04-005

REMOVAL OF CHROME DYES FROM WATER BY BIOSORPTION USING FISH WASTE

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The tannery industry was and continue to be a source of contamination for surface water bodies throughout the world. Its liquid discharges contain various dyes, some with heavy metals. The dyes in the water give it an unnatural color and make it harmful to the environment and to organisms that consume it. Previous studies have shown that different types of biomass, orange peel, rice hulls, algae, ground green tea leaves among others, can remove dyes from water. However, little has been studied about fish residues, since collagen is an important component within this residue, a promising adsorption capacity that should be studied is glimpsed. This study investigates the adsorption potential of different dyes by means of Tarpon (Prochilodus lineatus) scales. The dyes that were experimented with were: potassium chromate and potassium dichromate, which contain the element chrome in their composition. Exposing that the adsorption of dyes using fish scales is a passive and low-cost alternative that can be applied in different parts of the world with similar problems.

Keywords: Bioadsorption; collagen; dyes; heavy metals; safe water

REMOCIÓN DE TINTES DE CROMO DEL AGUA POR BIOADSORCIÓN USANDO RESIDUOS DE PESCADO

La industria de curtiembres fue y continúa siendo un foco de contaminación para cuerpos de agua superficiales en todo el mundo. Sus descargas líquidas contienen diversos tintes, algunos con metales pesados. Los tintes en el agua le otorgan un color no natural y la convierte en nociva para el medio ambiente y para los organismos que lleguen a consumirla. Estudios anteriores mostraron que, distintos tipos de biomasa, cáscara de naranja, cáscara de arroz, algas, hojas molidas de té verde entre otros, pueden remover tintes del agua. Sin embargo, existe poco estudiado sobre residuos de pescado, siendo el colágeno un importante componente dentro de este residuo se vislumbra una capacidad de adsorción prometedora que debe ser estudiada. Este estudio investiga el potencial de adsorción de diferentes tintes por medio de escamas de Sábalo (Prochilodus lineatus). Los tintes con los que se experimentó fueron: cromato de potasio y dicromato de potasio, mismos que contienen el elemento cromo en su composición. Exponiendo que la adsorción de tintes usando escamas de pescado, es una alternativa pasiva y de bajo costo, que puede aplicarse en diferentes partes del mundo con problemáticas similares.

Palabras clave: Bioadsorción; colágeno; tintes; metales pesados; agua segura

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1. Introduction

Water is an essential resource for life. Due to population growth and the increase in anthropogenic activities, it is essential to find a way to return it to the environment without degrading its quality (Ibáñez Hergueta, 2017). Water resources in growing and underdeveloped countries face unaddressed pollution problems, mainly due to the costs of implementing and maintaining treatment systems (Anastopoulos & Kyzas, 2015; Namasivayam & Sangeetha, 2006). It is estimated that around 90% of wastewater in developing countries is discharged without a treatment (Zaruma Arias et al., 2018). The preceding shows that industrial discharges are an essential source of degradation of the water quality available on earth.

Dyes impart color in the industry, particularly in textiles, paper, rubber, plastics, leather, cosmetics, pharmaceuticals, and the food (Chaparro et al., 2013; Varjani et al., 2020). Industrial effluents are composed of dyes that are discharged into bodies of water without prior treatment and / or control, degraded flora and fauna of aquatic ecosystems (Belpaire et al., 2015). The toxicity of dyes can even inhibit growth and cause cell deformation (Tkaczyk et al., 2020). In addition, it prevents aquatic plants from carrying out photosynthesis since light penetration is reduced (Mandal et al., 2009).

Some dyes are carcinogenic or have mutagenic levels. After transformation or degradation, others produce compounds such as aromatic amines, which can be toxic to the environment and risk the public health (Inforçato Vacchi et al., 2017; Maguire, 1992). Many countries, such as Bolivia, present contamination in their surface water bodies by dyes from the tannery industry (Escalera Vasquez et al., 2013). The tannery industry is characterized by using chromium compounds in its operations (Chávez Porras, 2010; Correa Delgado et al., 2013). Chromium is used in the tanning process because it can make the skin stable in a material such as leather, stopping its degradation (Correa Delgado et al., 2013). Bolivian tanneries emit liquid waste contaminated with chromium (Correa Delgado et al., 2013; Vargas Doria Medina & Amurrio Derpic, 2017). Water contaminated with chrome dyes used for irrigation can cause allergic reactions, ulcers, decreased immune system, kidney and liver damage, and even death (Chaparro et al., 2013; Lenntech, 2022; Namasivayam & Sangeetha, 2006). For this reason, it is essential to search for an effective, fast and sustainable removal method that can solve the existing problem around wastewater with chrome dyes.

