

Evaluation of the kinetic of Cu^{2+} adsorption in the Poly Vinyl Alcohol membranes crosslinked with sulfosuccinic and citric acids

Avaliação da cinética de adsorção de Cu^{2+} nas membranas de Alcool Poli Vinílico reticuladas com ácidos sulfosuccínico e cítrico

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Abstract

Soil contamination by wastewater containing polluting ions, such as Cu^{2+} , is of great concern to society. Therefore, it is necessary to invest in materials capable of containing or removing such contaminants from the soil. Polyvinyl alcohol (PVA) membranes crosslinked with sulfosuccinic acid (SSA) and citric acid (CA) were synthesized using the technique of pouring and solvent evaporation in order to absorb Cu^{2+} . After film formation, the membranes were characterized by moisture absorption (WU), infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and copper ion adsorption (Cu^{2+}). It was found that the membrane containing sulfosuccinic acid (SSA) presented a lower degree of swelling among the other membranes tested, with only 7.4% of water absorption. Therefore, it was the membrane with the best dimensional stability since the pure PVA presented 235% swelling. Furthermore, from the bands presented in the FTIR at 1400 cm^{-1} it was possible to verify the occurrence of the esterification reaction, which is another indication of the polymer crosslinking. Kinetic models of diffusional and chemical control were used to understand the ion adsorption interaction phenomena. The mixed control kinetic model was also evaluated, in which it was possible to evaluate different parameters related to interaction ions and membranes. From these results it was observed that the correlation coefficient of PSSA / Cu^{2+} 0.97; PCA / Cu^{2+} 0.91; thus indicating a possible tendency for the stage of adsorption rate controlled by the surface of adsorption of Cu^{2+} ions by the reticulated membranes.

Keywords:

Membranes, Poly (Vinyl Alcohol), Copper Adsorption, Crosslinked.

Resumo

A contaminação de solos por águas residuárias contendo íons poluidores, como por exemplo o Cu^{2+} , é de grande preocupação da sociedade. Logo, faz-se necessário o investimento em materiais capazes de conter ou remover tais contaminantes do solo. Membranas de álcool poli vinílico (PVA) reticuladas com ácido sulfosuccínico (SSA) e ácido cítrico (CA) foram sintetizadas através da técnica de vazamento e evaporação de solvente com objetivo de absorver Cu^{2+} . Após a formação do filme, as membranas foram caracterizadas pela absorção de umidade (WU), espectroscopia de infravermelho (FTIR), análise termogravimétrica (TGA) e adsorção de íons de cobre (Cu^{2+}). Verificou-se que a membrana contendo ácido sulfosuccínico (PSSA) apresentou menor grau de inchamento dentre as demais membranas testadas, somente 7,4% de absorção de água. Portanto foi a membrana com melhor estabilidade dimensional já que o PVA puro apresentou inchamento de 235%. Além disso, a partir das bandas apresentadas no FTIR em 1400 cm^{-1} foi possível verificar a ocorrência da reação de esterificação, sendo este mais um indicativo da reticulação do polímero. Modelos cinéticos de controle difusional e químico foram usados para entender os fenômenos de interação de adsorção de íons. O modelo cinético de controle misto também foi avaliado, no qual foi possível avaliar diferentes parâmetros relativos aos íons de interação e membranas. A partir desses resultados observou-se que o coeficiente de correlação de PSSA / Cu^{2+} 0,97; PCA / Cu^{2+} 0,91; indicando assim uma possível tendência para o estágio de velocidade de adsorção controlada pela superfície de adsorção de íons Cu^{2+} pelas membranas reticuladas.

Palavras-chave:

Membranas, Poli (Álcool Vinílico), Adsorção de Cobre, Crosslinked.

Como você deve citar?

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1 INTRODUCTION

Heavy metals present in industrial waste are a serious environmental concern at present, due to their toxicity and non-biodegradability (TEOW et al, 2018). Copper (Cu), in the form of Cu²⁺ ion, is one of these metals, widely used in the manufacture of batteries, coatings, metal finishes, metallurgy and chemical industry (LIU et al, 2016). Among the methods used for the removal of heavy metal ions are chemical precipitation, adsorption, filter membranes and electrochemical treatments (FU et al, 2011). In the specific case of Cu²⁺ ions, adsorption has shown to be attractive and promising due to its high efficiency, selectivity and low cost (LIU et al, 2016). The use of membrane separation processes allows the reuse of water from industrial processes, presenting advantages such as lower energy consumption, compared to other traditional separation processes, operational flexibility, because the system is more compact, and the reduction of use of chemical agents in the treatment, providing a final product of better quality (KUNZ et al, 2002).

