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Removal and desorption of chromium in synthetic effluent by a mixed culture in a bioreactor with a magnetic field

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ABSTRACT

Two chromium removal experiments were performed in bioreactors with and without a magnetic field under the same conditions. The release of the chromium present in the biomass was tested in two experiments one with the initial pH of the medium and one with pH 4.0. The objective was to remove Cr(VI) and total Cr from the effluent, this was carried out by placing biological treatments of synthetic effluent contaminated with 100 mg/L of Cr(VI) in a bioreactor with neodymium magnets that applied a magnetic field (intensity 85.4 mT) to the mixed culture. The removal of Cr(VI) was approximately 100.0% for the bioreactor with a magnetic field and 93.3% for the bioreactor without a magnetic field for 9 hr of recirculation of the synthetic effluent by the bioreactor. The removal of total Cr was 61.6% and 48.4%, with and without a magnetic field, respectively, for 24 hr. The desorption of Cr(VI) in the synthetic effluent was 0.05 mg/L, which is below the limit established by Brazilian legislation (0.1 mg/L) for the discharge of effluent containing Cr(VI) into bodies of water. The results obtained for the removal of chromium in synthetic effluent suggested that there was no significant influence on the viable cell count of the mixed culture. The desorption of Cr(VI) in synthetic effluent after bioadsorption of chromium by the mixed culture in the process of removal of chromium in bioreactors with and without a magnetic field was not significant in either of the experiments with different initial pHs.

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Introduction

In the environment, chromium is found in its natural form as trivalent chromium (Cr(III)), and during industrial processes hexavalent chromium (Cr(VI)) is generated by the oxidation of Cr(III) and is discarded as industrial waste (Pradhan et al.,

2017). This creates a serious environmental problem, because according to Thatoi et al., 2014, the higher oxidation states of metals are always more toxic than the lower oxidation states.

The standards for effluent discharge in the recipient body in Brazilian legislation are listed in CONAMA Resolution No. 430 as of May 13, 2011. For Cr(VI), the maximum value that is

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allowed is 0.1 mg/L and for Cr(III) it is 1.0 mg/L (BRASIL; CONAMA, 2018).

Cr(VI) to Cr(III) reduction techniques are of great interest for Cr(VI) detoxification due to the different toxicity of the two oxidation states (Xu et al., 2009). As Cr(VI) is persistent and bioaccumulative, and toxic to human health, living resources, and the ecological system, alternative treatment methods for the removal of Cr(VI) are needed. The use of microorganisms in treatment methods is sustainable (Ahmad et al., 2013). The challenge of Cr(VI) bio-reduction in the biological treatment of wastewater is the death of the bacteria due to metal toxicity (Joutey et al., 2015). However, bacteria use oxidation, reduction, or methylation as a protective means to transform toxic compounds into more volatile or less toxic forms, or rapidly precipitate forms (Dermou et al., 2005).

Chromate (CrO_4^{2-}) is a structural analogue of sulphate (SO_4^{2-}) and it enters the cells through sulfate absorption systems (Joutey et al., 2015). Cr(VI), when entering the cell, will be reduced to Cr(III) because of the reducing environment and the enzymes present inside the cell (Ahmad et al., 2013). Cr(VI) will be reduced to Cr(III) if the bacteria have intracellular chromate reductase.

In metal adsorption, speciation of the metal is important since it is influenced by pH (Cruz et al., 2017). Biosorption is a process that is independent of metabolism and, therefore, can be performed by living and dead microorganisms (Dermou et al., 2005). Cr(III) is transported from the liquid medium to the solid surface through the respective interface (Hintermeyer et al., 2008). Functional groups on the cell surface of the microorganism directly interfere in the ability of the species to adsorb metals (Sá et al., 2015).

Most microbial species are sensitive to Cr(VI). However, some species are resistant and tolerant to high chromate levels (Joutey et al., 2015). When present in a mixed culture, bacteria are more stable and better able to survive. This can be explained by the physiological and metabolic differences of each bacterial strain and by the different responses and resistivity to different metals, which would generate a dynamic, well adapted, and more resilient population due to the exchange of genetic material among the existing strains (Sannasi et al., 2006). The culture consortium organisms present greater competition and are more likely to survive when applied in the environment, in addition to being metabolically superior for the removal of metals (Kader et al., 2007).