Colorant removal is not an easy task. A large part of the dyes is of synthetic origin, highly soluble in water, and poorly biodegradable (Mansilla et al., 2001; Varjani et al., 2020). Currently, there is no single specific treatment due to the complex nature of these substances (Chaparro et al., 2013; Mansilla et al., 2001). There has been an increase in passive processes that use low-cost materials, such as orange peel, cotton, rice, pulverized study leaves, coconut shell, clay, and activated sawdust (Angulo Mercado et al., 2012; Jain & Sikarwar, 2008). In recent years, studies have confirmed that it is possible to remove dyes using theophylline, double-layered hydroxide, graphene oxide, shells, and algae (Anastopoulos & Kyzas, 2015; Angulo Mercado et al., 2012; Cervantes Tavera et al., 2018; Ramírez Llamas et al., 2015). Experiences such as Namasivayam & Sangeetha (2006), where removals greater than 90% of acid violet, methylene blue, carmine red, and carmine orange were obtained, using activated carbon from coconut fiber as an adsorbent. And even Bellatin et al. (2014) studied the ability to remove Yellow 57, Basic Blue 99, and Acid Red 18 hair dyes using ground green tea leaves.

Other studies have shown the adsorption capacity of fish scales to remove heavy metals from water, managing to remove lead, mercury, nickel, among others (Cuadros Evangelista & Viza Llenque, 2007; Delgado Huallpa, 2013; Quispe Auqui, 2017). The removal by scales is achieved by taking advantage of the percentage of collagen present in different fish species such as trout, sea bass, and tilapia (Guimarães Martins, 2009; Quintero & Zapata, 2017; Quispe Mendoza & Gutierrez Ramos, 2019; Serrano Gaona, 2011). Both collagen and chitosan are promising biopolymers due to their characteristics and comprehensive presence in nature (Vieira et al., 2018).

The present study proposes to use fish scales as a bioadsorbent to remove industrial effluents with chrome dyes. The chosen species is *Prochilodus lineatus*, commonly known as sábalo, present in the Plata Basin in Bolivia, Brazil, Paraguay, Uruguay, and Argentina (Van Damme et al., 2019; Volpedo et al., 2017). This research not only seeks to solve the existing problem in tannery discharges but also intends to do so by giving added value to the waste generated (scales) since they represent 30 to 70% of a fish (Toppe et al., 2018). The parameters that will be analyzed with special attention are the amount of adsorbent and the contact time. The adsorbent mass is essential to identify the quantity required to obtain a greater removal (Bellatin et al., 2014; Jain & Sikarwar, 2008; Ramírez Llamas et al., 2015). The contact time is also necessary when talking about adsorption since it seeks to obtain a more excellent removal in the shortest possible time (Jain & Sikarwar, 2008; López et al., 2007).

2. Objective

This research aims to evaluate the removal capacity of chrome dyes from aqueous solutions using tarpon scales as bioadsorbent.

3. Methodology

This section presents the methodology steps taken into account for the adsorption of potassium chromate and dichromate using tarpon scales. Figure 1 shows the diagram of the actions carried out for the experimentation.

Figure 1. Methodological scheme

Source: Own elaboration, 2022.

Figure 1 shows the scheme of the steps performed for the experimentation. These steps will be broken down throughout this section.

3.1. Fish scale collection

Scales of tarpon (Prochilodus lineatus) were collected. This species was selected because it is obtained mainly from the Pilcomayo River in Bolivia and because of the relative ease of extracting its scales (Van Damme et al., 2019). The scales were washed repeatedly with distilled water, dried in the sun, and refrigerated until use.

3.2. Determination of adsorption spectra of dyes

Potassium chromate and potassium dichromate were experimented with due to their wide use in the textile, wood, and tannery industries (González Pérez & Aportela Gilling, 2001; Valenteshop, 2019). The experiment was carried out in duplicate, and the most representative results were taken into account by Namasivayam & Sangeetha, 2006.

The analysis of the dyes studied was carried out by measuring the absorbance at their respective maximum wavelengths, which were obtained from the sweeps of the adsorption spectra of each dye at 20, 40, 60, 80, and 100 mg/L (Romero Cano, 2013).

3.3. Elaboration of calibration curves for potassium chromate and dichromate

To determine the concentration of each dye, a calibration curve was constructed using dye solutions in distilled water at known concentrations of 0, 20, 40, 60, 80, and 100 mg/L. The data was correlated according to equation (1) (Cuetocue et al., 2016; Ramírez Llamas et al., 2015).

$$C = k \cdot Abs + b \tag{1}$$

Where C is the concentration, Abs is the absorbance, *k* and *b* are the linear fit coefficients.

3.4. Experimental process of adsorption with fish scales

Synthetic waters of potassium chromate and dichromate were used for the adsorption process. Each solution had 250 ml of the contaminant at a concentration of 60 mg/L. The solutions were contacted with 5, 10, and 15 g of adsorbent. The solutions were taken to the magnetic stirrer at 400 rpm and a temperature of 25° C, collecting samples at 1, 3, 5, 24, 30, and 48 hours (Bellatin et al., 2014; Namasivayam & Sangeetha, 2006). The residual substance was analyzed spectrophotometrically by UV-visible using the supernatant after being centrifuged for 30 minutes at a 10,000 rpm (Namasivayam & Sangeetha, 2006; Romero Cano, 2013).

