Revista
Torreón Universitario
www.faremcarazo.unan.edu.ni / ISSN 2410-5708 / e-ISSN 2313-7215
Year 8 | No. 23 | p. 168 - p. 178 | October 2019 - January 2020

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Removal of hexavalent chromium in contaminated water using banana peel (Paradisiac musea) as adsorbent

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Submitted on December 20th, 2019 / Accepted on February 05th, 2020
https://doi.org/10.5377/torreon.v8i23.9534

Keywords: hexavalent chromium, biomass, isothermal models, removal, adsorption

ABSTRACT

This research aimed to remove the hexavalent chromium from contaminated water using the banana peel as an adsorbent. The study was realized in two stages: in the first stage, it worked with 1 g of the biomass at a particle size of approximately 600 µm, 5 minutes of contacts, 20 $mg.l^{-1}$ of hexavalent chromium and at pH 3, 3,5, 5 and 7. In the second stage, it worked with the mass and time conditions at pH 3 and 3.5, increasing the metal concentration from 20 to 40 and 80 $mg.l^{-1}$. The results obtained show that increasing the pH reduces the removal percentage and the adsorption capacity, however, at pH 3 and 3,5 the biomass removes almost 100% of the hexavalent chromium and increasing the

concentration increases the adsorption capacity of the banana peel. The experimental data fit more to the Langmuir model than to the Freundlich model, which shows monolayer adsorption of a homogeneous surface. Also, the separation factor R_L was between 0,809 and 0,383 which indicated favorable adsorption of the heavy metal in the biomass. The banana peel has great potential as an adsorbent for the removal of hexavalent chromium in water.

INTRODUCTION

The contamination of water by heavy metals represents a major environmental problem due to the toxic effects they cause to human health. The main sources of water contamination with heavy metals come from industrial wastewater such as metalized, mining, tanneries, paints, radiator manufacturing, foundry, alloy industries, among others. (Al-Azzawi, M.N.A., Shartooh, S.M., Al-Hiyaly S.A.K., 2013). The maximum permissible discharge for hexavalent chromium to receiving bodies must be less than 0.5 $mg.l^{-1}$ according to the regulations in which the dispositions for the discharge of wastewater executive decree No. 21-2017. (National Assembly, 2017). Chromium exists in more than one oxidation state from Cr (0) the metallic form, to its hexavalent form, Cr (VI). Especially, chromium in its oxidation state +6 is considered dangerous even in small concentrations, while Cr in oxidation state +3 is essential for health in moderate conditions. (Guertin J., 2004)

Hexavalent chromium can cause short-term and long-term adverse effects, the respiratory tract being the main organ affected after exposure. Hexavalent chromium can cause lung cancer, irritation or damage to the skin, eyes, nose, and throat. According to OSHA, the permissible exposure limit value of hexavalent chromium per day should be 5 $\mu g.m^{-3}$. (OSHA, 2009). Exposure by chronic inhalation to hexavalent chromium in humans causes perforations and ulcerations of the septum, bronchitis, decreased lung function, pneumonia, asthma, and nasal itching. High levels of hexavalent chromium can produce effects on the liver, kidneys, gastrointestinal and immune system. (EPA, 2000).

In sewage hexavalent chromium is in solution as CrO_4^{2}, which can be removed by reduction, chemical precipitation, adsorption and ion exchange. The most commonly used process is the addition of a reducing agent that converts hexavalent chromium to trivalent chromium and subsequently precipitation with basic $Cr(OH)_3$ solutions. Currently, the use of alternative methodologies such as the removal and/or reduction of hexavalent chromium to trivalent chromium by bacteria, algae, yeasts, and fungi has been analyzed. (Torres, L., Cárdenas, J. F., Moctezuma, M. G., Martínez, V. M., Acosta, I., 2012) Available agricultural waste is a viable option for the remediation of heavy metals since they are considered an important source for adsorption. In this context, the banana peel can be evaluated as an adsorbent for the removal of hexavalent chromium. (Díaz, M. R., Contreras, R., Guardiola, M. A., Mayo del Río, C., 2016