The use of a magnetic field with microorganisms to treat wastewater was shown to interfere with the biodegradability of microorganisms (Dias et al., 2016; Ji et al., 2010; Lebkowska et al., 2011; Moura et al., 2015; Tomska and Wolny, 2008). Evidence provided by recent studies has shown the positive effect of a magnetic field in wastewater treatment (Zieliński et al., 2018). Magnetic fields have been studied regarding their abilities that can be used to protect human health (Dini and Abbro, 2005). They have been shown to affect the responses to stimuli that living cells provide through intra and extracellular exchanges (Saffer et al., 1996) and they can change the conformation in transmembrane proteins and soluble proteins which produces significant biological effects (McLean et al., 2001). These reasons, as well as the biodegradability results, are why magnetic fields are studied regarding their influence on the removal of effluent chromium

by microorganisms. Working with permanent magnets is interesting because they do not require electric energy to generate the field, whereas in bioreactors with a field generated by coils electric energy is needed to generate the electromagnetic field. Thus, a system that uses permanent magnets for the treatment of effluents is economic and can last a long time (Dias et al., 2016).

In this study the construction of bioreactors with permanent neodymium magnets to generate a magnetic field, with the aim of influencing a mixed culture in the reduction and removal of chromium (Cr(VI) and total Cr) in the synthetic effluent was discussed. After the bioadsorption of chromium in synthetic effluent with Cr(VI) by the mixed culture in the bioreactors with or without a magnetic field, the desorption of Cr(VI) and total Cr in the synthetic effluent is quantified.

1. Materials and methods

1.1. Synthetic effluent

The synthetic effluent used to feed the bioreactors consisted of a mixed culture. The culture medium with a predefined composition was prepared by dissolving 1.0 g/L NH_4Cl , 0.2 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.001 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 6.0 g/L $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, 0.5 g/L K_2HPO_4 , 3.0 g/L of yeast extract, and 0.001 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 1 L of distilled water (adapted from Dermou et al., 2005). The initial pH of the synthetic effluent obtained with this composition was 6.8 ± 0.2 .

1.2. Mixed culture

The mixed culture microorganisms used in this study, obtained from industrial sludge, were adapted to concentrations of 40–150 mg/L of Cr(VI) under conditions of constant exposure. This culture was maintained every three days using the synthetic culture. The initial concentration of the inoculum used in the experiments was 5.0 ± 0.5 g/L, this was established based on preliminary experiments. The concentrations of the inoculum were determined by volatile suspended solids (VSS) (Apha et al., 2005).

1.3. Experimental apparatus for the desorption of chromium by a mixed culture

The synthetic effluent was contaminated with potassium dichromate (source of Cr (VI)) and chromium removal was carried out using a mixed culture in a bioreactor with a magnetic field generated by 600 neodymium magnets with a length of 10 mm, a width of 10 mm and a height of 2 mm. The magnets were purchased from the Neodimio virtual store (www.neodimio.com) and they consisted of neodymium-iron-boron and the direction of magnetization was by height (one pole on each face of the magnet). Two tubular bioreactors (laboratory scale) were made with nontoxic hose (1 cm in diameter and 330 cm in length). On the wall of a bioreactor the magnets were affixed with no space between them (Fig. 1).

The other bioreactor was built without magnets to perform the control test in order to verify the influence of the magnetic field on the mixed culture during the removal of the

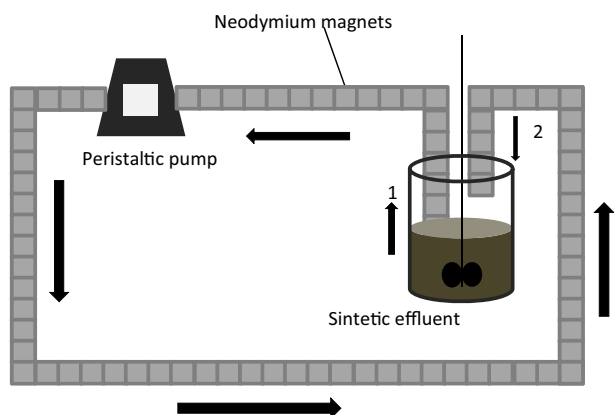


Fig. 1 – Simplified diagram of the bioreactor with the magnets. The input of the synthetic effluent is represented by the number 1, and the effluent outlet and collection point of the samples are represented by the number 2.

chromium. The volume of each bioreactor was 259.18 mL. This configuration of the reactor was the one that presented the best removal in comparison with other configurations that were previously studied.

A volume of 400 mL of synthetic effluent was pumped into each bioreactor by a Watson Marlow peristaltic pump (model 520S), ensuring recirculation of the effluent. Two mechanical stirrers (Ika RW20 and Ika RW16) were used to ensure that all the inoculum circulated through the bioreactors.

Twenty-four hours of synthetic effluent recirculation was considered in order to evaluate the behavior of the removal of Cr(VI), total Cr, and total organic carbon (TOC), with the microorganisms exposed to the effects of the magnetic field for 14 hr 8 min (the exposure time to the magnetic field was calculated as a function of the residence time of the bioreactor under which the magnetic field was applied and the number of times the synthetic effluent flowed through the bioreactor under magnetic field action). The intensity of the magnetic field of the bioreactor with magnets was 85.4 mT, measured using a Gaussmeter (model HT201). This magnetic field intensity was chosen, as in previous studies, this intensity produced the best chromium removal results.