3.5. Data collection and analysis

The absorbance measurement was performed with the JENWAY 6305 UV/Visible spectrophotometer. The concentrations were obtained with the calibration curve for potassium chromate and potassium dichromate. The adsorption capacity is calculated by equation (2).

$$q_e = \frac{C_i - C_e}{m} \cdot V \tag{2}$$

Where q_e is the adsorption capacity in mg/g, C_i y C_e are the initial and equilibrium concentrations in mg/L. m is the mass of the adsorbent in grams, and V is the volume of the dye solution in liters (Romero Cano, 2013; Vieira et al., 2018). n the same way, the percentage of discoloration (%D) was calculated using equation (3) (Shah, 2014).

$$\%D = \frac{Abs_{inicial} - Abs_{final}}{Abs_{inicial}} \cdot 100\% \tag{3}$$

3.6. Determination of adsorption isotherm models

By means of sorption isotherms, the equilibrium established between the adsorbate in solution and the molecules adhered to the surface of the biosorbent can be represented (Romero Cano, 2013). Isotherms show us the amount of adsorbent needed for a certain amount of adsorbate (Jain & Sikarwar, 2008). The most common theoretical models are the Langmuir and

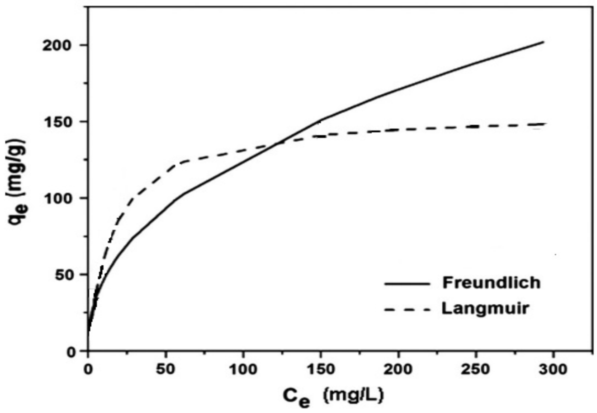
Freundlich models (Azari et al., 2020; Bellatin et al., 2014; Ramírez Llamas et al., 2015; Romero Cano, 2013).

Table 1. Isotermas de sorción

	Langmuir isotherm	**Freundlich isotherm**
	$q_e = \frac{q_{max} \cdot K_L \cdot Ce}{1 + K_L \cdot Ce}$	$q_e = K_F \cdot Ce^{\frac{1}{n}}$
Linearized model	$\frac{Ce}{q_e} = \frac{1}{q_{max}} \cdot Ce + \frac{1}{q_{max} \cdot K_L}$ **(4)**	$log\ q_e = \frac{1}{n} log\ Ce + log\ K_F$ **(5)**

Where from Table 1, K_L is the Langmuir adsorption constant, K_F is the Freundlich constant, q_{max} represents the maximum amount of dye that can be adsorbed per gram of adsorbent and n is related to the adsorption intensity (Jain & Sikarwar, 2008; Ramírez Llamas et al., 2015; Romero Cano, 2013). Figure 2 contains the theoretical behavior of the Langmuir and Freundlich isotherms.

Figure 2. Behavior of theoretical adsorption isotherms



Source: Avila et al., 2014

Figure 2 shows that in the Langmuir isotherm, the adsorbent becomes completely saturated as its slope decreases, while for the Freundlich isotherm the pores of the solid material are not filled when in contact with the contaminant molecules, having its slope without decrease (Avila et al., 2014).

4. Results

This section presents the results obtained from potassium chromate and dichromate adsorption with tarpon scales.

4.1. Fish scale collection

Tarpon scales were collected in local markets in the City of La Paz. They were rinsed with drinking water to remove impurities, and other fish remains. It was then rinsed with distilled water and placed in the sun to dry. They were in refrigeration until the moment of their use.

Figure 3. Tarpon scales

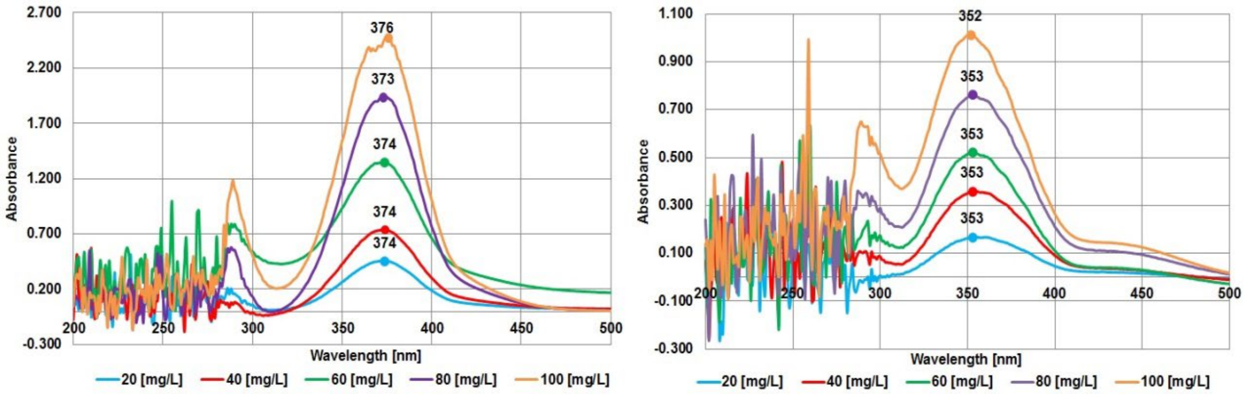
Source: Own elaboration based on Volpedo et al., 2017.