Poly (vinyl alcohol) (PVA) is a low-cost biodegradable polymer that has properties such as hydrophilicity and good film forming ability, which makes it suitable for membrane formation (AHMAD et al, 2012; BABU et al, 2017; TOYODA et al, 2019). The use of this polymer is not reported as a direct waterproofing system in sanitary landfills, but it has been widely used in desalination and ultrafiltration membranes (RHIN et al, 2004; SONKER et al, 2018). The use of crosslinking agents allows to improve the thermal and mechanical stability of PVA, which is low due to its solubility in water at 100°C (RHIN et al, 2004). Rhim et al (2004) observed and reported in studies that the addition of sulfosuccinic acid (SSA) improved ion exchange capacity (IEC), mechanical properties and thermal stability of membranes while it reduced the degree of swelling. Several crosslinking agents such as glutaraldehyde, formaldehyde and sulfosuccinic acid have been studied for membrane applications of pervaporation, nanofiltration and other treatments (AHMAD et al, 2012; EBENEZER et al, 2016).

Different studies demonstrate the potential for adsorption of heavy metals in different materials. For example, biomasses of dead fungi as *Pleurotus Pulmonarius* and *Schizophyllum Commune* (VEIT et al, 2005). Beppu et al. (2007) studied the removal of copper in macroporous chitosan membranes functionalized with an amino acid (histidine). According to Vieira et al (2007) in Cu²⁺ adsorption studies showed good adsorption capacity, the contact time required to reach equilibrium was 10 hours. The kinetic study indicated that the adsorption kinetics between the metal ions and the adsorbent material was controlled by chemical adsorption, according to the pseudo-second order adsorption mechanism.

In this work, the study focused on the preparation of two types of acid reticulated PVA membranes and the evaluation of their performance to remove the Cu²⁺ in liquid effluents. One of them with sulfosuccinic acid (SSA) and another one with citric acid (CA) containing the sulfonic and carboxylic groups, respectively. In addition, it evaluated membranes properties as dimensional stability, thermal resistance and potential of adsorption of Cu²⁺ ions to determine which membrane presented the best performance when crosslinked.

2 MATERIALS AND METHODS

The membranes analyzed in this work were synthesized from 5% of aqueous solution of PVA from Sigma Aldrich and 99% hydrolyzed. The chemical crosslinking thereof occurred by adding 30% of one type of acid. The acids used, sulfosuccinic acid (SSA) and citric acid (CA), were both from Sigma Aldrich. All reagents were used as received. After 2h of stirring the solutions, they were casted into petri dishes, dried in an oven at 50°C for solvent evaporation and thermal crosslinked at 130°C for 2h.

The evaluation of the chemical composition of the membranes was done using the infrared technique with attenuated total reflectance (FTIR) in a JASCO FT/IR-4700 spectrophotometer, in which the frequency range analyzed was 4000 to 400 cm^{-1} (THANGANATHAN et al 2012; THANGANATHAN et al 2015; NASCIMENTO et al 2021). The thermal decomposition study was performed on a TA Instruments thermogravimetric analyzer, model TG Q50. The temperature range was 25 to 800°C, with a heating rate of 10°C/min under nitrogen atmosphere (CADINELLI et al, 2018; NASCIMENTO et al, 2021). The evaluation of the water absorption was determined by the degree of swelling (WU) calculated through Eq 1. where: m_{wet} is the mass of the wet membrane; m_{dry} is the mass of the dry membrane.

$$\% \text{ swelling} = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (1)$$

Ion exchange capacity (IEC) was determined by the indirect acid - base titration method using sodium hydroxide (NaOH). The membrane sample was immersed in sodium chloride (NaCl) solution for 24h and then was titrated with (NaOH) phenolphthalein which was used as indicator. After titration, the number of moles of the ion is found through Eq 2., where V_{NaOH} (mL) is the volume of NaOH solution spent to reach the titration point, M_{NaOH} is the molar concentration of the NaOH solution (mol/L) and m_{dry} is the mass of the dry membrane sample (NASCIMENTO et al, 2021).

$$IEC = \frac{V_{NaOH} \times M_{NaOH}}{m_{dry}} \quad (2)$$

The number of water molecules per ionic group (λ) was determined by Eq 3. The values of degree of swelling and IEC used were those obtained in the previous tests.