The flow rate in each bioreactor was 7.07 cm³/sec because the best removal values of Cr(VI) and total Cr occurred at this flow rate in the study by [Dias et al. \(2016\)](#).

At the end of the chromium removal and TOC experiments in the bioreactors, the treated synthetic effluent (with approximately 100% removal of Cr(VI)) was centrifuged at 4000 r/min for 10 min. The biomass with the mixed culture was then separated from the supernatant and used in experiments to evaluate the desorption of chromium in a new synthetic effluent (without chromium), since desorption confirms the retention/removal of chromium.

A new synthetic effluent was created using the biomass with the mixed culture that had removed approximately 100% of the Cr(VI) from the synthetic effluent in the bioreactor with a magnetic field. A concentration of 5.0 ± 0.5g/L of this biomass with the mixed culture was placed in 400 mL of

culture medium, and this new synthetic effluent was put in the bioreactor with a magnetic field for a period of 120 hr to evaluate the process of the desorption of chromium.

The same approach was used for the biomass that treated the synthetic effluent in the bioreactor without a magnetic field, and the new synthetic effluent with the biomass and the mixed culture was put in the bioreactor without a magnetic field. In addition, the same concentration of biomass that went through the bioreactors to remove the chromium was placed in a new synthetic effluent in an Erlenmeyer flask to also evaluate the desorption process of chromium outside the bioreactors. A period of 120 hr was chosen to monitor the desorption process of chromium in the synthetic effluent so that evaluations could be carried out over a long enough period without causing damage to the microorganisms.

The following experiments were performed: (A) bioreactor with magnetic field, (B) bioreactor without magnetic field, (C) Erlenmeyer flask at rest, (D) bioreactor with magnetic field and pH 4, (E) bioreactor without magnetic field and pH 4, and (F) Erlenmeyer flask at rest and pH 4. The pH 4 was chosen to evaluate the chromium desorption in the synthetic effluent, since this pH range helps to maintain Cr(III) in the effluent and prevents its precipitation.

For experiments A–C, the samples were withdrawn after 24, 48, 72, 96, and 120 hr of residence time of the synthetic effluent in the bioreactors or in the Erlenmeyer flask. In experiments D–F with pH 4, the samples were withdrawn after 24, 48, and 72 hr of the synthetic effluent residing in the bioreactors or in the Erlenmeyer flask. The correction for pH 4 was performed after each sample was withdrawn for analysis, ensuring that the pH remained at 4. The pH of the medium was monitored in each sample that was collected to follow the behavior of the mixed culture in relation to the chromium desorption.

1.4. Analytical processes

During the period of effluent recirculation, the Cr(VI), total Cr, and TOC concentration were all quantified in the samples. Each collected sample was 10 mL, and all were filtered using a syringe filter with a 0.22 µm pore size (Kasvi brand). To guarantee the reliability of the results, the desorption chromium experiments were carried out in duplicate.

1.4.1. Hexavalent chromium

The concentration of Cr(VI) was defined using the colorimetric method with diphenylcarbazide from [Apha et al. \(2005\)](#) and with the use of a spectrophotometer (model Thermo Spectronic, brand Genesys 10 UV), with an absorbance reading taken at 540 nm. In this method, Cr(VI) reacts with diphenylcarbazide, producing a pink hue.

1.4.2. Total chromium

The concentration of total Cr was determined using a flame atomic absorption spectrophotometer (brand Shimadzu, model AA-7000).

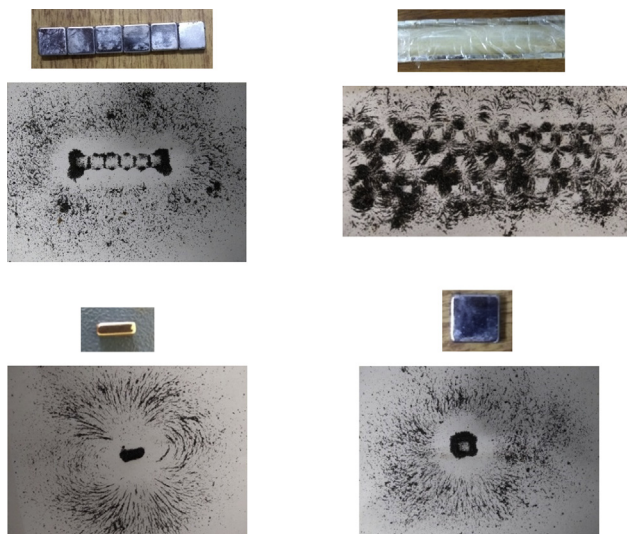


Fig. 2 – The neodymium magnets (size 10 mm × 10 mm × 2 mm) and their respective magnetic field lines in different positions.