Figure 3 shows the collected, washed, and dried tarpon flakes. They are off-white and semi-transparent. They are roughly circular in shape, 1.5 cm in diameter, and remain hard to the touch.

4.2. Determination of adsorption spectra of dyes

A sweep of the substances studied was performed at 20, 40, 60, 80 and 100 mg/L. Which can be seen in Figure 4.

Figure 4. Adsorption spectra of the substances studied at different concentrations



a) Potassium chromate b) Potassium dichromate

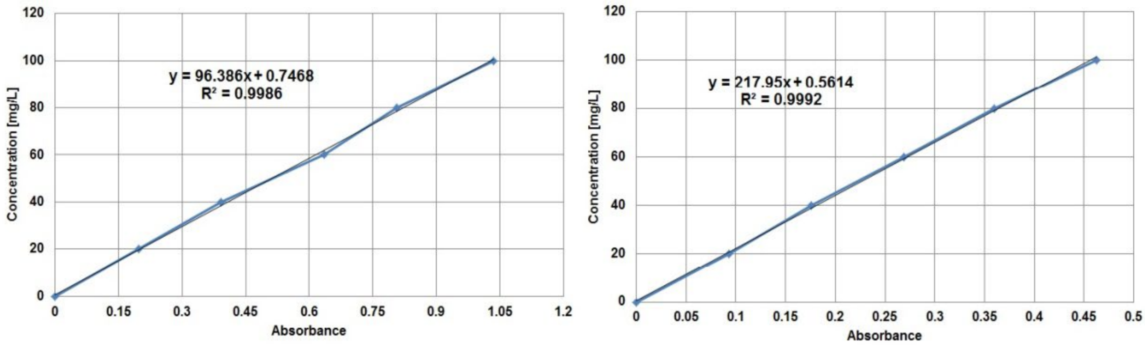
Source: Own elaboration, 2022.

Figure 4 shows the spectral scan of the pollutants studied. Where, the maximum wavelength was 374 nm for potassium chromate and 353 nm for potassium dichromate. These wavelengths were used for all the experimentation since they give us the absorbance of the contaminant with greater sensitivity.

4.3. Elaboration of calibration curves for potassium chromate and dichromate

The solutions were measured at 0, 20, 40, 60, 80, and 100 mg/L in the JENWAY 6305 UV/Visible spectrophotometer for the calibration curves.

Figure 5. Calibration curves Concentration vs. Absorbance



a) Potassium chromate b) Potassium dichromate

Source: Own elaboration, 2022.

Figure 5 shows the data scatter. According to equation (1), the fit coefficients for potassium chromate are k=96.386 and b=0.7468. And for potassium dichromate are: k=217.95 and b=0.5614.

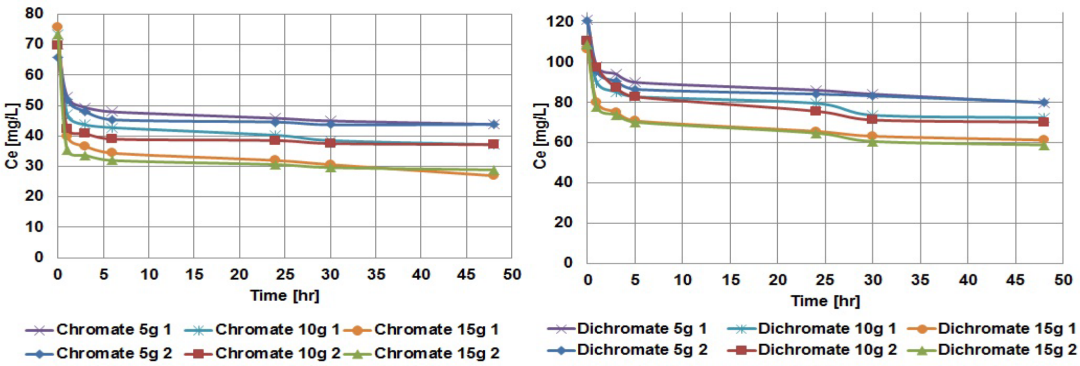
4.4. Experimental process of adsorption with fish scales

Different amounts of dry fish scales, 5, 10, and 15 g each, were contacted with 250 ml of the synthetic waters and in the same way with blank samples (distilled water + scales). The samples were placed on a magnetic stirrer at a temperature of 25°C. Absorbance data of the supernatant of the samples collected at 0, 1, 3, 5, 24, 30, and 48 hours were taken.

4.5. Data collection and analysis

Once the samples were collected and centrifuged, the absorbance of the supernatant was measured. The concentrations were calculated by substituting the absorbances in the calibration curves for the corresponding contaminant.

Figure 6. Equilibrium concentration vs. contact time



a) Potassium chromate b) Potassium dichromate

Source: Own elaboration, 2022.

