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Removal of Chromium, Iron and Manganese from contaminated waters using cryogels as adsorbent

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ABSTRACT

The aim of this study was to remove ions chromium (Cr^{3+}), iron (Fe^{3+}) and manganese (Mn^{2+}) from contaminated waters using polyacriamine gel macropores (MPAAG) called cryogels or hydrogel as adsorbent material. The cryogel MPAAG was prepared at a concentration of 7,5 % (w/v), the polymerization of which was performed at

-12 ºC for 1 hours. Amine and carboxyl ligand groups such as tris (2aminoethyl) amine (TREN) followed by bromoacetic acid (BA) were added. Cr^{3+}, Fe^{3+} y Mn^{2+} ions solutions at a concentration of 74 mg/L, 24 mg/L and 27 mg/L respectively were in contact with the adsorbent (MPAAG-TBA) adjusted to pH 2, 3 and 5 to Cr^{3+}, pH 3 y 5 to Fe^{3+} and pH 3, 5 and 7 to Mn^{2+}; the solution was shaken at 200 rpm for 3 hours; aliquots of 10 ml were taken at 5, 10, 30, 60, 120 and 180 minutes. The concentration of metals was determined using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique. The maximum adsorption capacity Cr^{3+} was determined (7.52 mg/g) at pH 3, Fe^{3+} (1.13 mg/g) at pH 5 and Mn^{2+} (1.51 mg/g) at pH 7 was determinated using Langmuir model. The results of adsorption isotherm of metallic ions on MPAAG-TBA were better represented by the Freundlich model, demonstrating an adsorption in multilayers of a heterogeneous surface. Also, the separation factor was equal to one, indicating a linear adsorption based on the Langmuir isotherm model. The results indicate that the cryogel MPAAG-TBA has chelating properties for the removal of Cr^{3+}, Fe^{3+} and Mn^{2+} in contaminated waters.

INTRODUCTION

Wastewater generated by the chemical industries contains pollutants that are very harmful to the environment. The excessive release of heavy metals into the environment due to industrialization and urbanization has projected a major problem worldwide (Al-anbakey, 2016). Heavy metal ions can be absorbed and accumulated by living organisms because they are not biodegradable and are highly soluble in aquatic environments. Some heavy metal ions, including Cr^{3+}, Fe^{3+} and Mn^{2+} are significantly toxic to humans if introduced into the food chain and ingested beyond pre-set concentrations (Fu et al., 2019; Li, Wang, Wu, Chen, & Wu, 2013).

In Nicaragua, the removal of these heavy metal ions from contaminated water is a difficult task for researchers, as most industries lack the technology and facilities to treat the wastewater before it enters the receiving bodies (Ur Rehman et al., 2019). Adsorption is one of the useful methods to reduce the heavy metal contaminant in the environment (Lesbani, Turnip, Mohadi, & Hidayati, 2015), and is widely adopted because of its simple operation, low cost and high efficiency (Fu et al., 2019). It has proven its efficiency and economic viability and has gained importance in industrial applications (El-Araby, Ibrahim, Mangood, & Abdel-Rahman, 2017).

The Biotechnology Laboratory of UNAN-Managua previously conducted laboratory-scale tests for the implementation of new technologies of supermacropore gels used as monolithic or chromatographic columns of nano and micro biological particles, which could be maintained by polymerization of sub-zero grade monomers (Plieva et al., 2006; Şarkaya, Bakhshpour, & Denizli, 2019). Cryogels also ensure suitability for working with highly viscous media such as metal ions contained in wastewater. The macroporous structures interconnected to cryogels represent the suitability for various applications (Şarkaya et al., 2019).

Therefore, this research aimed at removing chromium, iron and manganese ions from contaminated water using polyacrylamide cryogenic adsorbents which have an effective adsorption capacity for heavy metals, taking into consideration certain parameters that influence such as pH, metal concentration and contact time.

