI) sorption by coconut coir is shown in Fig. 2. Table 1 presents the constants q^0, b and β, for isotherm models that was fitted on experimental data. The Redlich–Peterson and the Toth models had best described the experimental data. The fitted q^0 constant was around 1.3 mmol g^{-1}, which is equivalent at a SC of 6.3 mg g^{-1} of Cr by biosorbent. This SC value confirms the possibility of the use of coconut fiber as biosorbent to employ in waste treatments. The b value indicates a high sorption affinity of Cr for the coconut coir sorption sites. The Redlich–Peterson model approximates the Freundlich equation for concentrated solutions and describes process of multilayer adsorptions [11,23,24]. On the
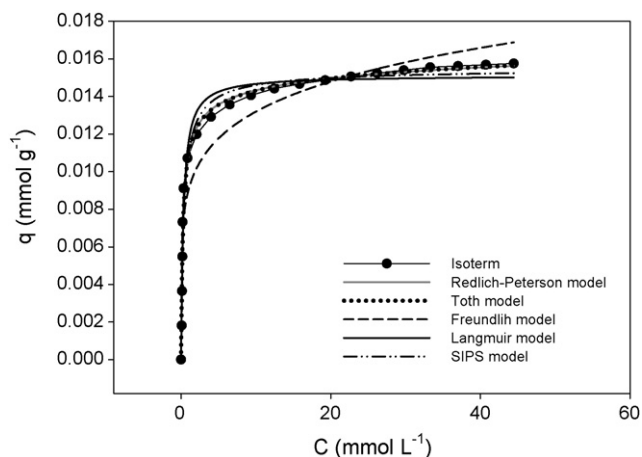

Fig. 2. Adsorption isotherm of Cr(VI) by coconut coir at pH 2.0 and fitted isotherm models. Solution of 200 mg L^{-1} of Cr(VI) at pH 2.0 and 6.25 g of biosorbent, $n = 6$.

other hand, Toth model presupposes a localized adsorption without lateral interactions between the adsorbed analyte and/or the sorption sites. This model can be used to solid heterogeneous adsorbents [23,25]. Both isotherms can describe the experimental conditions, since the used solutions presented high concentration of Cr(VI) and the biosorbent is probably heterogeneous, considering that it is a vegetal fibber which is formed by innumerous organic compounds.

3.3. Sorption sites studies

A discrete sites distribution model was used and the regressions were accomplished being considered a minimum of two and a maximum of six acid sites. Better data fit was obtained for a number of three sites, which was adopted for the biosorbent material characterization. Table 2 presents the average results of three titrations performed for the material acid–base characterization. This table presents pKa, acid concentrations, and the percentages of each sorption site and the related deviation. The experimental titration curve and theoretical (fit) data are available in Fig. 3.

As can be observed in Table 2, the discrete sites distribution model allowed the characterization of three classes of ionisable sites. A larger contribution was attributed to phenolic sites with an average of 88% of the sites, and conditional pKa's of 8.4 and 9.7. Phenolic groups of poliphenolic compounds are weakly basic groups, which could adsorb Cr(VI) from solution by a acid adsorption

Table 1
Theoretical parameters for isotherm models fitted on experimental data of Cr(VI) sorption in coconut coir

| Model	q^0 (mmol g^{-1})	b (L mmol^{-1})	β	r^2
Redlich–Peterson	1.3 ± 0.6	4.7 ± 0.8	0.95 ± 0.01	0.9839
Toth	1.25 ± 0.08	4.8 ± 0.9	0.975 ± 0.008	0.9842
Sips	1.55 ± 0.42	2.9 ± 0.4	0.8 ± 0.1	0.9774
Langmuir	1.51 ± 0.02	3.28 ± 0.35	–	0.9756
Freundlich	–	0.90 ± 0.05	0.17 ± 0.02	0.9097

Solution of 200 mg L^{-1} of Cr(VI) at pH 2.0 and 6.25 g of biosorbent, $n = 6$.