$$\lambda = \frac{\text{swlling}}{18 \times IEC} \quad (3)$$

The adsorption tests were performed through flame atomic absorption spectroscopy (FAAS), using a spectrophotometer VARIAN, Spectr AA-55B, air / acetylene flame (99.7 to 99.8% purity), current of lamp of 10 mA and wavelength equal to 766,5nm. For this, the membranes remained immersed and under stirring for 72h at room temperature in an aqueous solution of 5ppm containing the Cu^{2+} ions. After the adsorption equilibrium, Cu^{2+} concentration in the remaining solution was measured. The Cu^{2+} distribution coefficients (k_d) were calculated using Eq 4., where k_d is the distribution coefficient (in L.g^{-1}), Q_e is the adsorption equilibrium capacity (in mg.g^{-1}) and C_e is the concentration equilibrium (in mg.L^{-1}) (SHI et al, 2008; ZHANG et al, 2016; YOON et al, 2019; BEDIKO et al, 2019).

$$k_d = \frac{Q_e}{C_e} \quad (4)$$

After the values obtained in Eq 4, an isothermal curve adjusted to the Langmuir Eq 5 model was made, where: Q_e is the amount of solute adsorbed per gram of adsorbent at equilibrium, Q_{max} is the maximum adsorption capacity (mg.g^{-1}), adsorbate/adsorbent interaction constant (L.mg^{-1}) and C_e is the concentration of adsorbate at equilibrium (mg.L^{-1}). In order to evaluate the development of the adsorption

process, the separation factor (RI) was calculated from the results of Q_{max} and KI and C_0 initial adsorbate concentration of Eq 6 (ZHANG et al, 2016; BEDIAKO et al, 2019).

$$q = \frac{Q_{max} k C_e}{1 + k C_e} \quad (5)$$

$$RI = \frac{1}{1 + KI C_0} \quad (6)$$

2.1 Calculations of the copper removal speed controlling step.

Chemical kinetics encompasses factors that influence the speed of chemical reaction, identify the mechanisms in which it is processed. Thus for the calculation controlling step of adsorption of the chemical elements Cu²⁺ where they are adsorbed by the membrane surface the chemical control equation presented below is used Eq 7 and Eq 8.

$$1 - (1 - \alpha)^{1/3} = k_R \cdot t \quad (7)$$

$$K_R = \frac{bk[H_2SO_4]^n}{\rho r_0} \quad (8)$$

If the ion diffusion occurs through the membrane layer becoming the control rate step, Eq 9 and Eq 10 represent the diffusional control model.

$$[1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)] = k_D \cdot t \quad (9)$$

$$K_D = \frac{6bD_{eff}[H_2SO_4]^n}{\rho r_0^n} \quad (10)$$

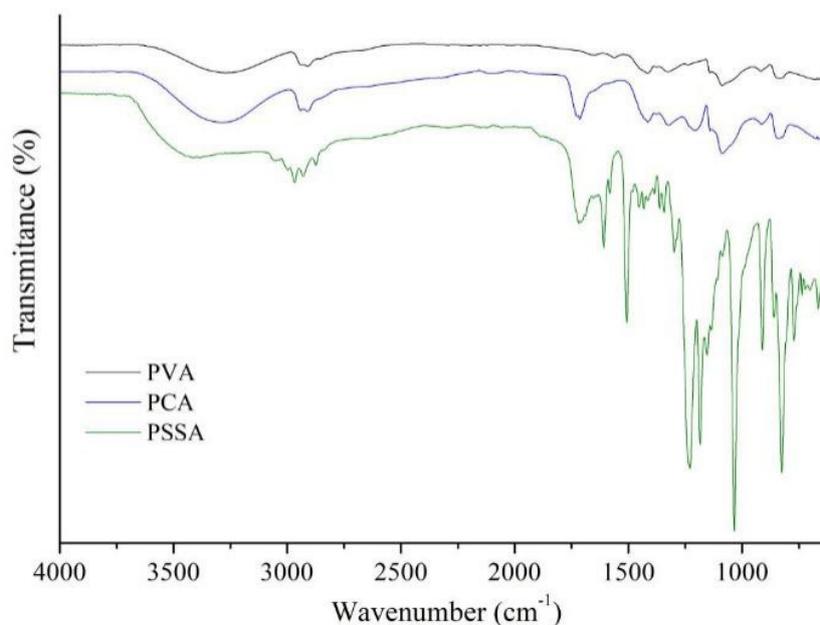
According to Equation 7 when the chemical reaction becomes the speed control step, the $[1 - (1 - \alpha)^{1/3}]$ versus time will approach a straight line with slope representing K_R . Similarly, for Equation 9 when plotting $[1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)]$ versus time and approaches the line indicates that the predominant control would be diffusional with the slope representing K_D .