MATERIALS AND METHODS

Reagents: Acrylamide (AAm, > 99. 9% pure, (APS) ammonium persulfate, (AGE) allyl glycidyl ether 99%, N,N,N-tetramethyl ethylenediamine (TEMED), N,N-methylene bis-acrylamide (MBAAm), (HCl, 37%) hydrochloric acid, (NaOH) sodium hydroxide, tris(2-aminoethyl) amine (TREN), bromacetic acid (BA), (TNBS) picrisulphonic acid, sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), iron sulfate heptahydrate ($FeSO_4$. $7H_2O$), manganese sulfate ($MnSO_4.H_2O$), potassium dichromate ($K_2Cr_2O_7$) and ethanol (96%).

Preparation of standards: For the analysis of Cr^{3+}, Fe^{3+} and Mn^{2+} the certified Inorganic Ventures standard of 998±4; 1,006±5 and 999±4 mg/l respectively was used, being used for the preparation of the working range.

Preparation of solutions from Chrome, Iron and Manganese salts: The experiment was carried out in batch mode using $K_2Cr_2O_7$, $FeSO_4.7H_2O$ and $MnSO_4$ salts. H2O for Cr^{3+}, Fe^{3+} and Mn^{2+} determination, the solutions were prepared at concentrations of 74, 24 and 27 mg/l respectively at a volume of 300 ml with de-ionized water, using Agilent 700 Series Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Epoxy pAAm polymerization

The methodology used to produce the pAAm-cryogels with epoxy functional groups (epoxy pAAm) has been previously described (Jarquín, M. & Lacayo M., 2020). The appropriate amounts of the monomer were the following: 7.6 g of acrylamide; 3.2 g of MBAAm and 2.0 ml of AGE, these reagents were dissolved in 170 ml of de-ionized water to obtain a final concentration of 7.5 w/v%. The solution was then degassed for 30 minutes and 190 µl TEMED was added. The content was placed in a cold bath for 30 minutes. Afterwards, 152.6 mg of APS was added, the mixture was quickly shaken and then poured into the glass columns (15 ml, ID 9 mm) containing the carriers (molds) and they were placed in a thermostatic bath at -12°C for 1 h, then they were transferred to a freezer at -12°C for 1 hour. The tubes containing the gel were left at room temperature for 30 minutes and cut according to the diameter of the carrier and placed in deionized water. Three washings were performed with agitation at 100 rpm for 1 hour to remove any reagent residue and finally, they were stored at 4 °C.

To understand the role of functional groups in the removal of Cr^{3+}, Fe^{3+} and Mn^{2+} ions using epoxy-MPAAG, carboxylic groups were added as follows: the first reaction consists of adding ligand groups which are the primary amines. It was prepared the carbonate buffer ($NaHCO_3$: Na_2CO_3) 0.2 M at pH = 9.2-9.4 to a volume of 800 ml, 5.04 ml of tris (2 aminoethyl) amine (TREN) was added, later the epoxy-MPAAG that was obtained from the cryogenic process, was left in agitation for 15 h at 200 rpm, then the cryogenic was washed with deionized water to remove the excess of the reagent.

To verify the binding of the TREN group in the epoxy-MPAAG it was necessary to take the gel at random, which was placed in a vial containing 1 ml of sodium carbonate pH = 8.5 and 2 μl of trinitro benzene sulfonic acid (TNBS) were added, the change in yellow color indicated that the ligand of the amine group was properly bound. After checking the binding of the amine group, the second reaction was carried out by adding a carboxyl group from bromacetic acid (BA) with a 4:1 ratio (bromacetic acid: MPAAG) at pH 8.7 to which the primary amines of the first reaction are bound. The reaction was carried out for 20 h at 300 rpm. The pH was adjusted with concentrated NaOH, which should remain above 8.5. The excess of reagent was eliminated by rinsing the MPAAG-TBA with deionized water (Jarquín, M. & Lacayo M., 2020).

Influence of pH and contact time on MPAAG-TBA

The aqueous solutions for each metal under study were prepared and brought the experimental process separately to a volume of 300 ml at concentration for Chromium 74 mg/L at pH 2, 3 and 5; Iron 24 mg/L at pH 3 and 5; and Manganese 27 mg/L at pH 3, 5 and 7 from the salts of $K_2Cr_2O_7$, $FeSO_4.7H_2O$ and $MnSO_4.H_2O$ respectively. Thirty carriers containing 0.672 g of MPAAG-TBA equivalent to its dry weight were added and shaken at 200 rpm during 3 hours. Aliquots of 10 ml were taken at 5, 10, 30, 60, 120 and 180 minutes at laboratory temperature of 25.5 ± 2 ° C. The concentrations of Cr^{3+}, Fe^{3+} and Mn^{2+} were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique.

