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Adsorption of hexavalent chromium in a continuous stirred tank using exhausted wheat stubble immobilized in sodium alginate

Adsorción de Cromo hexavalente en un Tanque Agitado Continuo Utilizando Rastrojo de Trigo Agotado Inmovilizado en Alginato de Sodio

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Abstract

Agricultural and agro-industrial waste are good adsorbents of heavy metals, whether used naturally, pretreated or immobilized in other biopolymers, due to their content of functional groups with positive and/or negative charges. In addition, they are characterized for being biodegradable and for their compatibility with other materials, and for their opportunity of reuse for the design of alternative technologies for the treatment of water contaminated with heavy metals, for example: cadmium (Cd), chromium (Cr), lead (Pb), among other metals, with negative impact on society and the environment. In this sense, the objective of the present work was to evaluate the adsorption capacity of hexavalent chromium, Cr(VI), by using three organic adsorbent materials (derived from residual materials from the production of *Pleurotus djamor*) and immobilized on alginate in continuous adsorption processes to evaluate the adsorption capacity of Cr(VI) on the adsorbents. For this purpose, the adsorption capacity of chromium ions in aqueous phase in a glass tank (glass reactor) with a controllable stirring system was evaluated, as well as the rate of Cr(VI) increase and the adsorption load of the metal on the adsorbents. The results show a better adsorption capacity on the adsorbent composed of depleted wheat substrate and immobilized on sodium alginate. In relation to the lowest Cr(VI) rate of increase in the tank volume, it was 0.1251 and 0.0072 mg Cr(VI) min^{-1}, respectively, 60 and 5 mg L^{-1} of Cr(VI) in the feed stream to the tank. Both results for depleted and immobilized substrate in sodium alginate. Finally, for the same adsorbent, the adsorbent loading capacity was higher. The adsorbents preliminarily analyzed showed good adsorption capacity.

Keywords: Chromium absorption, modeling, agro-industrial and agricultural wastes, continuous Cr(VI).

Introduction

In recent years, removal of heavy metals from aqueous solution has received considerable attention by health and environmental organizations around the world (Duan et al., 2020; M. Li et al., 2023). However, new procedures are now required to treat environmental systems contaminated with heavy metals, see for example, (Sarker et al., 2023). The priority metals for the world's environmental and health protection organizations are cadmium (Cd), lead (Pb), arsenic (Ar) and hexavalent chromium Cr(VI) (H. Li et al., 2021). This last metal is carcinogenic and mutagenic for humans. In contaminated sites, e.g. with hexavalent chromium, the common concentrations of this metal found in typical wastewaters are 50 - 100 mg L^{-1} (Thiripelu et al., 2024a). However, different concentrations of Cr(VI) in wastewater have been reported in different industrial processes (see Table 1). Because of the problem caused by the presence of this metal in the environment, the removal of Cr(VI) from the effluents of various industries is required (anthropogenic activities). In Table 2, some of the classical methods or techniques for the treatment of water contaminated with chromium are reported. These have advantages and disadvantages; however, the adsorption or bio-adsorption process is one of the most widely used to remove Cr(VI) due to the use of natural adsorbents, agricultural and agro-industrial wastes (Simón et al., 2022). Finally, the aim of these techniques is to reduce the concentration of chromium to the value required by the standard, that is, to reduce the concentration of chromium to the value required by the standard, according to the United States Environmental Protection Agency (USEPA) (Adams & Garman, 2024), for example, the concentration of chromium in drinking water has

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been regulated with a maximum allowable level of 0.1 mg L^{-1} for total chromium or value of 0.000050 g L^{-1} set by World Health Organization (WHO) (Bharagava & Mishra, 2018; Kinuthia et al., 2020).