The banana peel according to a study by Kamsonlian, S., Suresh, S., Majumder, CB, Chand, S., 2011 has irregular and porous surfaces, proteins and polysaccharides within its cell cover, some N-H and O-H functional groups, carboxyl groups, aromatic rings C = C and presence of silica that gives the biomass properties for fruitful use as an adsorbent in the treatment of contaminated water. Kamsonlian S. et al. (2011)

The objective of this research was to present an effective and low-cost alternative for the removal of hexavalent chromium in contaminated water, by using banana peel (*Musa paradisiaca*) as an adsorbent to remove hexavalent chromium, taking into account certain parameters that influence the removal process such as solution pH, metal concentration and contact time. The maximum adsorption capacity of the biomass was determined by the Langmuir and Freundlich isotherm models.

MATERIALS AND METHODS

Preparation of the banana peel

The banana peel was obtained from the Central dining room of the Universidad Nacional Autónoma de Nicaragua, Managua (UNAN-Managua) and from the dining room of Centro para la Investigación de Recursos Acuáticos (Center for Aquatic Resources Research, as in English) CIRA /UNAN-Managua, which were collected in sacks and taken to the Biotechnology Laboratory where they were cleaned with deionized water and cut into smaller parts. The shells were dried at room temperature for 3 days, then introduced into the oven Brand Thermo Scientific at 60 °C for 2 hours and finally crushed in a homemade manual mill, Brand Victor to obtain a particle size of approximately 600 μm. Banana peel flour was stored in Ziploc bags in an airtight jar for later use.

Experimental phase

To assess the adsorption capacity of the banana peel, the influence of pH on metal removal and the initial concentrations of hexavalent chromium were taken into account. Experimental tests were performed at a laboratory scale in duplicate to assess the repeatability of the analysis. In the first stage, a pH of 3, 3.5, 5 and 7 was worked with 1 g of banana peel per 100 ml of contaminated water at a concentration of 20 $mg.l^{-1}$ of hexavalent chromium for 15 minutes in the constant stirring of approximately 600 rpm on a stir plate Brand Cimarec. In the second stage, we worked with concentrations of 20, 40, and 80 $mg.l^{-1}$ of hexavalent chromium at pH 3 and 3.5 for 15 minutes under constant agitation. At each stage, aliquots were taken at 0, 2, 4, 6, 10 and 15 minutes of contact with the banana peel, which were passed through a Whatman 110 mm filter.

Hexavalent chromium was determined on a Varian Cary 50 UV-vis spectrophotometer at an absorbance of 540 nm, using the 1.5-diphenylcarbazide colorimetric method described in the

3500-Cr B Standard Methods. (APHA, AWWA, WEF, 2012). The SigmaPlot 14.0 software was used to obtain the graphics.

RESULTS AND DISCUSSION

The removal percentage of the hexavalent chromium ions and the number of ions absorbed in the banana peel (qe), was calculated using equations (1) and (2).

$$\% \ Removal = \frac{100\ (C0 - Ceq)}{C0} \quad (1)$$

$$qe = \frac{(C0 - Ceq)V}{m} \quad (2)$$

Where C_0 and C_{eq} are the initial and final concentrations of the metal ion in the solution, V the volume of the solution (L), m is the mass of the banana peel (g) and q_e is the adsorption capacity of the biomass (Abbasi, Z., Alikarami, M., Nezhad, ER, Moradi, F., Moradi, V., 2013).