Figure 6 presents the behavior of the concentration of the solutions over time. A pronounced downward slope is observed during the first hours that the scales contact the solutions. From hour 5 until the end of the experiment, the pitch continues to descend but is no longer very pronounced. The percentage of discoloration (%D) and the adsorption capacity (q_e) data were obtained, the ANOVA tables and the graphs of their effects that are presented in Table 2, were analyzed using the statistical program MiniTab 19.

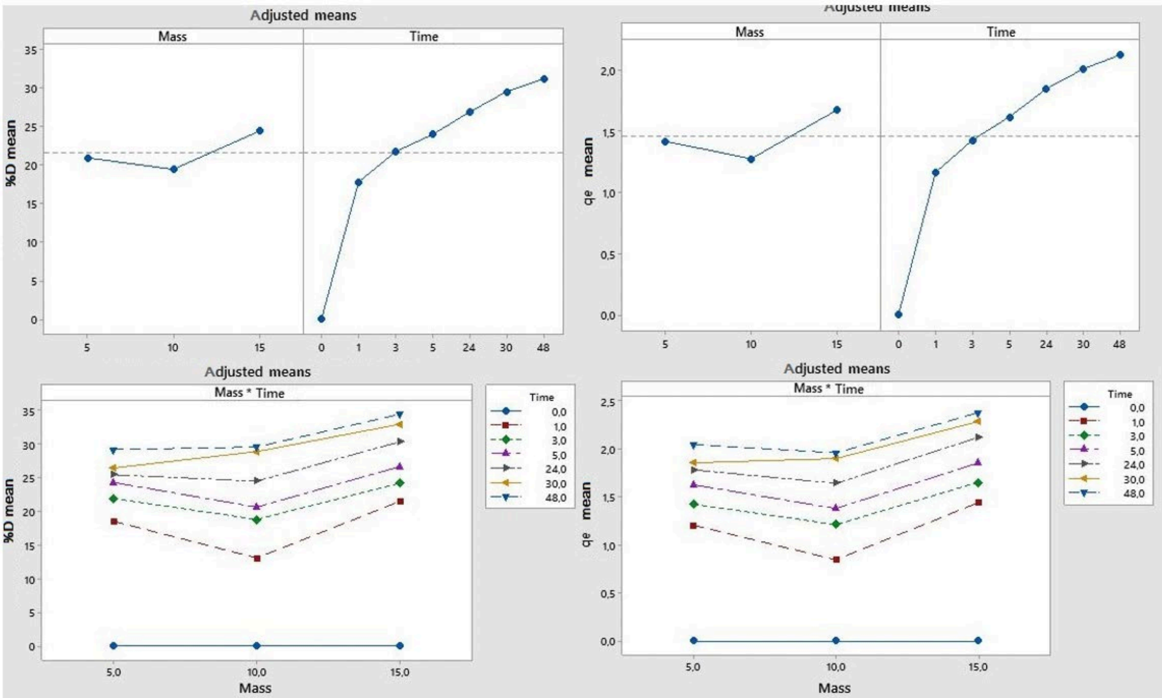
Table 2. ANOVA potassium chromate

	Source	DF	SC Adjust.	MC Ajust.	F Value	p Value
	Mass	2	181.05	90.527	25.78	0.000
	Time	6	3994.00	665.667	189.54	0.000
%D	**Mass*Time**	12	75.74	6.312	1.80	0.116
	Error	21	73.75	3.512		
	Total	41	4324.55			
	Mass	2	1.1459	0.57295	44.52	0.000
	Time	6	18.8484	3.14141	244.13	0.000
q_e	**Mass*Time**	12	0.2951	0.02459	1.91	0.093
	Error	21	0.2702	0.01287		
	Total	41	20.5597			

Source: Own elaboration, 2022.

Table 2 shows the analysis of variance for potassium chromate and the factors that were taken into account. The p-value shows us, both for the percentage of discoloration and the adsorption capacity (q_e), that the mass and time are significant. Since its p-value is less than 0.05. While the interaction of these factors is not significant, since there is a p-value of 0.116 for the %D and 0.093 for q_e.

Figure 7. Main Effects for Potassium Chromate

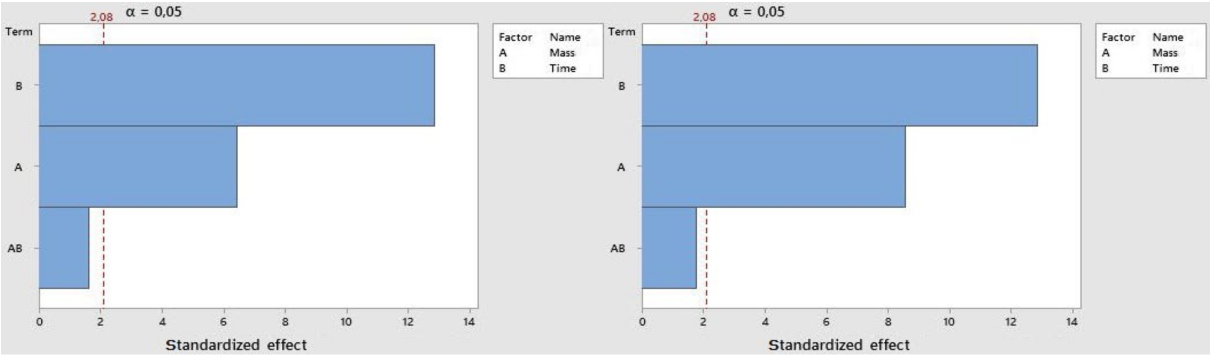


a) %D b) q_e

Source: Own elaboration, 2022.