3 RESULTS AND DISCUSSION

The crosslinking of PVA by acid groups occurs through the esterification of the carboxylic groups (COOH) present in the crosslinking agents and the hydroxyls (OH) of the polymer matrix. In addition, it is known that the use of temperatures above 100°C promotes the greatest number of crosslinks during esterification (NASCIMENTO et al, 2021). Through the FTIR analysis, Figure 1, it was possible to evalua-

te the changes in the chemical structure of the membrane and verify the bands corresponding to the esterification reaction.

Figure 1 - Evaluation of structure modification due to chemical crosslinking. Poly (vinyl alcohol) (PVA) crosslinked with sulfosuccinic acid (PSSA) and citric acid (PCA)

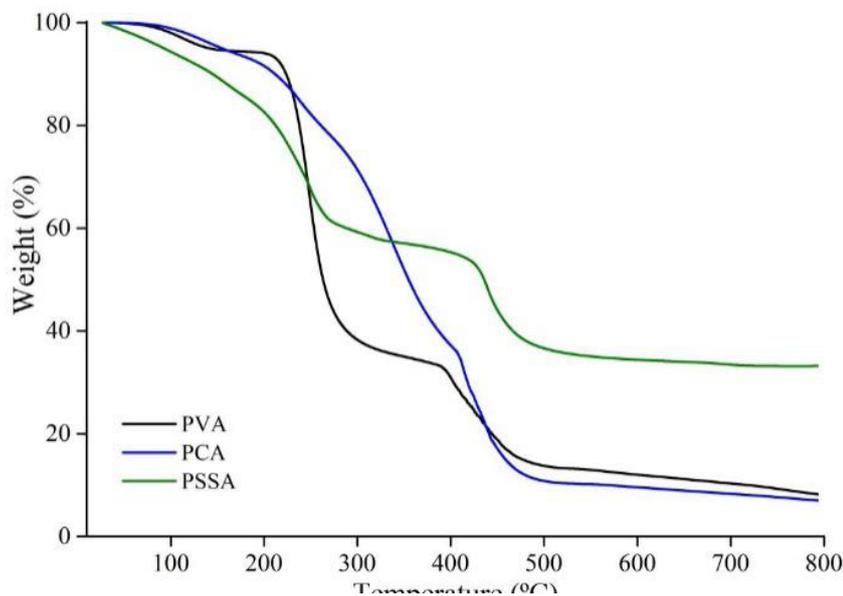


Source: Authors (2021)

The spectrum of the PVA exhibits an extensive band between 3500-3000 cm^{-1} relative to the stretching of the intra and intermolecular OH bond. The peak between 3000 and 2840 cm^{-1} and the two peaks near 1400 cm^{-1} are associated with the asymmetric and symmetrical stretching of the C-H alkyl groups, while the absorptions between 1700 and 1600 cm^{-1} and near 1200 cm^{-1} describe, respectively, the stretching of C=O bonds attributed to the presence of non-hydrolyzed residual PVA vinyl acetate groups. The band shown at 1100 cm^{-1} refers to the vibration of the -COH bond (SHI et al, 2008; NASCIMENTO et al, 2021).

Although the AC promoted the cross-linking of PVA, this acid has a large number of OH in its structure. Thus, the band maintenance in the 3500-3000 cm^{-1} region is observed in the spectrum of the membrane PCA. Bands between 1700-1600 cm^{-1} and between 1200-1000 cm^{-1} are related to C=O stretching and out-of-plane stretch of CA hydroxyls, respectively. In the PSSA membranes, the absorption band near 3000 cm^{-1} relative to the hydroxyl groups is less intense due to the reduction of free O-H by the more effective crosslinking compared to the membranes of the CA group. This membrane also presented bands between 1760 and 1700 cm^{-1} referring to the carbonyl group (REDDY et al, 2010; NASCIMENTO et al, 2021).

Figure 2 - Evaluation of the thermal degradation by TGA.