Table 1. *Different industrial processes that generate water contaminated with hexavalent chromium*

Industries	Reference
Electroplating:	(Suksabye et al., 2008; Worku et al., 2023)
Column study, electroplating wastewater	
Pigment manufacture:	(Gurgel et al., 2009)
Using cellulose and manganese oxides	
Leather tanning:	(Codreanu (Manea) et al., 2024; Hartati et al., 2024; Khatun et al., 2024)
For tannery sludge, electrocoagulation, extraction	
Metal finishing: green technology	(Xie, 2024)

Table 2. *Classical and alternative processes (methods or techniques) for the treatment of water contaminated with heavy metals.*

Industries	References
Chemical reduction:	(de Oliveira Marques Neto et al., 2024)
Magnetic composite film	
Precipitation:	(Misganaw et al., 2024)
Chemical precipitating agents	
Evaporation:	(Hamann et al., 2024)
Evaporation reactions	
Ion Exchange:	(Balram & Kaith, 2024; Thiripelu et al., 2024b)
Using agar-polyvinyl alcohol, ion-exchange	
Membrane separation:	(Bin Darwish & AlAlawi, 2024)
ultrafiltration	
Pyrolysis method:	(Philip et al., 2024)
Using reduced graphene oxide-zinc oxide composite	
Photochemical reduction:	(Long et al., 2020)
photocatalysts	
Adsorption:	(I. H. Ali et al., 2019; Fisher & Vreugdenhil, 2022; Islam et al., 2020)
Bio-polymeric beads made from bagasse, Activated Carbon, activated Carbon.	
Bioremediation (sulfate reducing bacteria: biological metabolic	(Cheung & Gu, 2007)
or non-metabolic process	
Reduction process:	(Peña-Caballero et al., 2016; Yang et al., 2017)
Sulfate-reducing bacteria	

To achieve a quantitative understanding of the adsorption mechanism and continuous processes the chromium onto immobilized exhausted wheat stubble in a continuous stirred tank reactor in this study, a series of experiments are conducted to obtain information about the adsorption phenomena. It is assumed that the temperature (27 °C) and pH (<2) will be constant. The research studies include the construction of adsorption

equilibrium isotherms; batch adsorption kinetics and adsorbent loading in a continuous stirred tank as a simple approach by using experimental observations with the least squares technique to estimate the isotherm, kinetics and adsorbent loading parameters (see Figure 1.). Therefore, specifically in this work the objective was to evaluate the adsorption capacity of Cr(VI), by using three organic adsorbent materials (derived from residual materials from the production of *Pleurotus djamor*) and immobilized on sodium alginate in continuous adsorption processes to evaluate the adsorption capacity of Cr(VI) on the adsorbents (see Figure 1D).

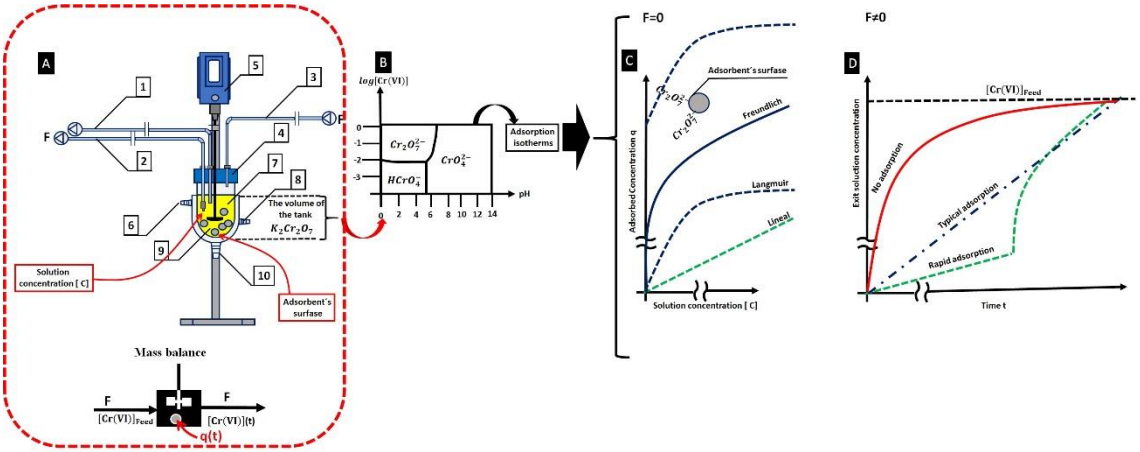

Figure 1. Schematic diagram of a continuous stirred tank (A) and adsorption isotherms (B): batch (C), and continuous (D).

Source: Own elaboration.

Background and Theory

Different scientific references have been reported to describe the modeling of the adsorption process in stirred tanks with continuous feed, that is, maintained at a constant volume (Parniske et al., 2024; Sarioglu Cebeci & Guler, 2024; Wosu Chimene Omeke et al., 2024). Then, to model the dynamics of Cr(VI) concentration in the aqueous phase in a continuous operation mode, the following mass (material) balances applied to the tank (see Figure 1A) are considered in the equations below.

