



Effect of pH on the simultaneous sorption of Cr(III) and Cr(VI) by magnetic nanomodified lettuce roots in aqueous medium.

Efeito do pH na sorção simultânea de Cr(III) e Cr(VI) por raiz de alface nanomodificada magnética em meio aquoso.

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RESUMO: O descarte incorreto de efluentes industriais contendo metais potencialmente tóxicos podem trazer consequências ao meio ambiente e aos seres humanos. Dentre estes poluentes encontra-se o cromo, um metal cujas espécies mais comuns e estáveis são o Cr(III) e o Cr(VI), que embora raramente seja encontrado na natureza na forma hexavalente, tem contaminado efluentes devido a ações antropogênicas, como o descarte industrial incorreto. Este trabalho realiza um estudo do efeito do pH na remediação de matrizes aquosas empregando raiz de alface *in natura* (LR) e nanomodificada com magnetita (LR-NP) como materiais biossorbentes na remoção simultânea de Cr(III) e Cr(VI). Para avaliação dos melhores parâmetros do processo de biossorção foram realizados testes de pH baseados na determinação dos valores de pH_{PZC} das espécies Cr(III) e Cr(VI), individual e simultaneamente. Com a variação do pH das soluções foi observado um processo de oxidação e redução entre as espécies, que passam a apresentar diferentes frações molares. Os valores ótimos de pH de sorção obtidos dentro da faixa de 1 a 6, estabelecido pelo pH_{PZC} , foram de 6 para Cr(III), 1 para Cr(VI), e 2 para a remoção simultânea destes íons. A porcentagem de retenção de Cr nas melhores condições de pH foi em torno de 50 a 80%, e os melhores resultados de adsorção foram obtidos para Cr(VI).

Palavras-chave: Biossorção. Cromo. Nanopartículas magnéticas. Descontaminação de água.

ABSTRACT: The incorrect disposal of industrial effluents containing potentially toxic metals is of great concern for the environment and humans. Among these pollutants, chromium is a metal present most commonly as Cr(III) and Cr(VI). Although rarely found in nature in its hexavalent form, it has been contaminating effluents due to anthropogenic actions such as incorrect disposal of industrial waste. This work conducts a study of the effect of pH on the remediation of aqueous matrices using *in natura* (LR) and nanomodified (LR-NP) lettuce as a biosorbent material in the simultaneous removal of Cr(III) and Cr(VI) species. The assessment of pH was performed based on the pH_{PZC} to evaluate the best parameters of the individual and simultaneous sorption of Cr(III) and Cr(VI) species. With the solutions' pH variation, the oxidation and reduction process was observed between these species, which start to present different molar fractions. The optimal pH values obtained within the range of 1 to 6, established by the pH_{PZC} , were 6 for Cr(III), 1 for Cr(VI), and 2 for the simultaneous removal testes, with the percentage of Cr retention in the best pH conditions around 50 to 80% with Cr(VI) exhibiting the best adsorption results.

Keywords: Biosorption. Chromium. Magnetite nanoparticles. Water decontamination.

Introduction

The treatment of water and effluents to remove potentially toxic metal ions, such as hexavalent chromium, is a process of increasing importance because, with industrial growth and the exploitation of natural resources, a great demand for environmental problems has been caused by inappropriate waste disposal (Jobby *et al.*, 2018).

Chromium is a transition metal found in various oxidation states depending on the pH of the medium, and the species Cr(III) and Cr(VI) are the most common and stable (Costa *et al.*, 2017; Jobby *et al.*, 2018). Chromium(III) is considered an essential metal ion but can be harmful to biological activities in high concentrations (Costa *et al.*, 2017). Cr(VI) is not commonly found in nature, but can be derived from industrial processes with improper disposal of residues from industries, generating high toxicity, and is considered quite aggressive to the environment (Conceição *et al.*, 2014; Jobby *et al.*, 2018).

Although classic methods of treating effluents are employed, they still have many limitations, such as economic infeasibility, long time for their implementation, and difficulties to be applied when pollutants are in large volumes of water (Santos *et al.*, 2011).