1.4.3. Total organic carbon (TOC)

Catalytic combustion at high temperature was used to determine the concentration of TOC using a total organic carbon analyser (TOC-L, Shimadzu).

1.4.4. Volatile suspended solids (VSS)

Analysis of the fixed and volatile suspended solids was used to determine the initial and final concentrations of the inoculum. This method is described by Apha et al. (2005) and involves igniting the solid samples at 550 °C in a muffle furnace (Quimis).

1.4.5. Viable cells

Counting the viable cells on plates verified the resistance of the microorganisms in the presence of the magnetic field and with chromium. For this, the method of Madigan et al. (2004) was employed. Several dilutions of the samples (10^0 to 10^{12})

were performed in triplicate, and the plates were incubated for 48 h at 30 ± 2 °C.

1.5. Lines of the magnetic field

The lines of the magnetic field generated by the neodymium magnets were identified using iron filings. The iron filings were distributed on a sheet of white paper over the magnet.

2. Results and discussion

2.1. Lines of the magnetic field of the magnets

The lines of the magnetic field generated by neodymium magnets (size 10 mm × 10 mm × 2 mm) can be seen in Fig. 2.

2.2. Removal of Cr (VI), total Cr, and TOC

The concentrations of Cr (VI), Cr (III), total Cr, and TOC after the application of the magnetic field and without a magnetic field in the bioreactors are presented in Fig. 3.

In Fig. 3 (a), it can be seen that the concentrations of Cr(VI), 0.04 ± 0.001 mg/L with a magnetic field and 0.05 ± 0.004 mg/L without a magnetic field, are below the concentrations allowed by the current Brazilian legislation CONAMA 430/2011 (0.1 mg/L), which indicates that the bioreactors were effective in removing Cr(VI). However, concentrations of Cr (III) were higher than that allowed by legislation, for Cr(III) the maximum value is 1.0 mg/L (BRASIL; CONAMA, 2018).

For the bioreactor with a magnetic field, the removal of Cr(VI) from the synthetic effluent was $99.96\% \pm 0.0013\%$ with 9 hr of recirculation of the synthetic effluent by the bioreactor (4 hr and 42 min of magnetic field), and for the bioreactor without a magnetic field the removal was approximately $93.3\% \pm 1.1\%$ in the same period. The removal rate of Cr(VI) for 9 hr was 11.2 mg/L/hr for the bioreactor with a magnetic field and 10.5 mg/L/hr for the bioreactor without a magnetic field. The removal of total Cr was $61.6\% \pm 0.9\%$ for the bioreactor with a magnetic field and $48.4\% \pm 1.4\%$ for the bioreactor without a

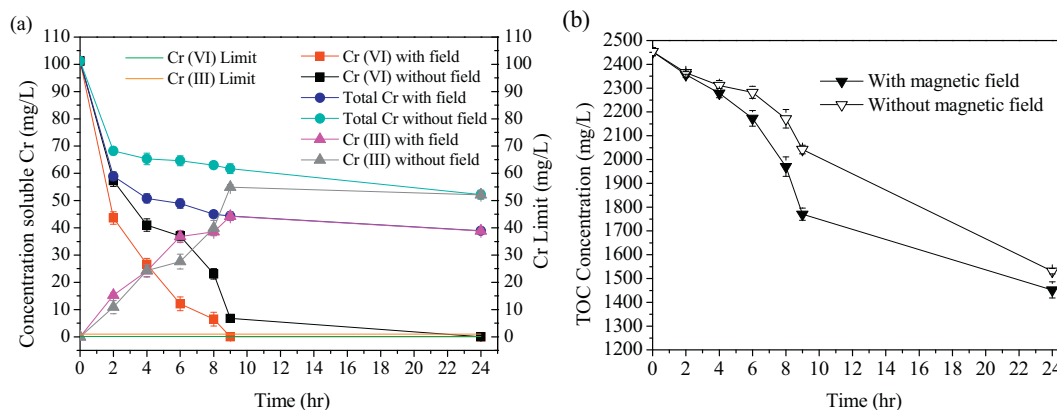


Fig. 3 – (a) Cr(VI), Cr(III), and total Cr concentrations for a magnetic field and no magnetic field for 24 hr of operation and 14 hr and 8 min of magnetic field application. (b) TOC concentrations for a magnetic field and no magnetic field for 24 hr of operation and 14 hr and 8 min of magnetic field application.

magnetic field for 24 hr of recirculation of the synthetic effluent by the bioreactor (14 hr and 8 min of magnetic field). The removal of TOC was $40.8\% \pm 1.5\%$ for the bioreactor with a magnetic field for 24 hr and $37.6\% \pm 0.8\%$ for the bioreactor without a magnetic field during the same period (Fig. 3 b).