According to the scientific evidence, the mass balance in the tank is given in Equation (1) for adsorption in a Continuous Stirred Tank (ACST),

$$\frac{d(\epsilon \cdot V \cdot [Cr(VI)])}{dt} = F \cdot ([Cr(VI)]_{Feed} - [Cr(VI)]) - \frac{d((1-\epsilon) \cdot V \cdot q)}{dt} \quad (1)$$

Where V is the volume of the tank (L), [Cr(VI)]and $[Cr(VI)]_{Feed}$ are the solute concentrations in the effluent and the feed (mg L^{-1}), respectively, F is the feed rate (L min^{-1}), and q is the adsorbed solute concentration (mg L^{-1}). A similar mass balance on the adsorbent gives

$$\frac{d((1 - \cdot\epsilon) \cdot V q)}{dt} = V \cdot r \quad (2)$$

Remark for common adsorption (abscissa and ordinate)

The analysis of adsorption is based on equilibrium (adsorption isotherms: the abscissa gives the solute concentration in the solution (units of mass of the solute (Here Cr (VI)) per volume of solution). The ordinate gives the solute concentration on adsorbent´s surface (units of mass of solute per mas of adsorbent)) and mass balance (see Figure 1C).

For the above equations, r is the rate of adsorption per volume of tank. According to Figure 2, we know the mechanism responsible for the kinetics of adsorption. Two limiting mechanisms are common:

Definition 1 (Abbasi et al., 2023; Paul A. Belter et al., 1988). Adsorption is controlled by diffusion from the solution to the adsorbent:

$$r = k \cdot a([Cr(VI)] - [Cr(VI)]^*) \quad (3)$$

where k is a mass transfer coefficient, a is the surface area of adsorbent per tank volume, and $[Cr(VI)]^*$ is a hypothetical concentration in the solution which would be in equilibrium with the adsorbent.

Definition 2 (Abbasi et al., 2023; Paul A. Belter et al., 1988). Adsorption is controlled by diffusion and reaction within the adsorbent particles.

$$\mathrm{r} = \sqrt{\mathrm{D\kappa}} \cdot \mathrm{a}([\mathrm{Cr(VI)}] - [\mathrm{Cr(VI)}]^*) \quad (4)$$

This is generally associated with the nature of the functional groups present in the materials used as adsorbents. Where the assumptions are represented by empirical and/or theoretical models (Sarioglu Cebeci & Guler, 2024). Figure 2 shows an empirical sketch of a sodium alginate bead (a natural polysaccharide, which consists of abundant hydroxyl (ROH) and carboxyl (hydroxyl and carboxyl, –COOH) groups, has been widely reported as the raw material for the adsorption of heavy metals from aqueous solutions (Gao et al., 2020; Lach & Okoniewska, 2024; Sun et al., 2021; Yasir et al., 2022) illustrating its nature on the surface. For this study, the immobilization of spent wheat residues from a mushroom production process.

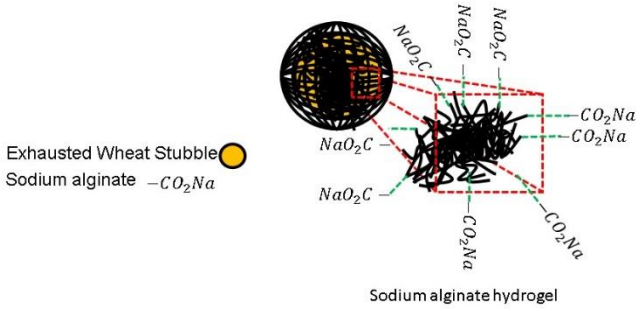

Figure 2. Scheme 1. (for more details, please consult (Tian et al., 2024)*)*

Source: Own elaboration.