RESULTS AND DISCUSSION

Effect of MPAAG-TBA composition

MAAP-TBA was prepared at a concentration of 7.5 % (w/v) as described by Jarquín et.al. (2020). The polymerization process was brought to a temperature of -12 ºC for one hour by using a thermostat. The addition of ligand groups was done first by the addition of amine groups giving positive by the yellow coloration and the second was the addition of carboxylic groups willing to accept the metals under study (figure 1).

Figure 1: Obtaining the cryogel and adding the iron functional groups

Effect of pH on MPAAG-TBA adsorbent

The content of Cr^{3+}, Fe^{3+} and Mn^{2+} ions in the water phase before and after the adsorption process was determined using the ICP-OES. The adsorption capacity Qe (mg/g) was calculated according to the following equation:

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

Where C_0 is the initial concentration of the metal in solution (mg/L); C_e is the concentration of the metal in equilibrium (mg/L); V is the volume of the solution (L) and m is the mass of the adsorbent (g) (Jarquín M. & Lacayo M., 2020; Pourjavadi, Abedin-Moghanaki, & Hosseini, 2016).

Figure 2 shows the effects of pH on the adsorption capacity on MPAAG-TBA for Cr^{3+}, Fe^{3+} and Mn^{2+} ions. The adsorption is closely related to the pH of the Manganese solution and the adsorption capacity increases as the pH increases, being observed that its maximum adsorption capacity was 1.51 mg/g at pH 7, however, for Chrome increasing its pH gradually decreases its adsorption capacity being the maximum of 7.52 mg/g at pH 3 and for Iron its maximum adsorption capacity was 1.13 at pH 5.