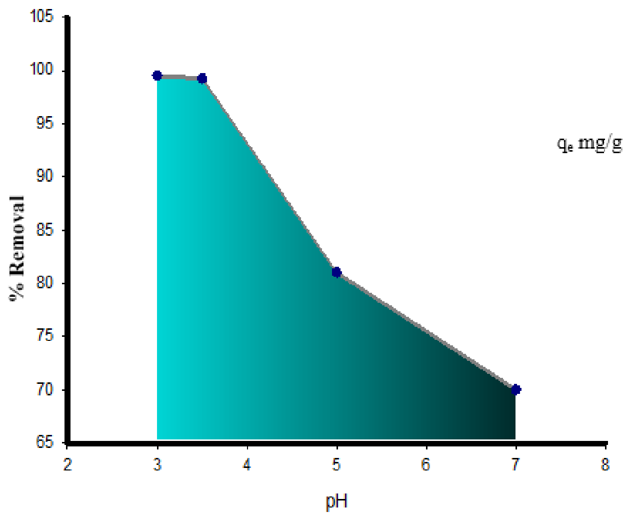

Figure 1. Effect of pH on % removal

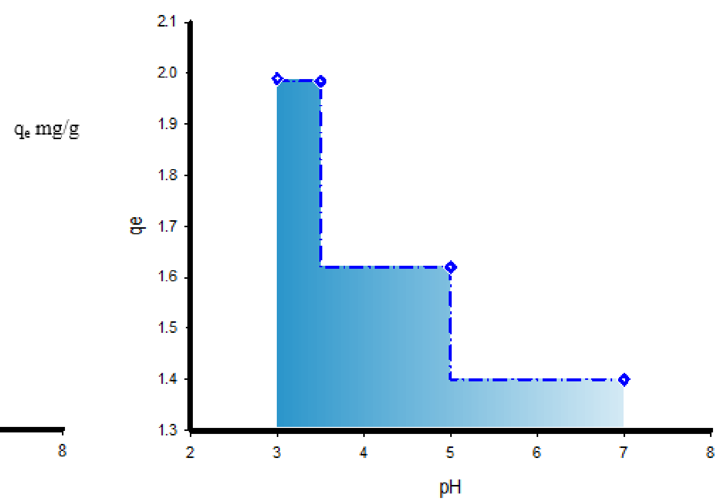

Figure 2. Effect of pH on adsorption capacity

In figure 1, it is observed that the removal of the metal is influenced by the pH so that the percentage of removal decreases to 70% as the pH increases to 7. Figure 2 shows that the pH also influenced the capacity of removal of the banana peel, this being inversely proportional. Ashraf A. et al. (2016), Memon J. R et al. (2009) and Kumar M. et al. (2014) obtained similar results to this study when evaluating chromium removal based on pH. Figure 3. (Ashraf, A., Khalid S. b., Fazal, M., 2016) (Memon, JR, Memon, SQ, Bhanger, MI, Khuhawar, MY, 2009) (Kumar, M., Majumder, CB, 2014)

Hexavalent chromium is found as $HCrO_4^-$, $Cr2O_7^{2-}$, CrO_{12}^-, $Cr4O_{13}^{2-}$, $Cr3O_{10}^{2-}$, a decrease in pH causes protonation of the adsorbent surface, which induces a strong attraction to the chromium ions of the solution negatively charged, so adsorption increases with increasing acidity of the solution. However, increasing the pH increases the concentrations of OH^- ions, inducing changes in the surface of the adsorbent, preventing the bioabsorption of negatively charged chromium ions, which decreases the absorption of the metal. (Torres, L., Cárdenas, J. F., Moctezuma, M. G., Martinez, V. M., Acosta, I., 2012).

