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Adsorption of chrome (VI) and mercury (II) in solution using hyacinth (*Eichhornia crassipes*)*

Adsorción de cromo (VI) y mercurio (II) en solución utilizando jacinto (*Eichhornia crassipes*)

Adsorção de crómio (VI) e mercúrio (II) em solução utilizando hiácito (*Eichhornia crassipes*)

TEJADA-TOVAR, CANDELARIA[1]; PAZ, ISABEL[2]; ACEVEDO-CORREA, DIOFANOR[3]; ESPINOSA-FORTICH, MARÍA[4]; LÓPEZ-BADEL, CRISTINA[4]

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1 University of Cartagena, Research Group IDAB. M.Sc. in Environmental Engineering. Cartagena, Colombia. https://orcid.org/0000-0002-2323-1544
2 University of Tolima, Research Group CEDAGRITOL. Ph. D in Engineering. Ibagué, Colombia. https://orcid.org/0000-0002-0935-8856
3 University of Cartagena, Research Group IDAA. Ph. D in Food Engineering. Cartagena, Colombia. https://orcid.org/0000-0002-1364-7044
4 University of Cartagena, Research Group IDAB. Bachelor of Chemical Engineering. Cartagena, Colombia

Correspondencia: dacevedoc1@unicartagena.edu.co

ABSTRACT

The existence of water hyacinth proliferation in wetlands of the Canal del Dique (Bolívar- Colombia) causes environmental problems because there is no final disposal of these. Therefore, it is necessary to study alternatives for its use. The objective of the study was to evaluate the behavior of the aquatic hyacinth as an adsorbent of Cr (VI) (VI) and Hg (II) (II) in a synthetically prepared solution. The lignocellulosic material was dried at 80°C for 24 h to remove moisture; then crushed and sieved with meshes of different particle sizes; characterized by elemental analysis to check for the presence of cellulose, hemicellulose, and lignin, as well as by Fourier Transform Infrared Spectrometry to verify the existence of functional groups responsible for the adsorption process. It was found that the best particle size was 1 mm, with a removal percentage of 73,4 and 79,3% for Cr (VI) and Hg (II), respectively. When establishing the adsorption kinetics, it was verified that the elimination percentage increases with time up to 5,5 h of contact with the Hg (II) solution and 3,8 h with the Cr (VI) solution.

KEYWORDS:
Residual Biomass; Adsorption; Heavy Metals; Freundlich model; *Eichhornia crassipes*.

RESUMEN

La existencia de proliferación de Jacinto acuático en los humedales del Canal del Dique (Bolívar-Colombia) causa problemas ambientales por no existir una disposición final de estos. Por lo tanto, es necesario estudiar alternativas para su uso. El objetivo del estudio fue evaluar el comportamiento del Jacinto acuático como adsorbente de cromo (VI) y mercurio (II) en una solución preparada sintéticamente. El material lignocelulósico se secó a 80°C durante 24 h para eliminar la humedad; luego se trituró y tamizó con mallas de diferentes tamaños de partículas; se caracterizó mediante análisis elementales para comprobar la presencia de celulosa, hemicelulosa y lignina, así como mediante espectrometría de infrarrojos por transformada de Fourier para verificar la existencia de grupos funcionales responsables del proceso de adsorción. Se encontró que el mejor tamaño de partícula era de 1 mm, con un porcentaje de remoción de 73,4 y 79,3% para el cromo y el mercurio, respectivamente. Al establecer la cinética de adsorción se comprobó que el porcentaje de eliminación aumenta con el tiempo hasta 5,5 h de contacto con la solución de mercurio y 3,8 h con la solución de cromo.

PALABRAS CLAVE:
Biomasa residual; Adsorcion; Metales pesados; Modelo de Freundlich; *Eichhornia crassipes*.

RESUMO

A existência de proliferação de jacintos de água nas zonas húmidas do Canal del Dique (Bolívar-Colombia) causa problemas ambientais porque não há disposição final dos mesmos. Portanto, é necessário estudar alternativas para o seu uso. O objetivo do estudo foi avaliar o comportamento do jacinto aquático como adsorvente de cromo (VI) e mercúrio (II) em uma solução sinteticamente

PALAVRAS-CHAVE:
Biomassa residual; Adsorção; Metais pesados; Modelo de Freundlich; *Eichhornia crassipes*.