The approximately 100% reduction in the concentration of Cr(VI) to Cr(III) in the synthetic effluent indicates that the bacteria used the transformation of toxic compounds into less toxic forms as a means of protection (Dermou et al., 2005). One possible mechanism for the removal of chromium by a microbial cell is the adsorption (extracellular) and reduction (intracellular) of chromium in the cell. Cr(VI) is adsorbed to the surface of the microbial cell through a chemical bond between the metal ion and the functional groups present in the cell surface structures and can be reduced to Cr(III) by the enzymes' chromate reductase activity (Jobby et al., 2018). The Cr(III) produced by the extracellular reduction of Cr(VI) is unable to pass through the cell membrane (Pradhan et al., 2017). Chromate enters the microbial cell through the membrane by the sulfate transport system (Jobby et al., 2018). In the cell, in the reduction mechanism of Cr(VI) for Cr(III), Cr(VI) initially accepts one electron of one NADH molecule (NAD(P)H in some species) and generates Cr(V) as an intermediate and, subsequently, Cr(V) accepts two electrons and forms Cr(III) (Suzuki et al., 1992). The studies done by Blank et al. (1995) suggest that the magnetic fields directly affect the electron transfer reactions.

The results obtained by Dias et al. (2016) can be compared with the results from the present study since the authors used a magnetic field generated by 170 neodymium magnets (size $10 \text{ mm} \times 4 \text{ mm} \times 2 \text{ mm}$). The intensity of the magnetic field was 25 mT, and the magnetic field frequency was 5 Hz, and they used a mixed culture and an initial concentration of Cr(VI) of 100 mg/L and 280 mL of synthetic effluent. For Cr(VI), approximately 100% was removed in the bioreactor with a magnetic field frequency of 5 Hz and approximately 82% was removed in the bioreactor without a magnetic field for the 9 hr of recirculation of the synthetic effluent by the bioreactor (equivalent to 4 hr and 17 min of magnetic field application). For total Cr, the removal was approximately 82% and 44% for the bioreactor with a magnetic field frequency of 5 Hz and for the bioreactor without a magnetic field, respectively, during the same period of evaluation. The removal of TOC was approximately 34% and 12% for the bioreactors with and without a magnetic field, respectively, during the same period.

There were no significant differences between this study and that of Dias et al. (2016) regarding the removal of Cr(VI) in the presence of a magnetic field. It is assumed that the highest removal of total Cr and lowest removal of TOC found in the bioreactors of Dias et al. (2016) occurred due to the difference in the process conditions, the size of the magnets, and the lines of magnetic field generated (Fig. 2).

Moura et al., 2015 studied the removal of hexavalent chromium using an electromagnetic field on a mixed culture. The authors constructed batch reactors, one with an electromagnetic field and one without. An approximately 100% reduction of Cr(VI) was observed with the application of an electromagnetic field, and there was a 72% reduction without an electromagnetic field; both experiments involved an effluent volume of 500 mL and an initial Cr(VI) concentration of 100 mg/L and a

recirculation time of 3 hr. After 5 hr of recirculation the authors found 38% and 25% removal of total Cr with and without the application of an electromagnetic field, respectively. Removals of chemical oxygen demand (COD) of 62% and 35% were observed with and without an electromagnetic field, respectively, with a recirculation time of 5 hr.

In the present study, when the microorganisms were submitted to the magnetic field, more chromium and TOC was removed from the synthetic effluent in comparison with the effluent whose microorganisms were not submitted to the field.