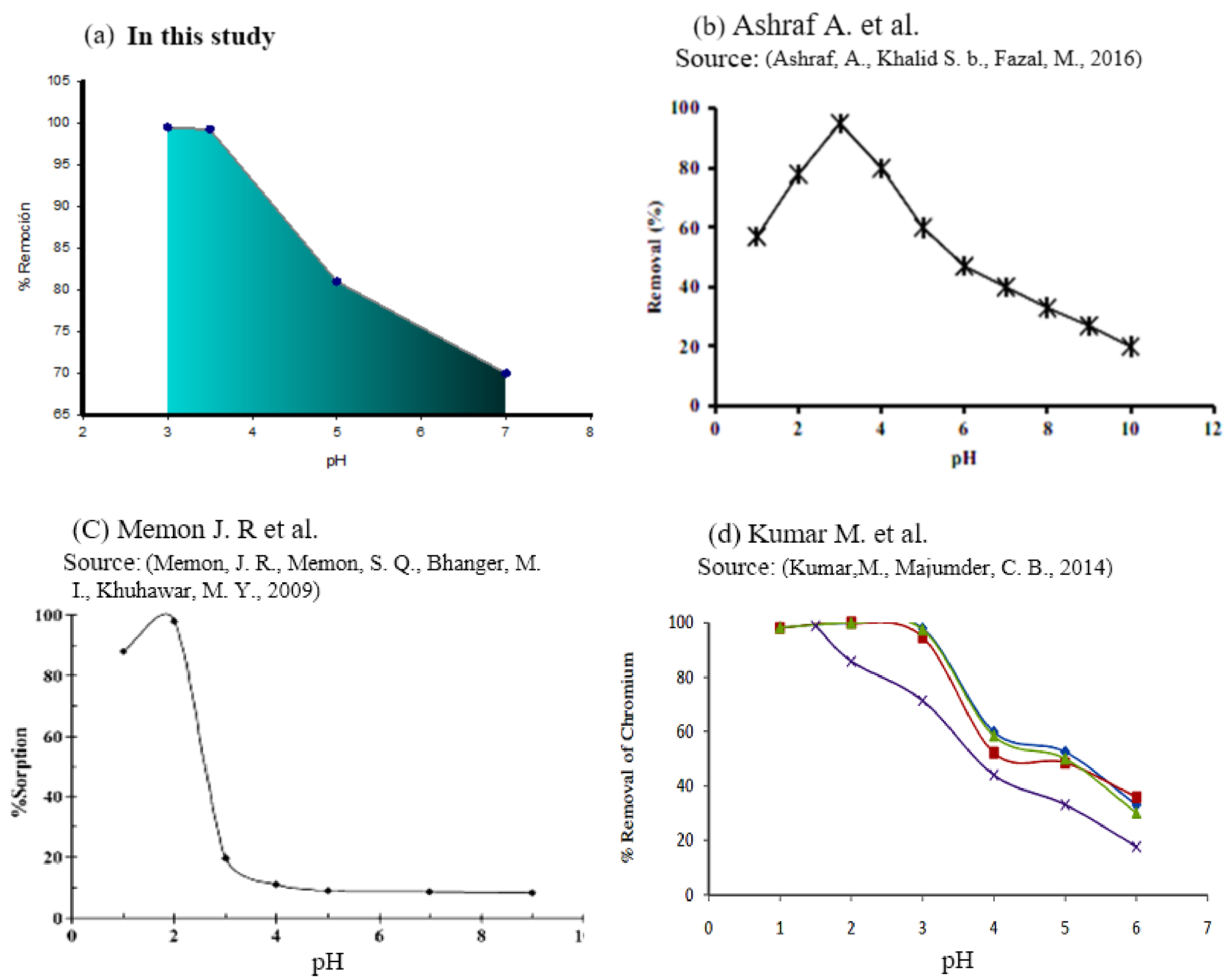

Figure 3. (a), (b), (c) y (d) Comparison of results obtained with other studies when evaluating % of Removal vs. pH using banana peel to remove Cr VI.