One of the most viable processes for removing potentially toxic metals in aqueous matrices is biosorption. This highly efficient process consists of the adsorption of contaminants through the use of biomass that can be derived from agricultural activities and several types of biological waste (Milani *et al.*, 2018; Labuto and Carrilho, 2016; Abilio *et al.*; 2021). In the biosorption technique, the interaction between adsorbate and adsorbent occurs by a passive process, with physical-chemical interactions between the analytes and the functional groups present on the surface of the biosorbent (Colla *et al.*, 2014).

The present work proposes the use of the hydroponic lettuce root by-product with the

use of ferromagnetic nanoparticles (Fe_3O_4) to remove the Cr(III) and Cr(VI) species in an aqueous medium, aiming at the remediation of water and effluents.

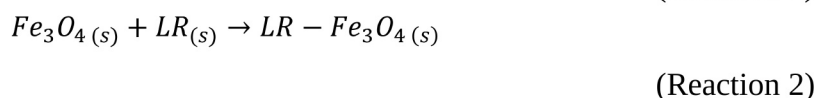
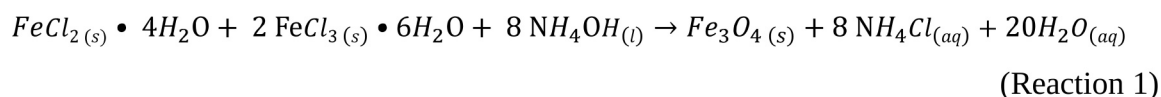
Material and Methods

Preparation of the lettuce roots (LR) biomass

The hydroponic lettuce roots (LR) samples were acquired at the Universidade Federal de São Carlos - *campus* Araras, where they were collected, washed, and rinsed with running and deionized water to remove solid residues. This material was then dried in an oven, ground in a rotor mill, sieved, and stored.

Preparation of magnetite nanoparticles (NP) and magnetic bionanocomposite (LR-NP)

The synthesis of magnetic nanoparticles was carried out using the coprecipitation method in which Fe(II) and Fe(III) salts, in the molar proportion of 1:2, respectively, were mixed in an acidic medium (HCl 1.0 mol/L) (Panneerselvam *et al.*, 2011; Carvalho *et al.*, 2020; Abilio *et al.* 2021). To this mixture, 0.7 mol/L NH_4OH solution was titrated under constant agitation for 30 min. Successively, powdered LR was added to the suspension containing the synthesized magnetite at 5:1 LR:NP ratio and kept under constant agitation, at 80 °C, for 30 min. The resulting magnetic bionanocomposite (LR-NP) was washed successively with distilled deionized water and dried in an oven at 50 °C, and ground. The synthesis of NP and LR-NP are exhibited in reactions 1 and 2:



Determination of pH at point of zero charge (pH_{PZC})

The pH_{PZC} indicates the pH at which the biosorbent surface charge is electrically zero, which indicates the ionization degree of the adsorbent surface, and the interaction with the adsorbate if this is possible. The determination of the pH_{PZC} is relevant to assess the pH in which the surface charge of the biosorbent is anionic (pH above pH_{PZC}) or cationic (pH under pH_{PZC}) (Carvalho *et al.*, 2020).

In the pH_{PZC} test, NaCl solution was used at initial pH values ranging from 2-12, which was adjusted with HCl or NaOH. To this solution, 100 mg of LR or LR-NP were added under constant stirring for 24h. The pH value corresponding to the pH_{PZC} was determined by the graphical representation of the initial pH variation as a function of the final pH. This procedure was performed in triplicate.

Sorption pH assessment

Monoelement and bielement solutions of 10 mg/L of Cr(III) and Cr(VI) were adjusted to the desired pH using 0.1 mol/L HCl or NaOH. These solutions were mixed with 100 mg LR or LR-NP, and the suspensions were kept under constant agitation at 185 rpm for 10 minutes. The supernatants from LR and LR-NP were collected with the aid of a pipette and a neodymium magnet, respectively, to be analyzed by Flame Atomic Absorption Spectrometry (FAAS, AAnalyst 400, PerkinElmer, USA) employing a 1.0 to 6.0 mg/L Cr(VI) and Cr(III) calibration curve. The operational parameters of the FAAS were: acetylene flow (3.3 L/min), nebulization flow (5.0 L min/L), air (10.0 L/min), and nebulizer flow rate (2.0 L/min), using a Cr cathode lamp at 357.87 nm. This procedure was performed in

triplicate.