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preparada. O material lignocelulósico foi seco a 80°C durante 24 h para remover a humidade; depois triturado e peneirado com malhas de diferentes tamanhos de partículas; caracterizado pela análise elementar para verificar a presença de celulose, hemicelulose e lignina, bem como pela Espectrometria de Infravermelhos por Transformada de Fourier para verificar a existência de grupos funcionais responsáveis pelo processo de adsorção. Verificou-se que o melhor tamanho de partícula era de 1 mm, com uma percentagem de remoção de 73,4 e 79,3% para o crómio e o mercúrio, respectivamente. Ao estabelecer a cinética de adsorção verificou-se que a percentagem de eliminação aumenta com o tempo até 5,5 h de contacto com a solução de mercúrio e 3,8 h com a solução de crómio.

INTRODUCTION

The increase of nutrients in water bodies due to poor environmental practices in agricultural and industrial activities causes eutrophication, which affects the socio- economic and ecological development of aquatic systems because of invasive plant species [1, 2]. This generates a decrease in dissolved oxygen, as well as the difficulty for the circulation of watercraft, fishing and the limited availability of water for treatment. Among the most invasive plants are the water fern (*Azolla filiculoides*), the Elodea (E*geria densa*), and the water hyacinth (*Eichhornia crassipes*), among others [1-3].

On the other hand, the presence of heavy metals in bodies of water implies risks for human public health, given their non- biodegradation and high toxicity [4, 5]. The most common metals present in water are: Cadmium, Cobalt, Copper, Manganese, Hg (II), Nickel, Lead and Zinc; which are produced in activities such as agriculture, metallurgy, energy production, microelectronics, mining, sewage sludge and waste disposal [6, 7]. These pollutants can affect aquatic systems through runoff, leaching and transport through mobile colloids; once released they dissolve to form ions or complexes, and their accumulation decreases water quality and alters the food chain as a consequence of the death of the species [8-10]. Several methods have been developed for the removal of heavy metals in solution among which stand out: chemical precipitation, chemical coagulation, oxidation, reduction, ion exchange, filtration, ultrafiltration, nanofiltration, adsorption (activated carbon, zeolites, silica gel), membrane technologies (reverse osmosis), electrochemical treatment (electrodialysis and electrocoagulation) and application of artificial wetlands (stabilization ponds), among others, which are costly for operating and installation costs [11, 12]. Biosorption is a physicochemical process that allows the retention of dissolved ions by plant materials that trap metal ions by attracting opposite charges, thanks to their lignocellulosic nature [7, 13].

In this context, adsorbents of vegetable residual origin have been used for water cleaning, among them: tea, coffee waste, watermelon seed husks, ceiba fiber, palm bagasse, yam and yucca husks, peat, fly ash, cellulose, fungi immobilized in nanosilica, orange peels, Kikuyo, among others [14-16]. Cu, Al, As, Hg (II), Fe, Ni, Ca and Pb, have been removed using bioadsorbents from water buffon, finding that this biomass of lignocellulosic origin has good percentages and removal capacities of metal ions as well as of phenolic compounds, due to its lignoelulósica nature and the presence of hydroxyl and carboxyl groups that benefits the removal [17, 18]. Therefore, in the present study the water hyacinth is used in the removal of Hg (II) and Cr (VI) from a synthetic aqueous solution in a batch system.

METHOD

Adaptation of lignocellulosic material

The experiments were carried out in the Environmental Laboratory at the Faculty of Engineering of the Universidad de Cartagena. Water hyacinth samples were used in the best possible state, from the Canal del Dique, Department of Bolívar (Colombia). Longitude 75.505553 and Latitude 10.402918, at room temperature (30°C), 1 atm, 2 m above sea level and a relative humidity of approximately 80%. Initially, the leaves and stems harvested with distilled water were washed to remove soluble compounds adhered to it and impurities, which can interve-

ne in the adsorption. Subsequently, they were dried in an oven at 80°C for 24 h and reduced in size in a knife mill for 20 min. Finally, it was classified into a sieve to obtain sizes of 0,355, 0,5 and 1 mm [19].

Characterization of the bioadsorbent material

The bioadsorbent material was characterized in order to identify the content of cellulose, hemicellulose by the TAPPI method T 203 os-74, which is a method for the determination of α-, β-, and γ-cellulose. For this, the pulp is extracted consecutively with 17,5 and 9,45% sodium hydroxide solutions at 25°C. The soluble fraction, consisting of beta and gamma-celluloses, is determined volumetrically by oxidation with potassium dichromate, and alpha-cellulose, as an insoluble fraction, is obtained by difference. In general, alpha-cellulose indicates a cellulose content of non-degraded molecular weight in the pulp; beta-cellulose indicates that a degraded cellulose, and gamma-cellulose is composed mainly of hemicellulose.