In figure 4, it is observed that in pH3, as the hexavalent chromium concentration increases from 20 to 40 and 80 $mg.l^{-1}$, the percentage of removal of the banana peel slightly varies, however, figure 5 shows that increasing the concentration increases the adsorption capacity of the banana peel. This same behavior is reflected for pH 3.5 (Figures 6 and 7). Abbasi Z. et al. (2013) in its publication mentions that “the adsorption capacity of the banana peel for Co^{2+} and Ni^{2+} increased with increasing equilibrium concentration”. (Abbasi, Z. Alikarami, M., Nezhad, E. R., Moradi, F. Moradi, V., 2013)

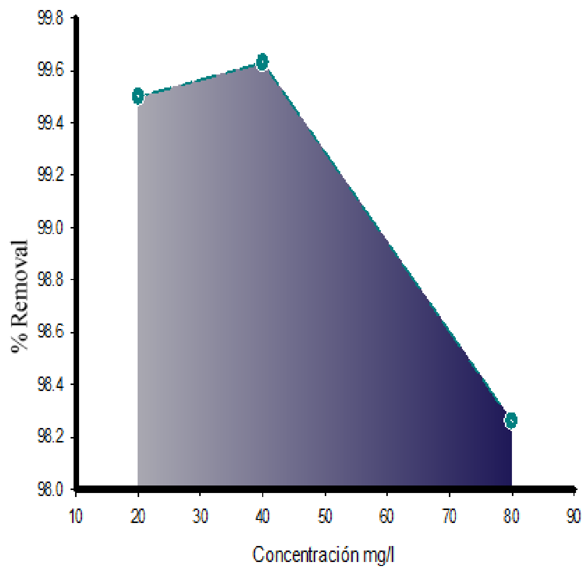

Figure 4. % of Removal versus concentration at pH3, second stage

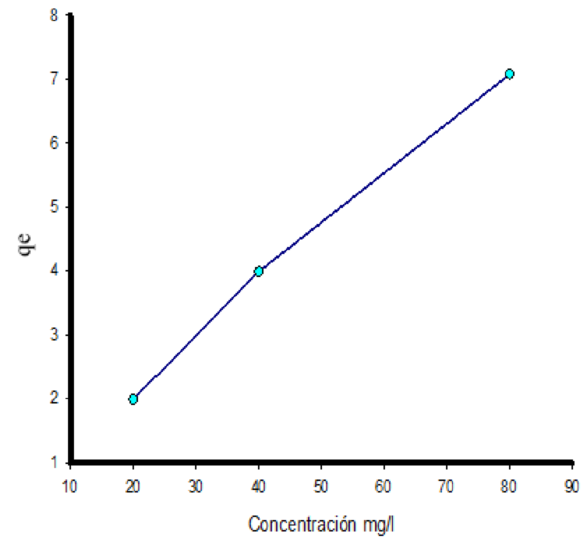

Figure 5. % Removal versus concentration at pH3, second stage

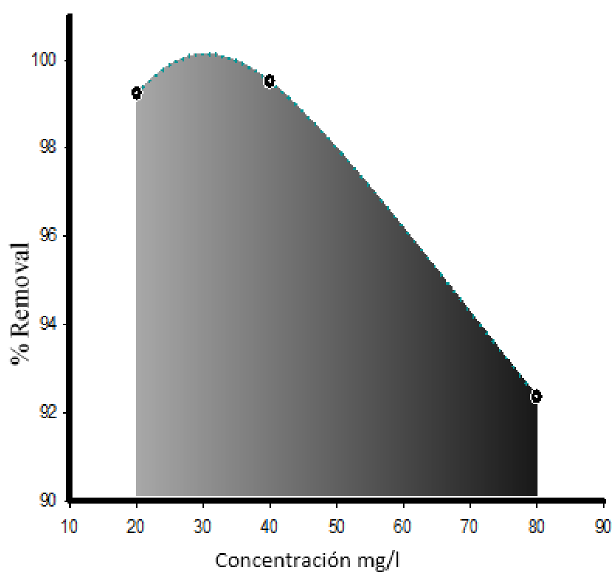

Figure 6. % of Removal versus concentration at pH3.5, second stage

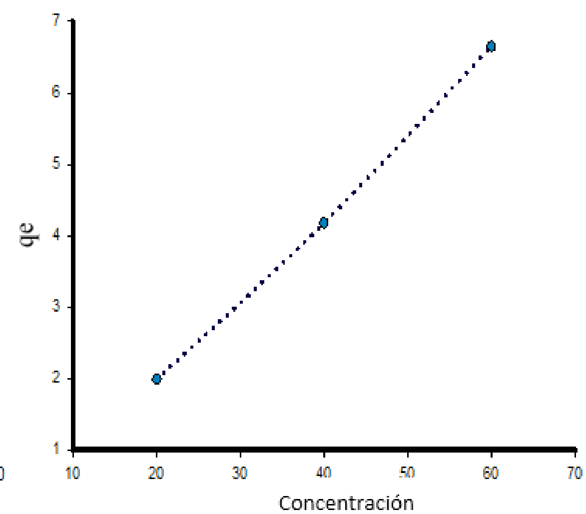

Figure 7. % of Removal versus concentration at pH3.5, second stage

According to the data obtained, the banana peel was able to remove more than 92% of hexavalent chromium in the solution. Another important aspect is that the biomass managed to remove almost immediately the highest concentration of the metal.

Adsorption isotherms