After determining the total chromium in the simultaneous sorption, the supernatants were analyzed by Ultraviolet-Visible Spectroscopy (UV-Vis) to determine each chromium species' concentration. For this, Cr(VI) was complexed with 1% diphenylcarbazide (DPC), forming a red-violet complex that absorbs at 540 nm. Cr(III) does not react with DPC; thus, with the results of Cr(VI) and total chromium concentrations found, it was possible to calculate the equivalent concentration of Cr(III) present. This procedure was performed in triplicate.

Results and Discussion

Synthesis of magnetite nanoparticles (NP) and the nanomodified lettuce roots composite (LR-NP)

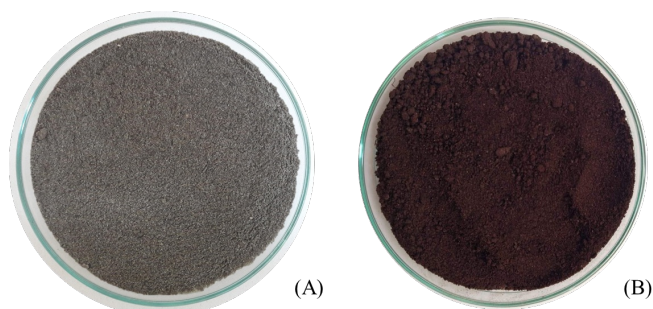
Clean and dried roots were ground and homogenized to 0.2 mm particle size (Figure 1).

The coprecipitation method used (Panneerselvam *et al.*, 2011; Carvalho *et al.*, 2020; Abilio *et al.*, 2021) is a simple procedure to obtain a paramagnetic material (Figure 1) efficiently. The magnetic nanomodified biomass (LR-NP) can be more efficiently used on a large scale and is easily removed using a magnet from the contaminated aqueous medium after sorption.

The magnetic properties of the magnetite used to produce LR-NP are derived from its inverted, cubic spinel structure. Its crystals have a high inverted polarity, considered a nanoparticle with excellent magnetic attributes (Carvalho *et al.*, 2020; Abilio *et al.*, 2021).

LR (A) and LR-NP (B) biomasses underwent granulometric analysis, so the particles were as homogeneous as possible, with size smaller than 0.250 mm.

Figure 1: Images of the (A) *in natura* (LR) and (B) magnetic nanomodified (LR-NP) lettuce roots.



The sorption pH assessment

The best sorption pH was assessed after determining the pH_{PZC} , calculated from the arithmetic mean of the constant values. The pH_{PZC} for LR and LR-NP were 5.96 and 6.50, respectively. In aqueous solutions at pH values below the pH_{PZC} , the material is positively charged. It indicates that sorption of anionic analyte will occur, while the reverse occurs if the material is exposed to pH higher than pH_{PZC} , where the material is negatively charged (Nascimento *et al.*, 2014). Thus, in aqueous solutions at pH below pH_{PZC} , Cr(VI) is present as $HCrO_4^-$ and will be attracted to the positively charged surface of LR and, therefore, adsorbed. As for trivalent chromium, Cr^{3+} form is predominant at pH around 1 and 2, and $Cr_3(OH)_4^{5+}$ form prevails up to pH values close to 6.5 (Pino, 2005). Commonly as a cationic species, its sorption would be favored at higher pH values; however, at pH above 6 Cr tends to precipitate as hydroxides.

Determination of Cr(III) and Cr(VI)

Chromium can assume different oxidation states, depending on the pH of the medium, which can interfere with the adsorption process (Costa *et al.*, 2017). Therefore, the procedure for determining the effect of the

sorption pH was carried out within the best pH range found (1-6) by determining the pH_{PZC} using Cr(III) and Cr(VI) monoelement e bielement solutions, in order to understand sorption under different pH for each of these conditions.