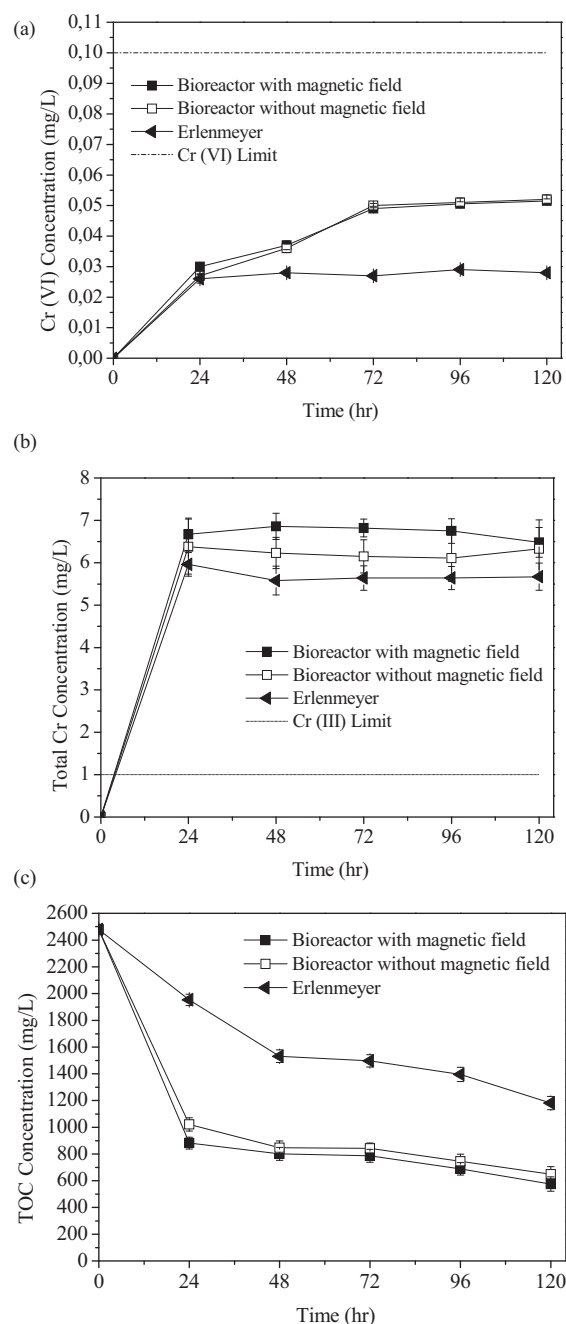


Fig. 4 – Desorption of Cr(VI) (a) and total Cr (b) in bioreactors with and without a magnetic field and in an Erlenmeyer flask (c) TOC concentrations during the desorption of chromium.

After the plates were incubated for a period of time, the viable cell counts had the same order of magnitude for the biomass concentration, $3.1 \pm 1.3 \times 10^{11}$ CFU/mL (colony forming unit per milliliter) with magnetic field application and $3.4 \times 10^{11} \pm 1.2$ CFU/mL without magnetic field application. At the start of the experiment in the bioreactor with the magnetic field, the biomass concentration was $1.7 \times 10^{11} \pm 0.7$ CFU/mL and it was $1.8 \times 10^{11} \pm 0.8$ CFU/mL for the experiment without the application of a magnetic field.

The largest amounts of Cr(VI), total Cr, and TOC that were removed in the experiments can be attributed to the effects generated by the magnetic field. This can be explained because in biological systems the action of magnetic fields is linked to the molecular structure of the membrane that has the potential to be influenced by these fields. An explanation for a general mechanism for the moderate intensity action of magnetic fields in biological systems involves the effect on the molecular structure of excitable membranes, which is sufficient to cause changes in the function of the specific ion channels found in these membranes. The rotation of the phospholipid molecules of the membrane can be affected by a magnetic field of moderate intensity due to their collective diamagnetic property, which explains the bioeffects attributed to these fields (Dini and Abbro, 2005).

2.3. Desorption of chromium

The desorption of chromium in synthetic effluent was evaluated at the end of the chromium removal and TOC experiments in the bioreactors with and without magnetic field application, since desorption can confirm the retention and

removal of chromium. Fig. 4a, 4b and 4c presents the concentrations of Cr(VI), Cr total, and TOC for experiment A (bioreactor with magnetic field), experiment B (bioreactor without magnetic field), and experiment C (Erlenmeyer flask) after 120 hr of evaluation of desorption of Cr(VI) in synthetic effluent by a mixed culture.

In Fig. 4a, it is observed that the concentrations of desorbed Cr(VI) were not significant, since the CONAMA resolution 430/2011 states that the maximum allowed value is 0.1 mg/L for Cr(VI) (BRASIL; CONAMA, 2018). The highest desorption of