The Langmuir and Freundlich equations are commonly used to describe the adsorption balance in contaminated water treatment applications. An important physicochemical aspect for the evaluation of the adsorption process is the balance of isotherms. The equilibrium relationships between the adsorbent and the adsorbate are described by the adsorption isotherms. Freundlich's isotherm model assumes that adsorption occurs on heterogeneous surfaces (Abbasi, Z., Alikarami, M., Nezhad, E. R., Moradi, F., Moradi, V., 2013). The nonlinear and linearized equation of Freundlich is expressed as:

(3) $$qe = a_F C_{eq}^{\,bF}$$

(4) $$\log qe = \log a_F + b_F \cdot \log C_{eq}$$

Where ***aF*** is the constant of the Freundlich isotherm and ***b*** is the Freundlich exponent that is obtained from the slope and the intercept when plotting $\text{Log}q_e$ vs $\text{Log}C_{eq}$. (M. Romero-Sevilla, S. Sánchez-Cuadra, M. Benavente Silva, 2018). (figure 8)

The Langmuir isotherm assumes that a metal monolayer is formed on a relatively regular adsorbent surface, using partially protonated groups of the adsorbent. (Abbasi, Z., Alikarami, M., Nezhad, E. R., Moradi, F., Moradi, V., 2013) The non-linear and linearized equation of Langmuir is expressed as:

(5) $$qe = \frac{qemax\,b\,Ceq}{1+bCeq}$$

(6) $$\frac{Ceq}{qe} = \frac{1}{qemax} Ceq + \frac{1}{qemax\,b}$$

Where q_{emax} is the maximum adsorption capacity (mg/g) and b is the Langmuir adsorption equilibrium constant, these two constants were obtained from the intercept and the slope when plotting C_{eq}/q_e vs. C_eq. (M. Romero-Sevilla, S. Sánchez-Cuadra, M. Benavente Silva, 2018). (figure 9).