Figure 7 shows that for potassium chromate the highest %D and highest q_e is obtained at a higher mass and with a longer contact time. This implies that a greater amount of bioadsorbent will be needed and more time will be needed to obtain good removal results. This is summed up in higher expenses and less water treated at a slower rate. The priority of the factors is shown in Figure 8.

Figure 8. Pareto charts for standardized effects for potassium chromate



a) %D b) q_e

Source: Own elaboration, 2022.

According to Figure 8, for both the %D and q_e main factor effects, mass and time are the most influential in the model, while their interaction is not. Which indicates that the control of the contact time and the mass have a higher priority at the time of experimentation. In the same way, the data on the percentage of discoloration and the adsorption capacity for potassium dichromate were obtained. Table 3 contains the ANOVA table of the model.

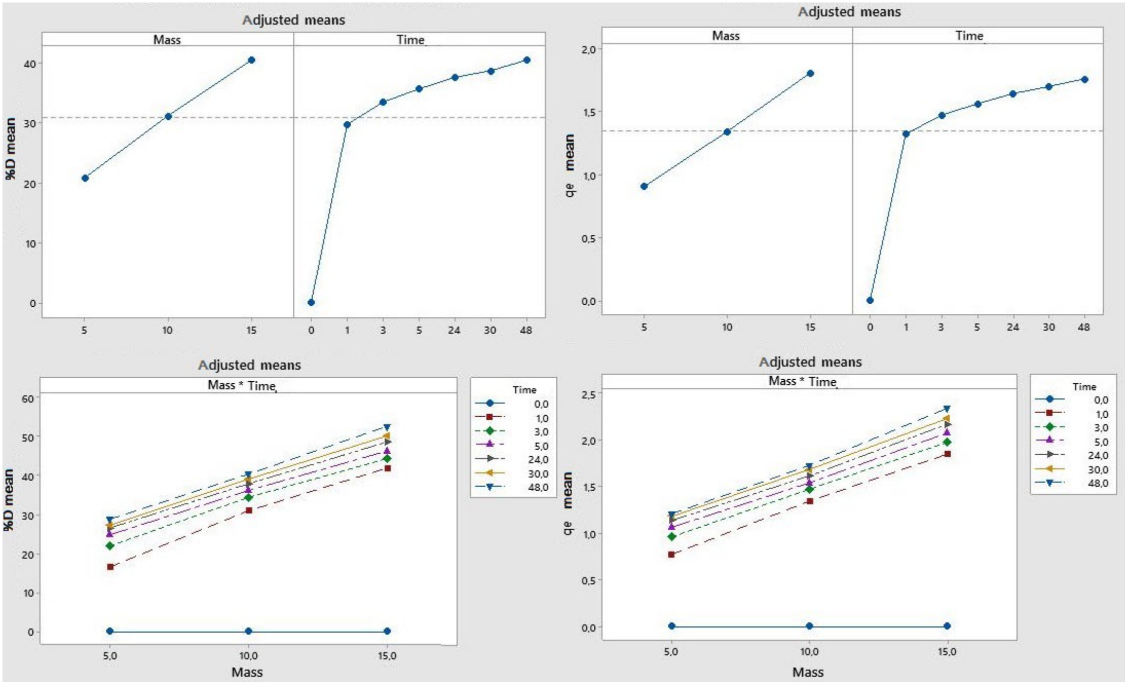
Table 3. ANOVA potassium dichromate

	Source	GL	SC Ajust.	MC Ajust.	Value F	Value p
%D	Mass	2	5.7000	2.85000	434.00	0.000
	Time	6	13.4926	2.24876	342.44	0.000
	Mass*Time	12	0.9662	0.08052	12.26	0.000
	Error	21	0.1379	0.00657		
	Total	41	20.2967			
q_e	Mass	2	2712.6	1356.29	475.02	0.000
	Time	6	7093.5	1182.26	414.07	0.000
	Mass*Time	12	465.2	38.76	13.58	0.000
	Error	21	60.0	2.86		
	Total	41	10331.3			

Source: Own elaboration, 2022.