The lignin content was determined by the TAPPI method T 222 om-83, for this the carbohydrates of the biomass are hydrolyzed and solubilized with sulfuric acid; the insoluble acid lignin is separated by filtration, dried and weighed.

The functional groups responsible for the adsorption were also identified by FTIR analysis (Fourier Transform Infrared Spectroscopy) [20, 21].

Adsorption tests

To perform the adsorption tests, a Shaking incubator IN-666 was used, which previously contained an Erlenmeyer with 0,5 g of biomass and solutions of Hg (II) and Cr (VI) at 100ppm with a pH of 6 and 2, which were prepared by adding 0,1 g of Merck brand $HgCl_2$ and 0,1 g of $K_2Cr_2O_7$ to 1 L of deionized water, respectively. We worked with 100 mL of the solution with a concentration of 100 ppm and 0,5 g of biomass of each particle size of the biomass already crushed (0,355 mm, 0,5 mm and 1 mm) placing them in a Beaker with stirring for 2 hours at 150 rpm, extracting samples of 3 mL at the end of the agitation. The analysis of the final concentration of the metal in the liquid phase is carried out by the method of diphenylcarbazide and ammonium diocyanate at 584 and 281 nm, for Cr (VI) and Hg (II) respectively, in a UV-vis spectrophotometer [5,18]. The experiments were carried out in duplicate.

Kinetics and adsorption isotherms

With the best particle size selected, a test was performed to establish the kinetics. 0.5 g of the biomass was weighed and the experimental assembly was made for the adsorption; both samples (main and replica) were kept in the shaker for 7, 5 hours, at 150 rpm and 25°C.

To determine the equilibrium time of adsorption, the kinetics were carried out taking aliquot of 3 mL every 30 minutes, performing independent experiments, so as not to affect the concentration of the metals in the solution. The adsorption isotherms were applied to analyze the metal adsorption equilibrium data in the evaluated adsorbent, for the realization of the assays initial concentrations of 25, 50, 75 and 100 ppm were used [5,22]. All the tests were carried out in triplicate, taking the arithmetic average of the data, the consistency of the data was verified by calculating the standard deviation and the analysis of the data was made using OriginPro 8 ®.

RESULTS

Characterization of the lignocellulosic material

The results presented in Table 1 allowed corroborating the content of lignocellulosic material is high. The main components of the lignocellulosic materials contain a variety of functional groups that play an essential role in metal sorption. This feature is due to the ion exchange between positive cations and sodium, potassium, cal-

cium, and magnesium present in the adsorbent. Being this mechanism next to the chelation, the main mechanisms that cause the sorption of metals in lignocellulosic sorbents sorbents [8,23,24]. The chemical composition of some common lignocellulosic materials studied in the processes of metal sorption are composed of cellulose (30-35%), hemicellulose (20-40%), lignin (15-25%), small amounts of water, ash, and cyclic hydrocarbons. Percentages of components depending on the type and part of the plant, the leaves contain a lower percentage of cellulose (15-25%), and lignin (5-10%). However, they have a higher percentage of hemicellulose (70-80%), while in stones and nuts, the lignin content is higher than cellulose and hemicellulose (30-40%) [13, 15, 25, 26].

Table 1. Results of the chemical analysis of the water hyacinth.

Sample	Stek	Sheet
Cellulose	26,94 ± 0,62	24,71 ± 0,72
Hemicellulose	27,82± 0,54	20,42 ± 0,87
Lignin	6,18± 0,32	12,91± 0,49

Evaluation of the effect of particle size

The particle size selection was carried out. The best particle size was 1 mm since was obtained the highest percentage of removal and adsorption capacity of both metals (Table 2). Therefore it was chosen to perform all the tests. The selection was based on choosing that particle size where there would be a lower absorbance, indicating the lower concentration of the metal in the solution after being in contact with the biomass; this, in turn, indicates a higher percentage of removal [7, 27, 28].

Table 2. Adsorption data of each particle size selected for Hg (II) and Cr (VI) tests.*

Particle size (mm)	Hg (II)		Cr (VI)	
	% removal	q_t (mg/g)	% removal	q_t (mg/g)
0,355	65,59	13.318	59,88	11.976
0,50	71,96	14.392	72,20	14.44
1,00	79,28	15.856	73,41	14.68

* The data presented in the table are averaged.