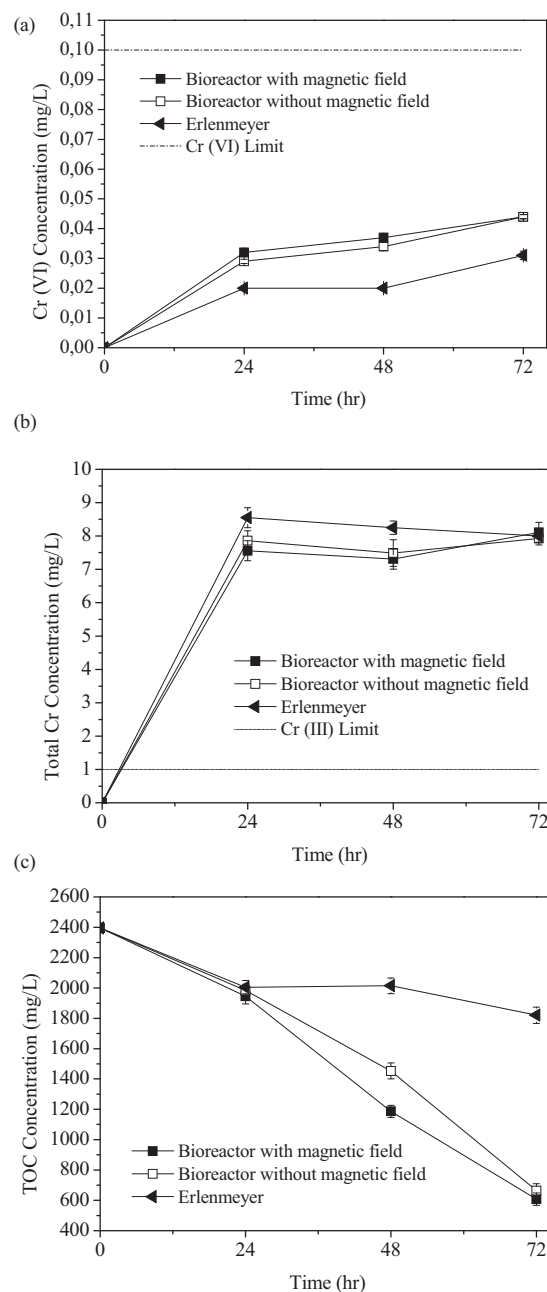


Fig. 5 – Desorption of Cr(VI) (a) and total Cr (b) in bioreactors with and without a magnetic field and in an Erlenmeyer flask at pH 4. (c) TOC concentrations during the desorption of chromium.

Table 1 – The pH values during the removal of Cr(VI) and the desorption of chromium in synthetic effluent.

Removal of Cr(VI)			
Time of effluent recirculation in the bioreactors (hr)	pH		
	BWMF	BWoMF	
0	7.0	7.0	
2	7.98	7.79	
4	8.14	7.90	
6	8.15	7.92	
8	8.18	8.01	
9	8.24	8.14	
24	8.81	8.58	
Desorption of Chromium			
Time of effluent recirculation in the bioreactors and rest of the effluent in the Erlenmeyer flask (hr)	pH		
	BWMF	BWoMF	Erlenmeyer flask
0	7.0	7.0	7.0
24	8.40	8.17	7.43
48	8.51	8.44	7.99
72	8.78	8.66	8.23
96	8.88	8.70	8.27
120	8.92	8.75	8.29

BWMF, bioreactor with magnetic field; BWoMF, bioreactor without magnetic field.

Table 2 – The pH values during the evaluation of chromium desorption in synthetic effluent with pH 4.

Chromium desorption			
Time of effluent recirculation in the bioreactors and rest of the effluent in the erlenmeyer flask (hr)	pH		
	BWMF	BWoMF	Erlenmeyer flask
0	4.0	4.0	4.0
24	4.45	4.38	4.29
48	6.65	5.45	4.13
72	6.28	6.24	4.24
BWMF, bioreactor with magnetic field; BWoMF, bioreactor without magnetic field.			

Cr(VI) in the synthetic effluent occurred in the bioreactors at 120 hr, with $0.05 \pm 7 \times 10^{-4}$ mg/L.

The desorption of total Cr was also evaluated during the 120 hr process for the same experiments. The total Cr concentrations are shown in Fig. 4b. For the total Cr, the concentrations were higher than those allowed by CONAMA resolution 430/2011, for Cr (III) the maximum value is 1.0 mg/L (BRASIL; CONAMA, 2018). The highest desorption of total Cr was 6.9 ± 0.3 mg/L after 48 hr in the bioreactor with a magnetic field.

As well as evaluating the desorption of chromium, the removal of TOC was also evaluated during the 120 hr process. Fig. 4c shows the TOC concentrations for the bioreactors with and without a magnetic field and in an Erlenmeyer flask. The highest removal of TOC occurred in the bioreactor with a magnetic field during 120 hr, with the concentration reduced from 2479 ± 29.7 to 575 ± 53.7 mg/L.

It was found that in the Erlenmeyer flask the removal of TOC was lower compared with the bioreactors, since the concentration was reduced from 2479 ± 29.7 to 1181 ± 49.5 mg/L. It is assumed that this occurred due to the influence of the process conditions and the stress generated in the cells of the microorganisms by the bioreactors. The bioreactors had a greater influence on the process that removed TOC, where the microorganisms were able to raise the pH faster due to the formation of bicarbonate. Table 1 shows the pH values during the removal of Cr(VI) from the synthetic effluent and during the desorption process of chromium in the new synthetic effluent.

The viable cell count was performed at the beginning and at the end (120 hr) of the period established for the evaluation of desorption of chromium in the synthetic effluent. The results are biomass concentrations of $1.3 \pm 0.8 \times 10^{11}$ CFU/mL with the application of a magnetic field, $1.5 \times 10^{11} \pm 0.5$ CFU mL⁻¹ without a magnetic field, and $2.3 \times 10^{11} \pm 0.8$ CFU mL⁻¹ in the Erlenmeyer flask. At the start of the experiments the biomass concentrations were $1.5 \times 10^{11} \pm 0.8$ CFU mL⁻¹ in the

bioreactor with a magnetic field, $1.6 \times 10^{11} \pm 0.8$ CFU mL⁻¹ in the bioreactor without a magnetic field, and $3.2 \times 10^{11} \pm 0.7$ CFU mL⁻¹ in the Erlenmeyer flask. It can be seen that the biomass concentration remained at the same order of magnitude for all the experiments.