Table 3 shows that both for the percentage of discoloration and adsorption capacity the main effects, mass and time, as well as their interaction is significant. It is interpreted in this way since the p-value for all factors is less than 0.05. Figure 9 shows the graphs for potassium dichromate. Both of the main effects and their interaction

Figure 9. Main Effects for Potassium Dichromate

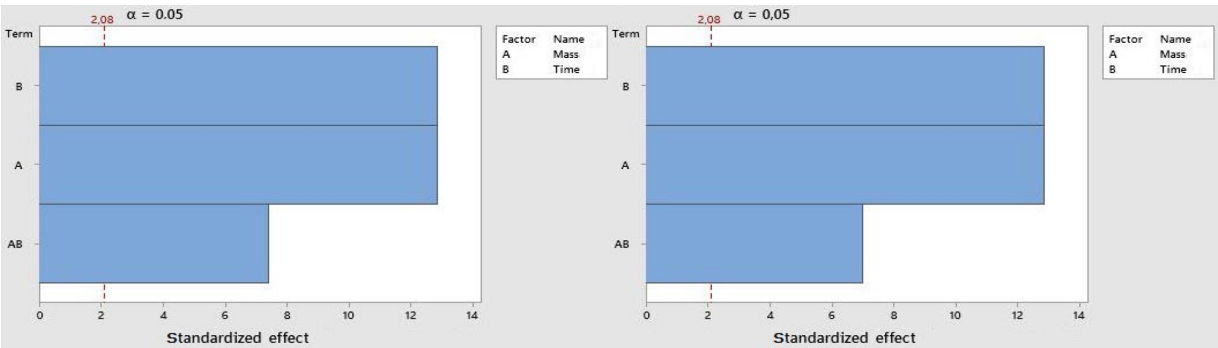


a) %D b) q_e

Source: Own elaboration, 2022.

Figure 9 shows that for potassium dichromate, the highest %D and q_e are obtained with a greater mass of adsorbent as time passes. And the interaction of the time-mass factors, it is observed that the higher %D and higher q_e are obtained in an ascending linear way, relating the amount of adsorbent mass and the contact time between adsorbate and adsorbate.

Figure 10. Pareto charts for standardized effects for potassium dichromate



a) %D b) q_e

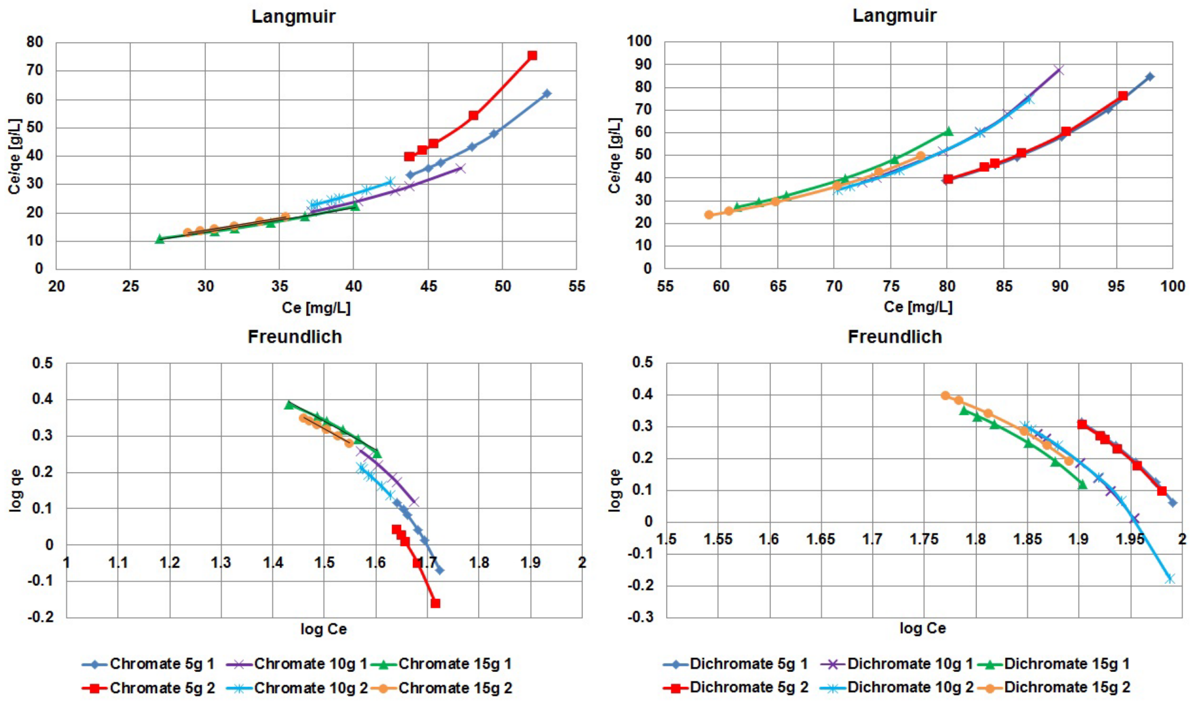
Source: Own elaboration, 2022.

Figure 10 shows that there is an equal priority between time and mass control, for the %D and the qe. Regarding the time-mass interaction, although it is lower than the priority of the main factors, at a confidence interval of 95% it is still a priority parameter. In other words, it still needs to be regulated to obtain good removal results.

4.6. Determination of adsorption isotherm models

Data for both adsorption isotherm models were fitted using equations (4) and (5).

Figure 11. Adsorption isotherms of fish scales in potassium chromate and dichromate



a) Potassium chromate b) Potassium dichromate

Source: Own elaboration, 2022.