In the size selection for adsorption, it would be expected that at a smaller particle size, there would be an increase in surface area and thereby a greater adsorption of the metal would be evidenced. However, the results obtained for the water hyacinth show that adsorption was favored for the larger particle size. It is important to note that the metals are located in the active sites of the biomass, which causes the pores to close as they capture the pollutant; these pores are made of lignocellulosic material, which degrades as it begins. To decrease the particle size, the active sites are destroyed and, therefore, adsorption does not occur, or at least in the expected degree [17, 29, 30].

This effect can be appreciated from the characterization carried out by FTIR analysis on the biomass after the contact with hyacinth, comparing it with that made to the biomass before adsorption. The peaks around 1733,70 cm^{-1} in the biomass spectrum are produced by the stretching of the C=O carbonyl group which indicates the vibration of the carboxyl groups of pectin, hemicellulose and lignin in the biomass studied. The stretching of C=C, possibly as a result of the presence of benzene or aromatic rings in lignin, can be seen in the peaks 1615,60 cm^{-1} and 1684,04cm^{-1}. The presence of aliphatic groups can also be observed at 1558,97 cm^{-1}. (CH), aromatic groups, the vibrations of methyl, methylene and methoxy groups, while in the intense band comprised between 1238,28 cm^{-1} to 602,49 $cm^{-1,}$ the presence of alcohols and carboxylic acids is evidenced [15, 31]. When comparing the before and after the adsorption process, most of these peaks show an increase in the intensity and width of the bands due

to a variation in the frequency of adsorption. It could be attributed to the union of the ions Cr^{+6} with the different groups present in the biosorbent, as evidenced by the change of the adsorption peak to 2927,87 cm^{-1}.

After Hg adsorption, greater peak intensity was observed around the 3000-3600 cm-1 band, corresponding to the hydroxyl groups and the bandwidth of 2361,93 cm^{-1} to CH vibration. Finally, the peaks of this range 1238,28 cm^{-1} to 602,49 cm^{-1}, which represent the groups of alcohols and carboxylic acids, are no longer shown after adsorption. It was concluded that the groups involved in the elimination of metals in this research are hydroxyl, carboxylic and aliphatic groups [9,32, 33]. These results confirm the information found in the literature for the characterization.

Statistical analysis

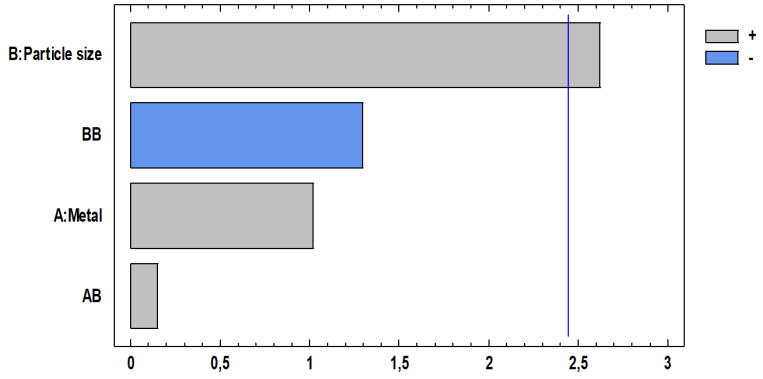
The results obtained from the analysis of variance (ANOVA), carried out to establish the statistical significance of the effect of the metal and the particle size, comparing its mean square with an estimate of the experimental error can be shown in Table 3. Thus, the values of the significant parameters in the process of adsorption of Cr (VI) and Hg (II) over water voids were obtained, and a 95% confidence level was established.

Table 3. Analysis of variance for the adsorption capacity of Cr (VI) and Hg (II) on hyacinth.

Font	Sum of sqaures	Gl	Half square	F- value	P Value
A:Metal	2,06622	1	2,06622	1,03	0,3491
B:Particle size	13,7516	1	13,7516	6,86	0,0396
AB	0,0431556	1	0,0431556	0,02	0,8881
BB	3,36831	1	3,36831	1,68	0,2424
bloques	0,970102	1	0,970102	0,48	0,5126
Error total	12,024	6	2,004		
Total (corr.)	29,3795	11			

Independently of the metal evaluated, the particle size of the adsorbent is the variable with the greatest positive influence on the process (Figure 1), establishing a standard error of 1,42. On the other hand, since the P-value is more significant than 5,0%, there is no indication of serial autocorrelation in the residues with a significance level of 5,0% [34, 35].