The oxidation and reduction processes among Cr(III) and Cr(VI) species, simultaneously in solution, were evaluated by Ultraviolet-Visible Spectroscopy (UV-VIS). For this, work solutions containing 5mg/L of Cr(III) and 5mg/L of Cr(VI) at each pH value were analyzed by FAAS to determine the total chromium after sorption. Chromium(VI) was then determined by UV-Vis after its complexation with diphenylcarbazide (DFC).

Figure 2 illustrates this reaction of Cr(VI), remaining in the supernatants, and DPC, after Cr sorption in 5 mg/L of Cr(III) + 5 mg/L of Cr(VI) solution, at pH 1 to 6. The color variation of the complex formed by Cr(VI) reaction with DPC indicates the different molar fractions of Cr(VI) in each test tube. It also implies the occurrence of chromium oxidation and reduction processes at different pH, as shown in Figures 3 and 4, which depict the speciation of Cr(III) and Cr(VI) in aqueous media, respectively.

Figure 2: Cr(VI)-diphenylcarbazide complex formation using a bielement solution of 5mg/L Cr(III) and 5mg/L Cr(VI), at pH range 1 – 6.

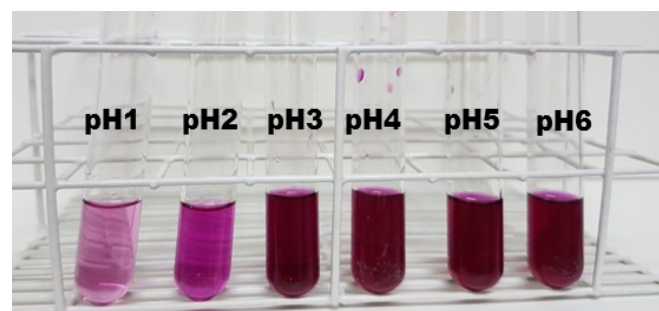
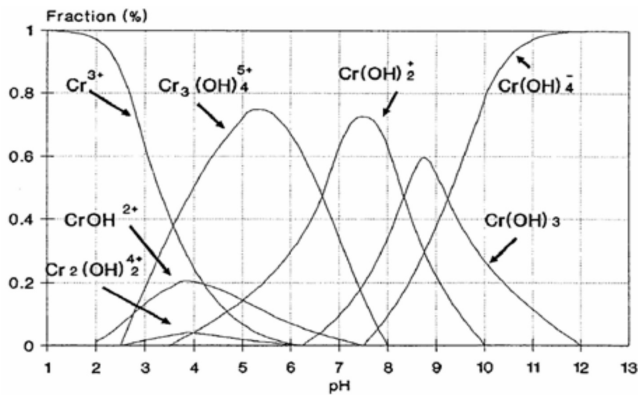
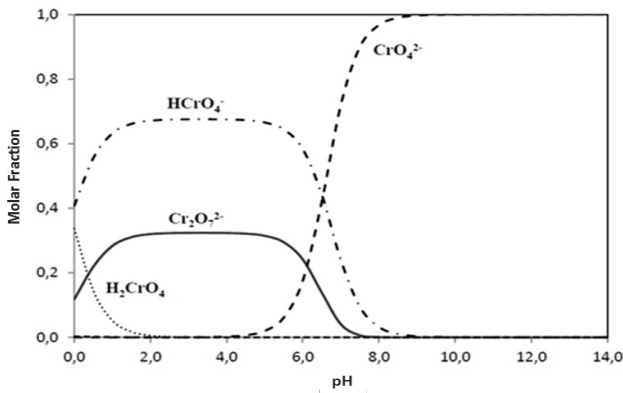


Figure 3: Speciation diagram of Cr(III), as a function of the molar fraction and pH of the medium.



Source: Pino, 2005

Figure 4: Speciation diagram of Cr(VI) as a function of the molar fraction and pH of the medium.



Adapted from: Pina, 2011.

Figure 5 and Figure 6 show the effect of pH variation on the sorption of Cr(III) and Cr(VI) species for LR and LR-NP biomasses, respectively.