Figure 11 shows the trend of the data already adjusted to the isotherms, in the upper part are the data of the Langmuir isotherm. Where the final or equilibrium concentration Ce [mg/L], was placed on the ordinate axis, and the relationship $\frac{Ce}{q_e}$[g/L]. While for the Freundlich isotherm $log\ C_e$ is found on the ordinate axis and $log\ q_e$ on the abscissa. The parameters obtained for both isotherms are found in Table 4 and Table 5 for potassium chromate and potassium dichromate, respectively.

Table 4. Parameters of the Freundlich and Langmuir isotherm for the adsorption of potassium chromate in aqueous solution to different masses of adsorbate

	Langmuir			Freundlich		
Mass	**5 [g]**	**10 [g]**	**15 [g]**	**5 [g]**	**10 [g]**	**15 [g]**
q_{max}	0.3213	0.6566	1.15367			
	0.2341*	0.6416*	1.1578*			
K_L	-0.0298	-0.0414	-0.0675			
	-0.0288*	-0.0441*	-0.0713*			
n				-0.4436	-0.7459	-1.2732
				-0.3720*	-0.7544*	-1.2900*
K_F				6691.14	234.05	33.00
				28747.49*	197.79*	30.37*
R^2	0.9835	0.9901	0.9900	0.9913	0.9926	0.9869
	0.9857*	0.9976*	0.9980*	0.9931*	0.9982*	0.9974*

*= duplicate

Source: Own elaboration, 2022.

From the data in Table 4, the average R^2 for the Langmuir isotherm is 0.9908. While for the Freundlich isotherm the average of R^2 is 0.9933. Therefore, for potassium chromate, the Freundlich isotherm had a better correlation of the data. However, by obtaining a negative n, it does not give a real parameter related to the intensity of adsorption. In addition, there is similarity in data behavior. Therefore, the Langmuir model is adopted. Obtaining that q_{max}==1.1578 mg/g], which is the highest adsorption capacity obtained if all the pores of the material were occupied under the best conditions.

Table 5. Parameters of the Freundlich and Langmuir isotherm for the adsorption of potassium dichromate in aqueous solution to different masses of adsorbate

	Langmuir			Freundlich		
Mass	**5 [g]**	**10 [g]**	**15 [g]**	**5 [g]**	**10 [g]**	**15 [g]**
q_{max}	0.3957	0.3688	0.5710			
	0.4201*	0.4346*	0.7305*			
K_L	-0.0152	-0.0168	-0.0214			
	-0.0155*	-0.0179*	-0.0235*			
n				-0.3663	-0.3076	-0.5951
				-0.3536*	-0.3608*	-0.5033*
K_F				326061.86	2172701.18	2398.28
				508979.16*	276949.13*	8226.21*
R^2	0.9722	0.9648	0.9787	0.9903	0.9565	0.9905
	0.9801*	0.9825*	0.9843*	0.9869*	0.9848*	0.9884*

*= duplicate
Source: Own elaboration, 2022.

With the data in Table 5, for potassium dichromate the Freundlich isotherm had a better correlation of the data. For Freundlich the average of R^2 is 0.9829 and for Langmuir the average of R^2 is 0.9771. However, although there is a better data fit, the Langmuir isotherm better represents the adsorption behavior, according to the similarity in the behavior of the theoretical data. In addition to obtaining unreal data for the adsorption intensity n.

5. Conclusions

With the results obtained in the experimentation, it is shown that the scales of the species Prochilodus lineatus have the capacity to retain contaminants on their surface. Which means that they are potential bioadsorbents for the removal of effluents with chrome dyes. Similarly, the use of a local species such as tarpon is important when applying it to a problem in the area. Due to the easy access to the material and the reduction of import expenses of other bioadsorbents. In addition, an added value is given to waste that is disposed of without first obtaining any benefit.

Figure 8 and Figure 10 highlight the priority of controlling mass and time factors when experimenting with bioadsorbents to remove chromium compounds. Figure 6 highlights that in the first 5 hours of experimentation a more abrupt removal was obtained. In addition, the data analysis shows that the scales continue to adsorb the contaminants but in less quantity. To improve the removal process, some pre-treatment of the scales should be evaluated where good results are obtained in less time.

In the case of experimentation with fish scales, the Freundlich isotherm fits better for both pollutants studied. However, in order to know the real conditions that would exist at the temperature experienced (25° C), the Langmuir isotherm must be followed. When comparing the results, for the Langmuir isotherm a high correlation was obtained with an average of R^2 = 0.9771 and with positive q_{max} values. While the Freundlich isotherm, although it has a greater linear trend, the values of n are not real numbers for adsorption intensity, which is why the model is discarded for this experiment.

The use of bioadsorbents of uniform size is recommended to avoid variations at the time of data collection. Future research should evaluate the influence of pH on shad scale removal. In addition, evaluate if the removal is carried out purely by adsorption or if chemical reactions occur between the adsorbent and the adsorbate. The behavior of the model must also be studied by varying the temperature. Finally, it is very important to conduct tests with effluent water from tanneries to validate the results in natural conditions.

6. References

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