Figure 1. Pareto chart for Cr (VI) and Hg (II) removal capacity.



Kinetics and adsorption isotherms

Once the optimum particle size was established to perform the adsorption tests, the adsorption kinetics for each metal was established. For this, absorbance data were taken at different times of contact with the hyacinth. It was observed that as time passes, the percentage of removal of Hg (II) and Cr (VI) increases gradually (Figure 2), indicating the accumulation of metals in the available active sites until they are saturated. Once this happens, a maximum percentage of removal was obtained, and in the future a constant behavior will be observed. The percentage of removal is greater for the case of Hg (II) adsorption; taking as an example adsorption at 100 min, where the percentage of removal of Cr (VI) is 65% and that of Hg (II) is approximately 82% [34-36].

The data obtained from the adsorption tests were fitted to the Pseudo-First Order (PFO) [6], Pseudo-Second Order (PSO) [9] and Elovich [11] kinetic models. Figure 1 shows the fit to the above mentioned Cr (VI) and Hg (II) waterbottle models.

From the adjustment of the obtained data and the correlation coefficient (R^2) (Table 4), it was established that the Pseudo- Second Order model describes the behavior of the adsorption process. Therefore, it was establi-

Figure 2. Fitting of adsorption kinetics models of Hg (II) and Cr (VI) on water hyacinth.

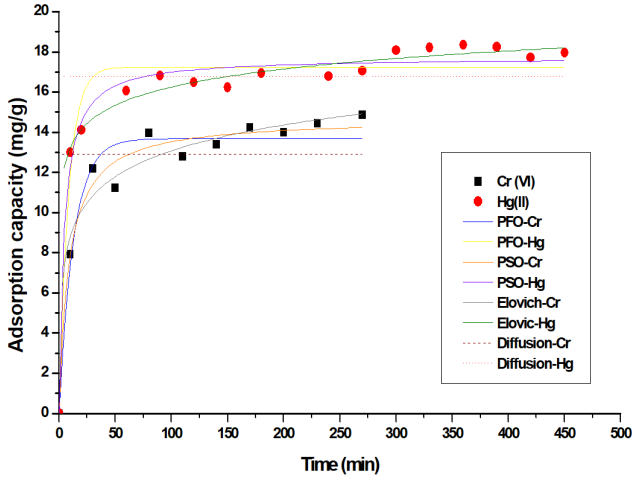


Table 4. Adjustment parameters for Cr (VI) and Hg (II) deadsorption kinetic models on water bucket.

Model	Parameters	Metal	
		Cr(VI)	Hg(II)
Pseudo-First order	q_e (mmol/g)	13,6839	17,2437
	k_1 (min^{-1})	0,0769	0,1194
	R^2	0,9503	0,9586
Pseudo-Second order	q_e (mmol/g)	14,691	17,726
	k_2 (g^{-1} min^{-1})	0,0078	0,0129
	R^2	0,9748	0,9812
Elovich		0,5388	0,7689
		21,2832	3461,69
	R^2	0,9699	0,9901
Intraparticle diffusion	K	12,9012	16,7988
	R^2	0,7961	0,8884

shed that Cr (VI) can be adsorbed by two active sites in the biomass and that the process occurs by chemisorption due to the formation of chemical bonds between adsorbent and adsorbate at the surface [30].

The Elovich model presents a good fit of the adsorption data of both metals, so it can be said that the process also takes place inside the particle pores of bioadsorbent materials and that their active sites are heterogeneous. Thus, exhibiting different activation energies throughout the adsorption process [36]. Furthermore, this suggests that the rate- limiting passage of this adsorption system can be controlled by chemisorption involving valence forces through the sharing or exchange of electrons between sorbent and sorbate [23, 31, 34].

To establish the adsorption isotherms for each metal, absorbance data were taken at different concentrations for the solutions in contact with the biomass, with which the adsorption isotherms were constructed according to the Langmuir and Freundlich models to compare them with the behavior obtained [37, 38]. For each model, their respective constants were found according to the adsorption of each metal, specifically, as reported in Table 5.

The constants allowed the construction of the adsorption isotherms for Cr (VI) and Hg (II) according to each model (Figures 3 and 4).

The isotherm that best describes the experimental behavior related to the type of adsorption is the Freundlich model (Figures 3 and 4). This model was chosen according to the highest R^2 found using the OriginPro®, which allows to

Table 5. Constants of the Langmuir and Freundlich models.