Table 2
Characterization of acid and basic sorption sites by potentiometric titration for coconut coir: S1 = site 1; S2 = site 2; S3 = site 3; Cc = total carbonate concentration, $n = 6$

Parameters	mol/L	% Sites	pKa	Type of sorption site
S1	7.14E−05	11.5 (±1.09)	6.6 (±0.19)	Amine
S2	9.45E−05	15.3 (±7.01)	8.4 (±0.49)	Phenolic
S3	4.54E−04	73.2 (±8.10)	9.7 (±0.05)	Phenolic
Cc	2.58E−05			

mechanism [10,26]. The stoichiometric relationship for complete oxidation of phenol to carbon dioxide coupled to reduction for Cr(VI)–Cr(III) was suggested by Shen and Wang [27]:

$$C_6H_6O + 9.3CrO_4{}^{2-} + 40.7H^+ \rightarrow 9.3Cr^{3+} + 6HCO_3{}^- + 20.3H_2O$$
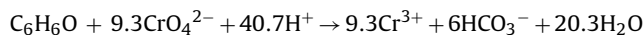
The cells of the biosorbent material were old and dead, being occupied by lignin, which is hydrophobic, and substitute the water in the cell wall [28]. Lignin, a rich phenolic compound is the major component of wood and vegetal old cell walls, and is the main phenolic component present in the coconut coir. Previous work related lignin as the main source of phenolic groups for Cr adsorption. The presence of the phenolic groups could be associated to the lignin, a phenolic polymer, which is deposited in cell walls after growing up interruption [29]. The 12% of the remaining sites can be attributed to amine groups at the surface, which could be related to proteins and glycoproteins that form the cell wall [30]. This remaining percentage also can be related to dissolved carbonic gas (carbonic acid system), or it can be associated to the sum of those two cited factors. Benedetti et al. [31] reported that great part of the metal associated to organic complex, which in that case, are humic substances, and could be attached to O-containing sites (–COOH and –OH phenolic) and N (–NH$_2$).

Some characteristic functional groups were identified using FT-IR. As could be observed in Fig. 4, the broad band between 3000 and 3750 cm^{-1} means the presence of OH groups on the coconut coir. This region is associated axial stretching of OH groups of cellulose and lignin. Other OH band within 2940 and 2820 cm^{-1}, confirmed the methyl radical. These groups are common in the lignin structure [32]. The peaks in 1511 cm^{-1} can be associated with aromatic rings and could be associated to phenolic groups from lignin. The difference obtained among samples in 1730–1640 cm^{-1} characterizes carbonyl groups stretching from aldehydes and ketones. It could be due to the changes on the stretching promoted by Cr adsorption or due hydrolyses of sorption sites promoted by the acidity of analytical solution.

3.4. Treatment of acid laboratory wastewater

The initial concentration of total Cr of sulphochromic waste was 4650 ± 5 mg/L, which 98% as verified as Cr(VI) by diphenylcarbazide [19] method. At the end of sorption experiment, around 17% of Cr had been removed from sulphochromic wastewater solution by
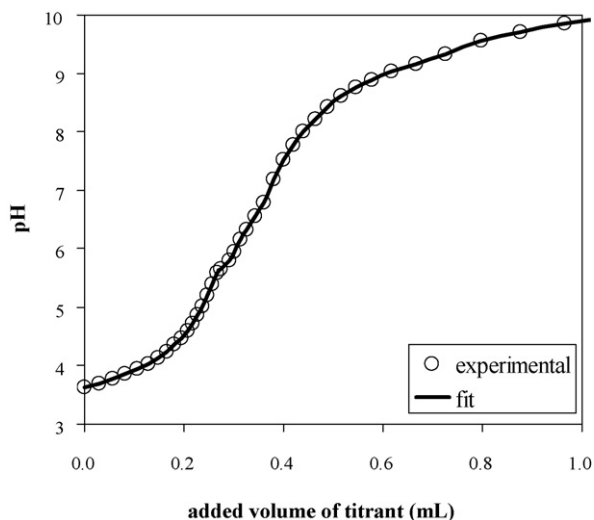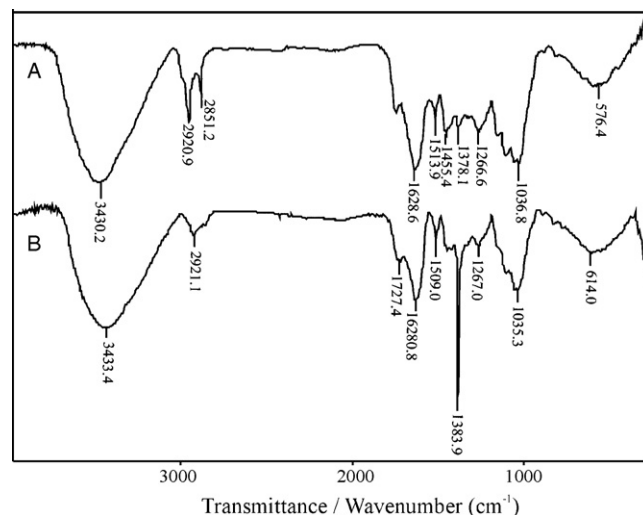