The best sorption pH for Cr(III) and Cr(VI) mono-element solutions were 6 and 1, respectively. The choice of pH lower than pH_{PZC} will favor the sorption of anionic species, such as Cr(VI), that produces neutral or anionic species by its hydrolysis, which are better adsorbed at pH 1. Higher pH will favor the sorption of cationic species, such as Cr(III), whose best sorption pH was 6 (Pina, 2011; Pino, 2005).

In the simultaneous sorption assessment, the best results were achieved at pH 2, which can be explained due to the influence of the solution pH on chromium speciation. At pH

values close to this, Cr(VI) species present in the solution are $HCrO_4^-$ and $Cr_2O_7^{2+}$. At the same time, Cr(III) prevails in the free form of Cr^{3+} until pH 2, where its molar fraction begins to decrease and increase the concentration $CrOH^{2+}$ of (Pina, 2011; Pino, 2005), the most favorable point of simultaneous sorption of species.

Figure 5: Effect of pH on the removal capacity of Cr(VI) and Cr(III) by *in natura* (LR), using 10 g/L dosages of LR with 10 mg/L Cr(VI) solution, n = 3.

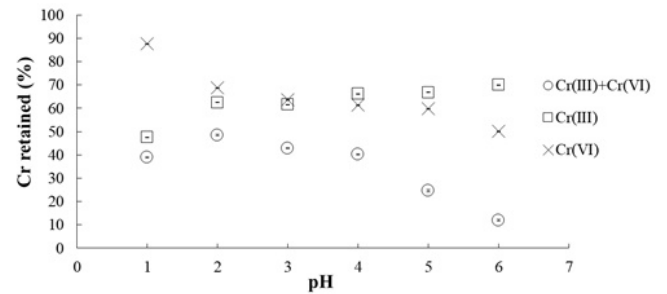
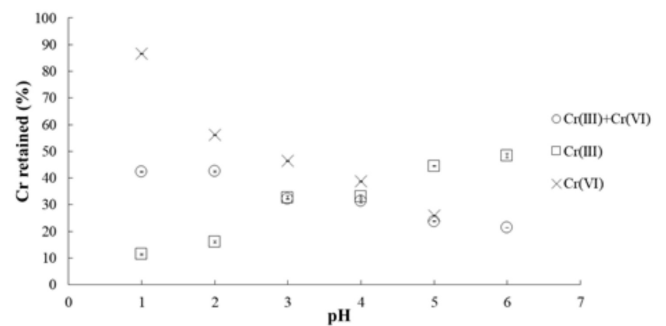


Figure 6: Effect of pH on the removal capacity of Cr(VI) and Cr(III) by nanomodified lettuce roots (LR-NP), using 10 g/L dosages of LR-NP with 10 mg/L Cr(VI) solution, n = 3.



Conclusion

The lettuce root (LR) presents itself as a biosorbent potential for adsorption of Cr(III) and Cr(VI) in aqueous matrices, its values obtained for the pH_{PZC} test were similar for both materials, obtaining the values of 5.96 and 6.50 for LR and LR-NP, respectively. The efficiency of magnetization is verified using a neodymium magnet to observe its attraction for the nanoparticle and magnetized nanocomposite.

In the assessment of the pH effect on the sorption of Cr(III) and Cr(VI), a process of oxidation and reduction between Cr(III) and

Cr(VI) was observed, as reported in the literature. The best sorption pH of Cr(III) and Cr(VI) was 6 and 1, respectively. However, in the simultaneous study, the best sorption pH for both species was 2, which is explained by the oxidation states chromium assumes at different pH values. The percentage of Cr retention in the best pH conditions was around 50 to 80%, with Cr(VI) exhibiting the best adsorption results. Therefore, these adsorbents are promising materials for Cr sorption in an aqueous medium.

The proposed materials LR and LR-NP are potential biosorbents for the sorption of toxic Cr(VI) in the presence of Cr(III) from contaminated aqueous matrices. After sorption, the Cr-containing LR-NP can be easily removed from the medium after with a magnet.

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