With the pH of the synthetic effluent adjusted to 4 in the evaluation of the desorption of chromium in new synthetic effluent, the Cr(VI), total Cr, and TOC concentrations for experiments D–F are visualized in Fig. 5a, b and c.

From Fig. 5a, it can be seen that the highest desorption of Cr(VI) in the synthetic effluent occurred in the bioreactors at 72 hr, with $0.04 \pm 7 \times 10^{-4}$ mg/L of Cr(VI). The concentrations of Cr(VI) that were desorbed were not significant in comparison with the CONAMA resolution 430/2011 which states a maximum value of 0.1 mg/L (BRASIL; CONAMA, 2018).

The desorption of total Cr was also monitored for the same process conditions (Fig. 5b). The highest desorption occurred in the Erlenmeyer flask at 24 hr, with 8.5 ± 0.3 mg/L of total Cr. The concentrations of total Cr were above that allowed by CONAMA resolution 430/2011, which is 1.0 mg/L of Cr(III) (BRASIL; CONAMA, 2018).

The removal of TOC was observed during the desorption of chromium in the synthetic effluent, as shown in Fig. 5c. The highest removal of TOC occurred in the bioreactor with a magnetic field at 72 hr, with the concentration reduced from 2395 ± 21.2 to 608 ± 40.7 mg/L.

Microorganisms were able to raise the pH faster in the experiments in the bioreactors. It was observed that in the desorption with pH 4, the pH helped with the removal of TOC. When microorganisms were able to raise pH, this improved the removal of TOC. It is therefore assumed that the microorganisms were able to consume acid, and this led to more TOC being removed, thus these conditions are clearly favorable for the removal of TOC. Table 2 shows the pH values during the evaluation of chromium desorption.

The viable cell count was performed at the beginning and at the end (72 hr) of the period established for the evaluation of chromium desorption in synthetic effluent. The results are presented in Table 3.

The same order of magnitude for the biomass concentration is observed in all experiments. In the process of cationic sorption, the pH has an important role because it influences the chemical speciation of the metal in solution and the ionization of chemically active sites in the sorbent. Thus, in sorption processes the net load of the sorbent surface can perform a decisive function and the characterization of the protonation/deprotonation behavior of the sorbent materials in aqueous media can be favorable in the clarification of the sorption mechanism (Belattimania et al., 2015). One of the parameters that interferes the most in the biosorption process is the pH of the solution (Dönmez and Aksu, 2002) since the pH strongly influences solubility and adsorption capacity (Akkaya and Özer, 2005).

Table 3 – Colony count for chromium desorption experiments at pH 4.

Time (h)	Bioreactor with magnetic field	Bioreactor without magnetic field	Erlenmeyer flask
	Number of Colonies (CFU/mL)	Number of Colonies (CFU/mL)	Number of Colonies (CFU/mL)
0	$(7.8 \pm 0.7) \times 10^{11}$	$(8.0 \pm 0.9) \times 10^{11}$	$(8.8 \pm 0.7) \times 10^{11}$
72	$(6.8 \pm 0.7) \times 10^{11}$	$(7.3 \pm 0.5) \times 10^{11}$	$(8.0 \pm 0.9) \times 10^{11}$

The results of the minimal desorption of Cr(VI) in aqueous suggest that the biological treatment of industrial effluents, so they can be discharged, is a highly efficient method.'

3. Conclusion

The results indicated that in the presence of a magnetic field more chromium and TOC were removed in comparison with the experiments without a magnetic field.

In the presence of a magnetic field, $7.1\% \pm 0.1\%$ more Cr(VI) was removed after 9 hr of recirculation of the synthetic effluent, and $27.3\% \pm 0.2\%$ and $8.5\% \pm 0.15\%$ more total Cr and TOC were removed, respectively, during 24 hr of recirculation of the synthetic effluent.

The highest desorption occurred in the Erlenmeyer flask at 24 hr and with an initial pH 4.0, with 8.5 ± 0.3 mg/L of total Cr. In the chrome desorption process at initial pH 4.0, slower carbon consumption was observed at the beginning indicating a preadaptation of the culture to the new pH condition. The desorbed Cr(VI) concentrations were below 0.1 mg/L (limit established by Brazilian legislation) in both experiments with different initial pH.

The viable cell count of the mixed culture in the chromium removal and desorption experiments indicated that the culture was not influenced by the presence of the magnetic field or chromium.

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