Fig. 4. Fourier transformed infrared spectra: a comparison between main functional groups of A = coconut coir before Cr adsorption and B = coconut coir after Cr adsorption. Resolution: 4 cm^{-1} with 21 scans min^{-1}.

dried coconut coir, while around 72% of Cr was removed by hydrated coconut coir, remaining in the supernatant around 520 ± 10 mg L^{-1} of Cr. The solution resultant from treatment with hydrated coconut was analyzed by diphenylcarbazide method to verify the remaining Cr species. Total absence of Cr(VI) was observed with results under the method detection limit (<0.003 mg L^{-1}); the equation of analytical curve was: $y = 0.0865x - 0.0063$, $r^2 = 0.9988$. The absence of Cr(VI) suggests that the hydrated coconut coir can uptake Cr in a course drove by a Cr(VI)–Cr(III) oxidation–reduction process. However, we cannot assure that a Cr(III) following adsorption occurs for the modified biosorbent surface because experiments with Cr(III) adsorption by coconut coir has not evidenced Cr removal from analytical solution. The experimental SC for sulphochromic waste was 26.8 ± 0.2 mg g^{-1}, around 4.3 higher than the SC found by isotherm studies, which employed standard solutions. The differences between SC obtained for experiments using Cr(VI) solution and sulphochromic wastewater solution could be explained by the following hypothesis: (1) the acidity of sulphochromic wastewater solution was considerably higher (pH < 0) than Cr(VI) solution prepared with controlled conditions. Kratochvil et al. [10] related that the sorption of Cr(VI) is strongly dependent on H$^+$, increasing the sorption when the pH decreases; (2) the sulphochromic wastewater presented a Cr(VI) concentration around 23 times higher than analytical solutions. According Kiran et al. [33], the increasing of metal concentration could increase the electrostatic interaction, which involves sites of progressively lower affinity for metal ions up to saturation point. In the case of sulphochromic waste, probably an interaction effect between its high acidity and high Cr concentration favored the increase in the SC of the biosorbent. Thereafter biosorption procedure, the supernatant of sulphochromic wastewater solution was analyzed by diphenylcarbazide method and no Cr(VI) was observed.

The acidity of solution proceeding from the treatment of sulphochromic wastewater with coconut coir was neutralized with hydroxide to precipitate Cr(III). It is important emphasize that the hydroxide consumption was reduced; owing the proposed treatment consumes part of the acid from sulphochromic wastewater to organic matter reduction.

In order to propose a final treatment for the used biosorbent, it could be burned to energy generation. The used material was calcinated, resulting 367 g of ash from 1000 g of original sample, indicating around of 60% of mass reduction.

Fig. 3. Acid–base potentiometric titration curve for coconut coir sorption sites evaluation with experimental and fitted data, $n = 3$.

The results showed that coconut coir is a good biosorbent to sulphochromic wastewater treatment, removing Cr(VI) presenting in solution, even biosorbent pretreatment. The obtained SC, 26.8 ± 0.2 mg g^{-1}, was better than almost 58% of a total of 247 different Cr(VI) biosorbent materials, with range of 0.00028–371 mg g^{-1}, related by Mohan and Pittman [29]. Otherwise, the coconut coir adsorption capacity could be improved with the ground of the raw material, increasing the superficial area. Among the main advantages of coconut coir use are (1) the use of a cheap and plentiful residue to treat another residue; (2) the velocity of the treatment; and (3) the reminiscences of only Cr(III) in solution after treatment.

Acknowledgements

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