Now, if it is considered that the volume in the tank remains constant in Eq. (1) to find the adsorbent loading q (the research objective in this contribution), then, if the equation (1) is integrated analytically with the result in equation (5):

$$\mathrm{q} = \mathrm{q}_0 + \frac{F}{(1-\epsilon)V}\left([\mathrm{Cr(VI)}]_{\mathrm{Feed}} \cdot t - \int_{t_0=0}^{t=t} [\mathrm{Cr(VI)}]dt\right) - \left(\frac{\epsilon \cdot V}{(1-\epsilon)\cdot V}\right)[\mathrm{Cr(VI)}(t)] \quad (5)$$

where $(1-\epsilon)\cdot V$ is the volume of liquid in the tank, which at $t = 0\ hr$, the concentration of hexavalent chromium is zero, i.e., $t = t_0 = 0\ hr$; $[Cr(VI)(t)] = 0\ g\ L^{-1}$, $\epsilon \cdot V$ is the volume occupied by adsorbent and in tank both in L. and q_0 is the initial adsorbent loading.

Remark for Eq. (5). In Eq. (5) q values, e.i., adsorbent loading can be found by numerical integration. For example, using numerical integration in MatLab (MathWorks) or Octave (A. J. Ali & Abbas, 2022): (see Eq. (6))

$$\text{Create the function } f([\text{Cr(VI)}]) = \text{Eq. (5)}$$
$$fun = @([\text{Cr(VI)}])Eq.(5) \quad (6b)$$
$$\text{Evaluate the integral from } [\text{Cr(VI)}] = [\text{Cr(VI)}]_{t=0} \text{ to } [\text{Cr(VI)}] = [\text{Cr(VI)}]_{t=f} \quad (6c)$$
$$q = integral(fun, [\text{Cr(VI)}]_{t=0}, [\text{Cr(VI)}]_{t=f}) \; or \; q = integral(initial, final) \quad (6d)$$

Based on equation (1), it is considered that there is no adsorbent mass, e.i., $\frac{\mathrm{d}((1-\epsilon)\cdot \mathrm{V}\cdot \mathrm{q})}{\mathrm{dt}} = 0$, then, the mass balance is as equation (7)

$$\frac{\mathrm{d}(\epsilon \cdot \mathrm{V} \cdot [\mathrm{Cr(VI)}])}{\mathrm{dt}} \equiv \frac{\mathrm{d}(\mathrm{v} \cdot [\mathrm{Cr(VI)}])}{\mathrm{dt}} = \mathrm{F} \cdot ([\mathrm{Cr(VI)}]_{\mathrm{Feed}} - [\mathrm{Cr(VI)}]) \quad (7)$$

In continuous regime, it is considered constant volume in the tank if the mass inflow and outflow is equal, then from Equation (7) we obtain Equation (8).

$$\frac{\mathrm{d}([\mathrm{Cr(VI)}])}{\mathrm{dt}} = \beta \cdot ([\mathrm{Cr(VI)}]_{\mathrm{Feed}} - [\mathrm{Cr(VI)}]) \quad (8)$$

where $\beta \equiv \mathrm{F/v} \in \mathbb{R}_+$

$$\underbrace{\frac{d([Cr(VI)])}{dt}}_{mg\,L^{-1}h^{-1}} - \underbrace{\beta}_{L\,min^{-1}L^{-1}} \cdot \underbrace{[Cr(VI)]}_{mg\,L^{-1}} = \underbrace{\beta}_{L\,min^{-1}L^{-1}} \cdot \underbrace{[Cr(VI)]_{Feed}}_{mg\,L^{-1}} \quad (9)$$

The solution of Equation (9) in equation (10)

$$[\mathrm{Cr(VI)}] = [\mathrm{Cr(VI)}]_{\mathrm{Feed}}\left(1 - \exp(-\beta \mathrm{t})\right) + [\mathrm{Cr(VI)}_0]\exp(-\beta \mathrm{t}) \quad (10)$$

Now, it if t = ∞

$$[\mathrm{Cr(VI)}] = [\mathrm{Cr(VI)}_0] \quad (11)$$

The result in Equation (10) models the Cr(VI) concentration in the tank volume at any instant of time t. Then, when operating the tank in a continuous regime with feed and outlet chromium equal to $[Cr(VI)]_{Feed}$ and $[Cr(VI)]$, therefore, if t is infinite ($t \to \infty$), equation (12) is satisfied, i.e., the maximum Cr(VI) concentration in the tank volume will be the feed concentration see the curve trajectory in red in Figure 1D).

$$\|[Cr(VI)(t)]\| \leq \|[Cr(VI)]_{Feed} = Cte.\| \quad (12)$$

With $[Cr(VI)(t)]$ and $[Cr(VI)]_{Feed} \in \mathbb{R}_+$.