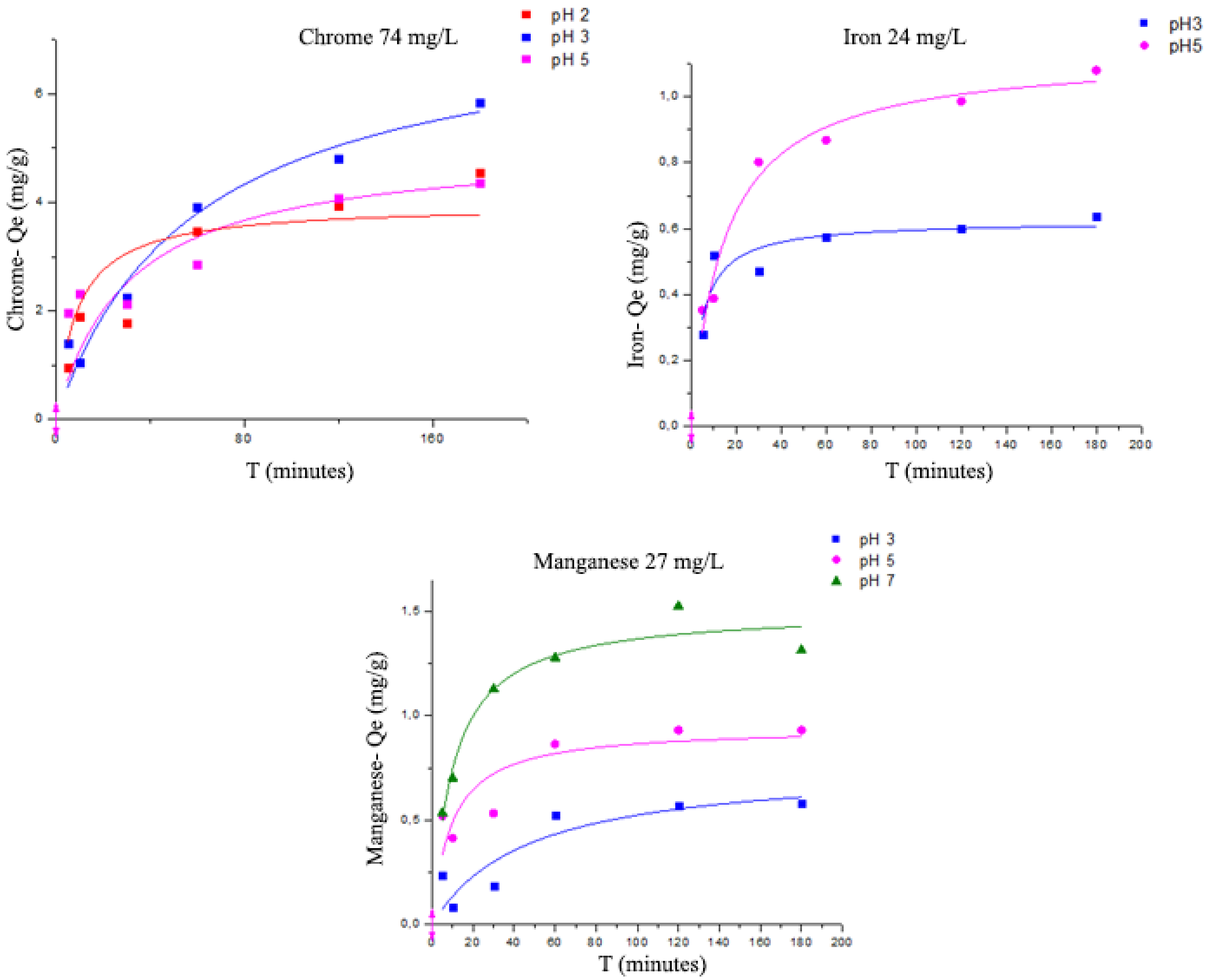

Figure 2. Effect of pH and contact time with MPAAG-TBA on the maximum adsorption capacity of Chromium (74 mg/L), Iron (24 mg/L) and Manganese (27 mg/L), Langmuir, m=0.672 g in 300 ml at 24.5 °C, 200 rpm, 180 minutes Software origin pro8 V2019 non linear analysis.

Adsorption model

The Langmuir and Freundlich equations are commonly used to describe the adsorption balance in contaminated water treatment applications. The isothermal equilibrium is an important parameter for the evaluation of the adsorption process, which relates the equilibrium between the adsorbent and the adsorbate. Freundlich's isothermal model assumes that adsorption occurs on heterogeneous surfaces (Lopez, M. & Lacayo, M., 2020). Freundlich's non-linear, linearized equation is expressed as:

(2) $$Qe = K_F C_e^{1/n}$$

(3) $$\log Q_e = \log K_F + \frac{1}{n}\log C_e$$

Where K_F and n are Freundlich's findings related to the adsorption capacity (mg/g) and the adsorption intensity respectively. Adsorption intensity (n) is the equilibrium constant of adsorption, whose value is indicative of the heterogeneity of the surface of the adsorbent (Jarquín, M. & Lacayo M., 2020; Pliego-Arreaga, Regalado, Amaro-Reyes, & García-Almendárez, 2013); that is, the values indicate the degree of non-linearity between concentration and adsorption as: Adsorption is linear if $n = 1$; adsorption is a chemical process if $n < 1$, adsorption is a physical process if $n > 1$ and if n is in the range of 1-10 it indicates that the adsorption is favorable; K_F (mg/g $(L/mg)^{1/n}$) represents the amount of metal ions adsorbed on the adsorbent for a unit of concentration at equilibrium and Ce (mg/L) is the concentration at equilibrium (Borhade & Kale, 2017; Desta, 2013; Jarquín, M. & Lacayo, M., 2020).