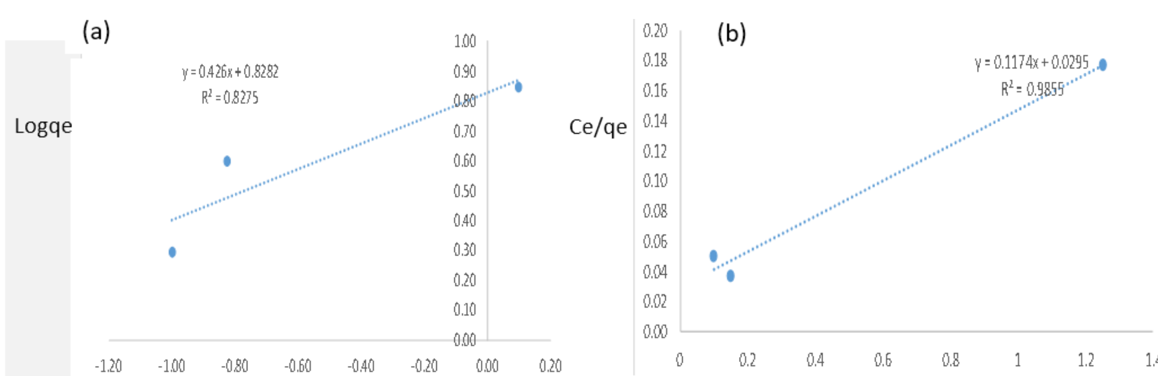

Figure 8. a and b Linear equation of adsorption isotherms of Freundlich and Langmuir pH3.

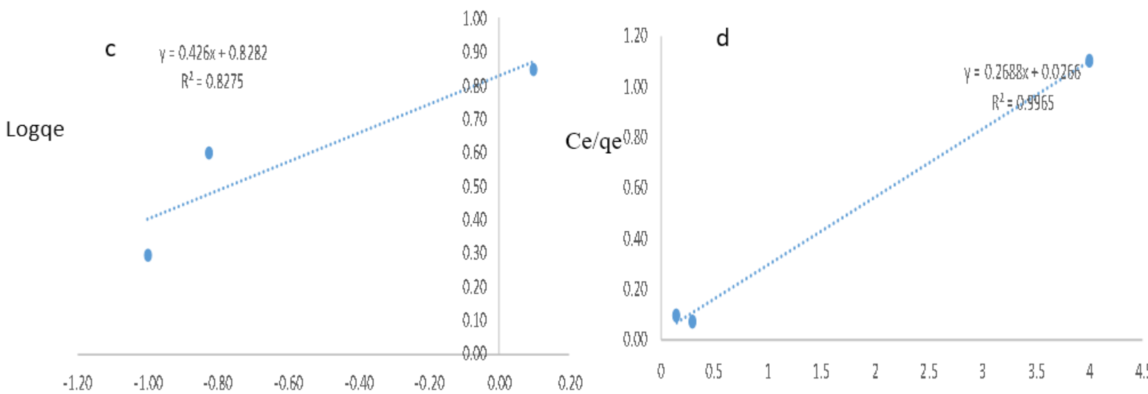

Figure 9. c and d Linear equation of adsorption isotherms of Freundlich and Langmuir pH3.5

Figures 8 and 9 show the linearized equations of both models, of which the best equilibrium model was determined based on the correlation coefficient (R^2). The metal adsorption equilibrium is best represented by the Langmuir isotherm, which assumes the existence of monolayer adsorption on a homogeneous surface. The highest adsorption capacity was obtained for pH 3, which indicates that the pH influences the adsorption capacity of the metal. The results correspond to that described by Abbasi Z. et al. (2013) in its publication, where the best isothermal model for the removal of Co^{2+} and Ni^{2+} using banana peel conforms to Lamguir. (Abbasi, Z. Alikarami, M., Nezhad, E. R., Moradi, F. Moradi, V., 2013). Table 1 shows the values of R2 and the maximum adsorption capacity of the banana peel for both models.

Table 1. Adsorption isotherms constants of Freundlich and Langmuir

	Isotherm Freundlich			Isoterma Langmuir		
PH	**a_f mg/g**	**b**	**R^2**	**q_{max} mg/g**	**b**	**R^2**
3.0	6.894	0.426	0.8275	8.5179	0.0118	0.9855
3.5	4.723	0.324	0.8184	3.7202	0.0072	0.9965

The Langmuir isotherm can be expressed in terms of a dimensionless constant called the separation factor (R_L, also called the equilibrium parameter) that is defined by the following equation:

$$R_L = 1 / 1+bCo$$

Where C_0 (mg / L) is the initial concentration of hexavalent chromium and ***b*** is Langmuir's constant related to adsorption energy. The value of R_L indicates that the shape of the isotherms is: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). (B. Meroufel, O. Benali, M. Benyahia, 2013). Figures 9 and 10.