Material and Methods

Generation of wheat stubble exhausted residues

Wheat stubble residues from the production of *Pleurotus djamor* were used (the reader is referred to the source (Arredondo et al., 2023) for further information), briefly:

Propagation and production of the fungus

Three hundred grams of sorghum grain (*Sorghum vulgare*) were placed in polypropylene bags with 225 mL of potable water and sterilized in an-autoclave at 121 °C for 15 min (Ecoshel® CVQ-B35L autoclave). Once room

temperature was reached in the bags, they were inoculated with mycelium previously grown on PDA (Potato Dextrosa Agar) medium. In the production stage, to regulate the pH, a mixture of quicklime (CaO) and gypsum ($CaSO_4 \cdot 2H_20$) (3:1) was prepared and added in the proportion of 70 g per kg of stubble, then 5 L of water was added and left to stand for 15 minutes, then sterilized for 15 min at 121 °C (Ecoshel ® CVQ-B35L autoclave). Once the mixture was ready, the stubble was inoculated, and an opening was made and subsequently plugged with a gauze (model FN17100) for mycelium oxygenation. It was incubated in the dark for 15 days at 25 °C.

Exhausted wheat stubble

The exhausted wheat stubble was washed twice with sterile deionized distilled water (sterilization for 20 min, 15 lbs.121 °C) and dried in an oven at 60 ± 2 C for 24 h.

Preparation of the chromium solution

Chromium solutions of 1000 mg L^{-1} were prepared by dissolving 0.245 mg $K_2Cr_2O_7$ in 1 L of double-distilled water. The required operational solutions of different concentrations (5-60 mg L^{-1}) were prepared by proper dilution of the stock solution.

Entrapment in calcium alginate (Preparation of the adsorbent)

A 2% (w/v) slurry of sodium alginate was prepared in hot (60 °C), sterile, deionized, distilled water. After cooling, a constant amount (2%, w/v) of exhausted wheat stubble (biomass) were added and stirred. The alginate–biomass slurry was then extruded into 50 mM $CaCl_2 \cdot 2H_2O$ for polymerization and bead formation. The resultant beads were of 3 mm diameter and were cured in the polymerizing medium for 5 h (Lilhare et al., 2021).

Results and discussion

Residual Cr(VI) concentration in tank without adsorbent Cr(VI) accumulation reference in tank)

The results of Cr(VI) accumulation in the tank operating volume for a constant linear feed flow (9×10^{-3} L min^{-1}) and constant Cr(VI) concentration (60 and 5 mg L^{-1}) are shown in Figure 1. The values obtained for Cr(VI) concentrations for a continuous feed time of 150 min were 36.7 and 3.12 mg L^{-1} for the feed stream and 60 and 5 mg L^{-1} for the tank outlet stream, respectively. This This considers perfect mixing conditions (200 rpm, working volume of 0.15 L, temperature of 27 °C, and adsorbent mass of m=0 g). The results obtained in this preliminary experimental evidence confirm that, for a very large time, i.e., the time tends to infinity ($t \rightarrow \infty$), the chromium concentration in the tank will be the concentration of the metal in the feed stream ($[Cr(VI)]_{Feed}$). Finally, the dynamics of chromium in the tank is equal to the discharge and will depend on i) the tank design variables and ii) the operating variables. In addition, for the purpose of the investigation, also iii) the nature of the adsorbent and the loading (mass) these assumptions are widely verified in the scientific literature (Hajiahmadi et al., 2024; Melo et al., 2024; Paul A. Belter et al., 1988).