The Langmuir isotherm assumes that a monolayer of the metal is formed on a relatively regular adsorbent surface, using the partially protoned groups of the adsorbent (López, M. & Lacayo, M., 2020). The Langmuir non-linear and linearized equation is expressed as:

(4) $$Qe = \frac{Q_{max} b C_e}{1 + bC_e}$$

(5) $$\frac{C_e}{Q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_e}$$

Where Q_{max} represents the maximum adsorption capacity of the metal (mg/g) and b is the adsorption constant (L/mg) and is related to the affinity and energy of the binding sites. The numerical values of Q_{max} and b are obtained from the slope and the intercept, respectively (Ayawei, Ebelegi, & Wankasi, 2017; Bulut & Baysal, 2006; Foo & Hameed, 2010; Özcan, Gök, & Özcan, 2009; Sari, Tuzen, Citak, & Soylak, 2007).

Figures 3 show the linearized equations of the Langmuir and Freundlich model, for the different treatments, of which the best equilibrium model was determined based on the correlation coefficient (R^2). The metal adsorption equilibrium is best represented by Freundlich's isotherm for the three metals, Cr^{3+}, Fe^{3+} and Mn^{2+}, which implies the existence of multilayer adsorption on a heterogeneous surface. The maximum adsorption capacity (Q_{max}) was obtained for pH 3 in the case of chrome, pH 5 for iron and pH 7 for manganese, which indicates that the adsorption capacity of MPAAG-TBA is influenced by pH, presenting different behaviors for each metal, that is, it requires either low or high pH depending on the metal of interest to be removed. Table 1 shows the R^2 values and maximum adsorption capacity of MPAAG-TBA for both models.

Table 1. Parameters of Langmuir and Freundlich isotherms for Cr^{3+}, Fe^{3+} and Mn^{2+} adsorption on MPAAG-TBA.

Metal ion	**pH**	**Langmuir**			**Freundlich**			
		Q_{max} (mg/g)	**b (L/mg)**	**R^2**	**K_f (mg/g (L/mg)$^{1/n}$)**	**n**	**1/n**	**R^2**
Chrome	2	5,07	0,03	0,79	0,63	2,60	0,38	0,94
	3	7,52	0,02	0,81	0,48	2,07	0,48	0,94
	5	3,96	0,11	0,96	1,12	3,89	0,26	0,99
Iron	3	0,62	0,22	0,95	0,29	6,37	0,16	0,98
	5	1,13	0,07	0,95	0,25	3,43	0,29	0,98
Manganese	3	0,77	0,02	0,66	0,1	2,36	0,42	0,93
	5	0,80	0,11	0,49	0,21	3,59	0,28	0,97
	7	1,51	0,09	0,92	0,45	4,27	0,23	0,98