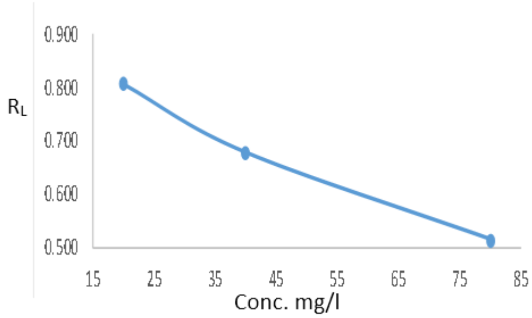

Figure 10. RL factor of banana peel for pH3

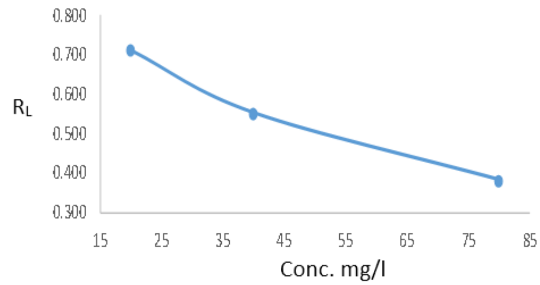

Figure 11. RL factor of banana peel for pH3.5

According to figures 10 and 11, the R_L values are lower at higher concentrations (C_o) of hexavalent chromium, that is, the higher the concentration, the lower the separation factor (R_L), this behavior is similar in both pH. The R_L values obtained ranged from 0.809 to 0.383, indicating a favorable adsorption of hexavalent chromium in the banana peel. The results correspond to those described by Meroufel B.et al. (2013) in its publication where the R_L factor tended to zero as the concentration increased. (B. Meroufel, O. Benali, M. Benyahia, 2013). Besides, Deshmukh P. D. et al. (2017), in his research he obtained a favorable adsorption of cadmium in the banana peel with a separation factor of less than 1. (Deshmukh, PD, Khadse, GK, Shinde, VM, Labhasetwar, P., 2017) Similarly, Memon J. R et al. (2008) in its publication, mentions that it obtained R_L values < 1, which shows a favorable adsorption of trivalent chromium in the banana peel. (Memon, J. R., Memon, S. Q., Bhanger, M. I., Khuhawar, M. Y., 2009). Based on the above, the banana peel has a favorable adsorption capacity for the removal of hexavalent chromium in contaminated water.

CONCLUSIONS

The highest percentage of hexavalent chromium removal was obtained with pH 3 and 3.5 reaching a removal percentage greater than 92.

The adsorption capacity of the banana peel increased as the metal concentration increased, both being directly proportional.

The adsorption equilibrium at pH3 and 3.5 was better represented by the Langmuir isotherm than that of Freundlich, obtaining greater maximum adsorption capacity (q_{emax}) at pH3.

The separation factor was less than 1 (R_L < 1), which indicates favorable adsorption of hexavalent chromium in the banana peel.

The banana peel is an excellent material to remove the hexavalent chromium content in contaminated water, which could be used for the treatment of wastewater contaminated by this heavy metal.

THANKS

To the Vice-Rectory of Research, Postgraduate and University Extension, and the Research Directorate of UNAN-Managua for financing through the Funds for Research Projects (FPI).

To the Central Dining Room of the Universidad Nacional Autónoma de Nicaragua, Managua (UNAN-Managua) and to the Dining Room of the Center for Aquatic Resources Research (CIRA-UNAN) for providing the banana peels necessary for research.

Mr. Jorge Esquivel Quezada for his valuable technical collaboration during the research process.

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