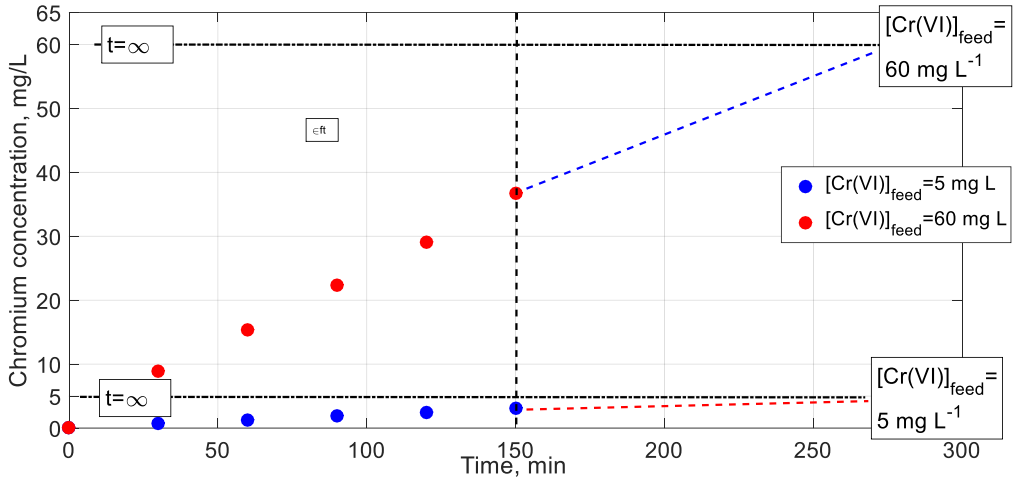

Figure 3. Dynamics of residual Cr(VI) concentration in tank without adsorbent at constant pH (2), temperature (27 °C), agitation (200 rpm), volume (0.15 L), and linear Cr(VI) feed (9 mL min with 5 and 60 mg L-1).

Source: Own elaboration.

Adsorption of chromium (VI) from the synthetic aqueous solution in a continuous stirred tank

The results of the continuous Cr(VI) adsorption studies on

i) sodium alginate (SA as a control),

ii) immobilization of substrate (wheat stubble) on sodium alginate (S-SA),

iii) depleted substrate and sodium alginate are shown in Figure 3. In the three experimental treatments, in relation to control and to the accumulation of chromium mass in the tank volume (see Figure 2, same markers in Figure 3) turn out to be low values, this is due to the corresponding adsorbent loading (m=mass= 9 g), i.e. chromium adsorption by SA, S-SA and EWS-SA. In addition, treatment iii) reports the lowest residual chromium concentration in the aqueous phase for the two metal concentrations.