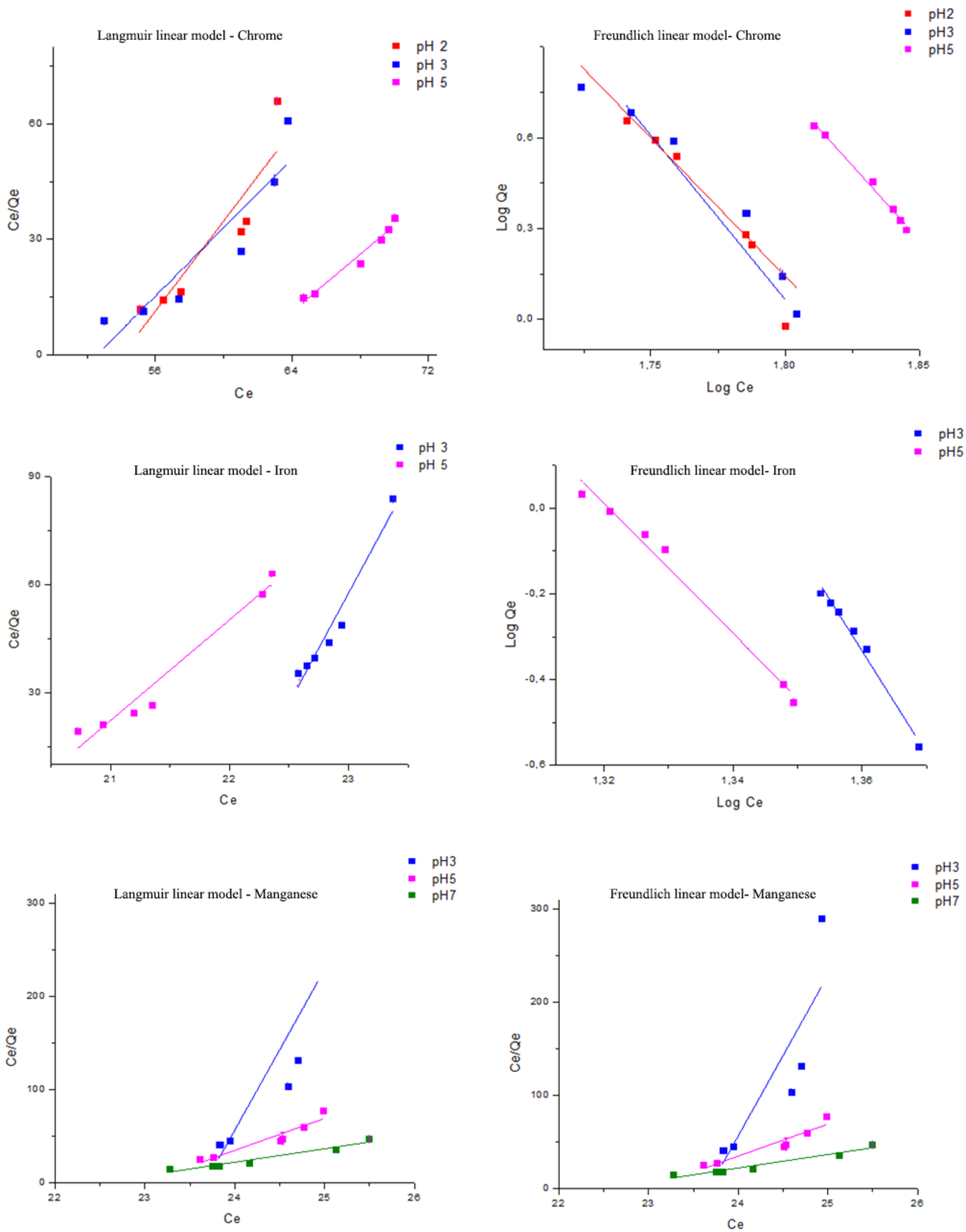

Figure 3: Isothermal experiment of chromium, iron and manganese adsorption linearized by the model of Langmuir and Freundlich different pH.

Adsorption according to Langmuir's isotherm can be expressed in terms of a dimensionless constant called the separation factor (R_L), also called the equilibrium parameter (Lopez, M. and Lacayo, M., 2020) which is defined by the following equation:

$$R_L = \frac{1}{1+bC_o} \tag{6}$$

Where b is the adsorption constant of Langmuir (mg/g) and C_o is the initial concentration of the adsorbent (mg/L). The R_L values indicate the nature of the adsorption and are considered the most reliable indicator for an isothermal adsorption. There are four probabilities of the separation factor or equilibrium (R_L) value, it is unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$ and irreversible when $R_L = 0$ (Jarquín, M. and Lacayo, M., 2020).

Table 2 shows that the results obtained by the Langmuir isotherm model the adsorption equilibrium (RL) for chromium, iron and manganese on MPAAG-TBA are RL=1, which indicates that it is linear for the different pH studied of each metal; that is, it is neither favorable nor unfavorable.

Table 2. Equilibrium factor (RL) of MPAAG-TBA for different pH

pH	**Cr^{3+}**	**Fe^{3+}**	**Mn^{2+}**
	RL		
2	1,00	-	-
3	1,00	1,00	1,00
5	1,00	1,00	1,00
7	-	-	1,00

CONCLUSIONS

The adsorption capacity of the cryogel for chrome increases when the pH decreases, being the pH 3 more optimal, however, for manganese and iron it is higher when the pH increases to 7 and 5 respectively, reaching an adsorption balance after 60 minutes.

The adsorption balance of the cryogel for chromium, iron and manganese was best represented by Freundlich's isotherm, indicating a multilayer adsorption of a heterogeneous surface.

The separation factor was equal to one (R_L=1), showing a linear adsorption of MPAAG-TBA for the three metals at the studied pH.

MPAAG-TBA is a polymer with chelating properties that could be useful for chromium, iron and manganese adsorption in contaminated water.

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