Isotherm model	Parameters	Cr (VI)	Hg (II)
Langmuir	q_{max}	217,710	8,58
	B	$3{,}60\times10^{-1}$	$2{,}942\times10^{-3}$
	SS	5,985	1,92
Freundlich	Kf	$5{,}99\times10^{-4}$	0,73
	1/n	2,205	0,49
	SS	0,396	1,29

Figure 3. Adsorption isotherms of Langmuir and Freundlich for the adsorption of Hg (II).

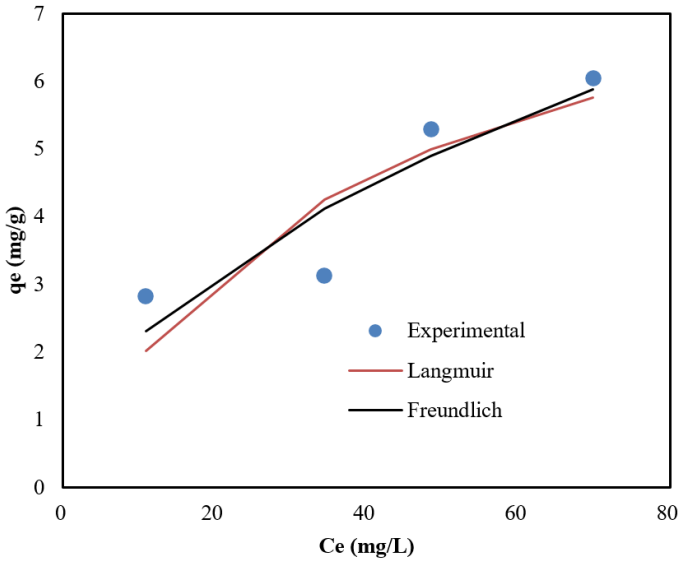
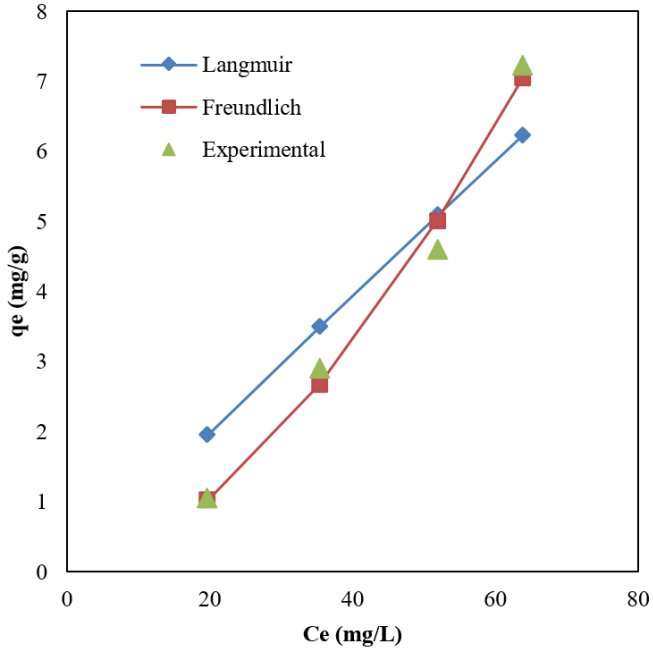


Figure 4. Langmuir and Freundlich Adsorption Isotherms for Cr (VI) Adsorption.



affirm that the adsorption of Cr (VI) and Hg (II) in the water hyacinth occurs in a microporous surface, where unlike the model of Langmuir does not assume the formation of a monolayer, but is applied in multiple layers of adsorption.

For this reason, it is said that there is an energetically heterogeneous distribution of the available active sites for the adsorption of the metal [39-42]. On the other hand, the value of Freundlich's constant n is in the range 1-10 for Hg (II). This indicates that the adsorption process is favorable [11], [12]

CONCLUSION

The best particle size for adsorption corresponds to 1 mm, obtaining a 79.2% removal of Hg (II) and 73,4% of the Cr (VI) present in the solution. By establishing the adsorption kinetics, it was found that the percentage of adsorption increases with time until the active sites available for adsorption are saturated. The saturation of the biomass occurred after being in contact with the solution 5,5 h for Hg (II) and at 3,8 h for Cr (VI). According to the analysis of the adsorption isotherms, the Freulinch absorption model was the best at fitting the data. The water hyacinth is a good material to remove metal contaminants such as Cr (VI) and Hg (II), present in aqueous solutions.

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