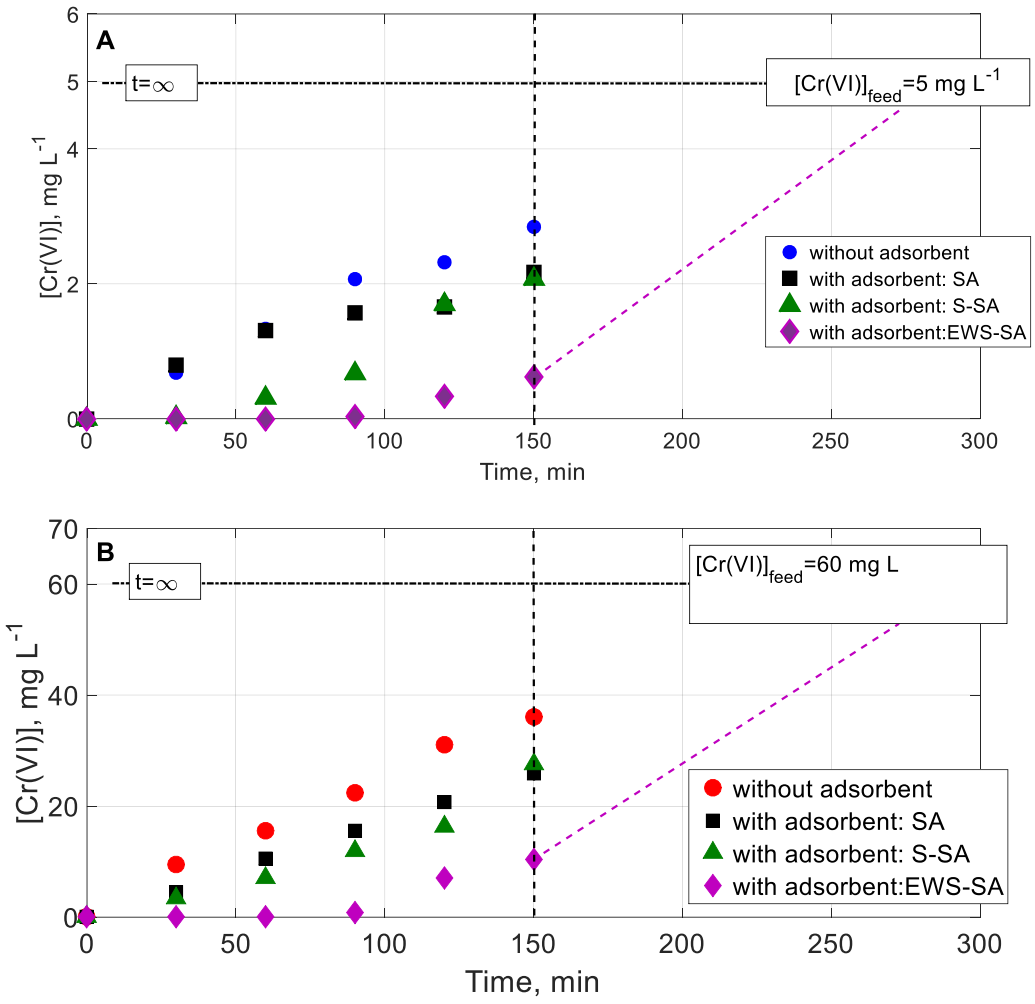

Figure 4. Adsorption of hexavalent chromium in a continuous stirred tank with different adsorbents (9 g wet weight with a 95.75% water content or 0.492 g of adsorbent) at pH (2), temperature (27 °C), agitation (200 rpm), volume (0.16 L), and linear Cr(VI) feed ($9x10^{-3}$ L min^{-1} with 5 and 60 mg L^{-1}) constant.

Source: Own elaboration.

Cr(VI) adsorption rate

The results of the removal rate of chromium ions on the adsorbent materials are shown in Table 3. These results correspond to the slope (rate of change=derivative=chromium concentration/time) of the experimental observations (see Figure 2). Which are low values for the slopes (in mg Cr(VI) min^{-1}) compared to the mass accumulation of the mental in the tank (without adsorbent) and the control (SA), as mentioned due to the materials used and immobilized on sodium alginate. In addition, using the exhausted wheat substrate from the *Pleurotus adjamor* production bioprocess improves metal removal in the aqueous phase in contrast to the other treatments. The latter due to the properties of SA, in this sense, due to the versatility of the biomaterial, different authors report adsorption values in batch and continuous (Tian et al., 2024). Furthermore, in this research the improvement of Cr(VI) removal with the residue used.

Table 3. Rate of increase of Cr(VI) concentration in the tank volume for the proposed adsorbents (see Figure 1).

	Adsorption tank without adsorbent	Adsorption tank with adsorbent	Adsorption tank with adsorbent	Adsorption tank with adsorbent
Adsorbent	-	SA	S-SA	EWS-SA
Operation time, Min	150	150	150	150
Feed, mL min^{-1}	9	9	9	9
Figure	3	4A-B	4A-B	4A-B
$[Cr(VI)]_{Feed}$	linear change rate, mg Cr(VI) min^{-1}	linear change rate, mg Cr(VI) min^{-1}	linear change rate, mg Cr(VI) min^{-1}	linear change rate, mg Cr(VI) min^{-1}
5 m L^{-1}	0.0189	0.013	0.015	0.0072
R^2	0.9831	0.9281	0.9020	0.9175
60 m L^{-1}	0.240	0.1741	0.1727	0.1251
R^2	0.9945	0.9990	0.9441	0.9305

Source: Own elaboration.

The experimental evidence is important at this stage of the research and are novel in relation to the laboratory system used for the development of the process, the substrates used and the versatility of sodium alginate to immobilize these materials (Bustos-Terrones, 2024; Farshidfar et al., 2023). Likewise, the results of batch (data not reported here) and continuous adsorption of chromium are key elements for continuous adsorption of the metal in packed bed columns.

Conclusions

The removal of hexavalent chromium in aqueous phase from synthetic solutions of this metal in continuous using a pyrex glass tank (Borosilicate glass) on wheat stubble exhausted from edible mushroom production processes (*P. djamor)* and immobilized in sodium alginate was improved. The value of the residual Cr(VI) concentration decreased from 0.1741 to 0.1251 mg Cr(VI) min^{-1} and 0.013 to 0.0072 mg Cr(VI) min^{-1}, respectively for 60 and 5 mg $L^{-1}$of chromium in the tank feed. That is, with respect to the control (SA). With these preliminary results, the Cr(VI) adsorption process will be designed in packed columns with the proposed adsorbents.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Supporting Information associated with to the development of numerical codes can be requested via E-mail (vicente.caballero@ugto.mx, and jl.zarate@ugto.mx).

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