Source: Authors (2021)

In the PCA membrane almost no distinction was made between degradation phases 1 and 2, this fact can be associated to the hydrophilic character of the CA since it has a higher number of hydroxyls, so the water is more retained by the structure of the polymer due to the hydrogen bonds. Despite the small improvement in thermal stability, since the third stage started at 400°C, crosslinking cannot be considered efficient because at the end of the test the residue content was lower than that of the PVA. Thus, the first mass loss occurred in the range of 25-340°C, associated with loss of side chain groups, such as the sulfonic group. The last phase occurred between 340-880°C being the degradation of the main chain. It is worth mentioning that the residue content for this membrane was considerably higher than that of the other membrane (PSSA). Therefore, the crosslinking of PVA with SSA was more efficient than the crosslinking (BOROGLU et al, 2011) with CA, which is a more thermally stable membrane.

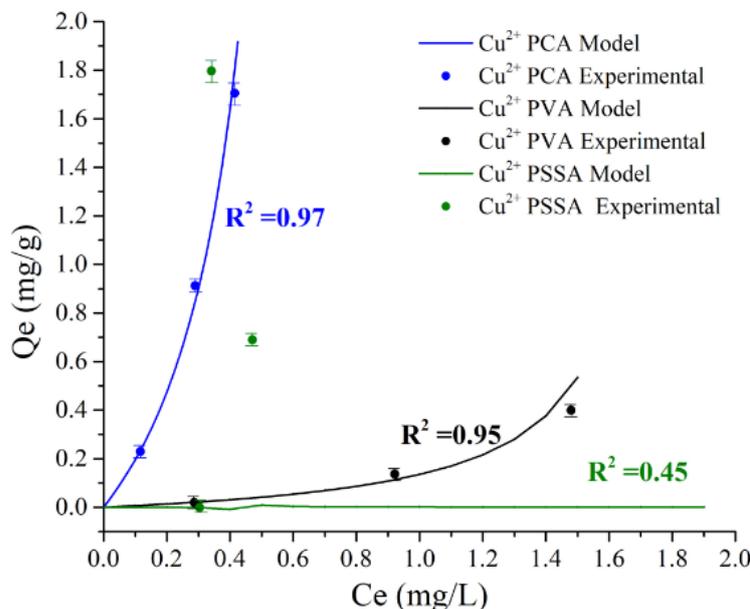
The values of λ , λ were presented in Table 1. Due to the lower swelling of the acid containing membranes, it was noted that the PVA chains were crosslinked. As demonstrated in the FTIR result, it was noted that the PSSA membrane has the most crosslinked chains as a function of the lower swelling. Figure 3 shows the isotherms according to the Lagmuir model. Through the mathematical treatments it was possible to calculate the value of the separation factor (λ).

Table 1 - Representation of values λ , λ and λ

Samples	WU (%)	IEC	λ	RI
PVA	235,5	0,07	189,28	0,074
PCA	35,4	1,07	1,84	0,43
PSSA	7,44	1,71	0,24	0,078

Source: Authors (2021)

Figure 3 - Langmuir adsorption isotherms: PVA, PCA and PSSA.



Source: Authors (2021)

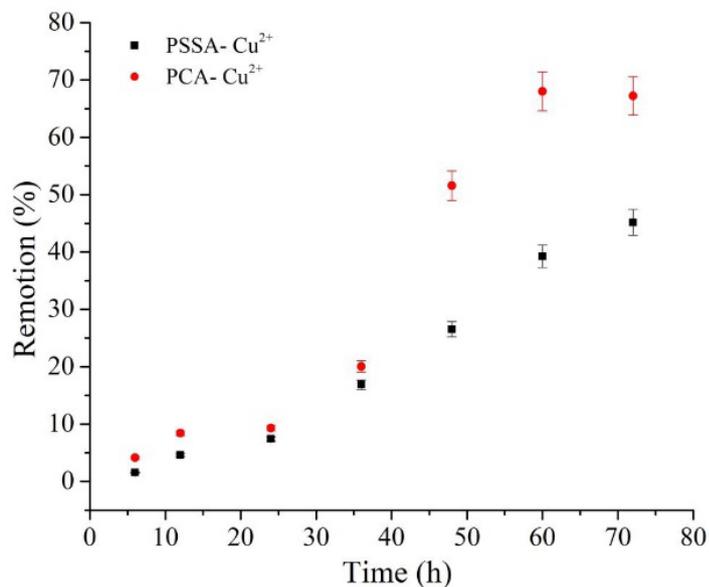
The behavior of the PVA isotherm and the PSSA membrane indicates a high adsorbate retention in a low and in the liquid phase, so an inference can be made by the concave profile of the curve. For the range of the adsorption is considered favorable (THANGANATHAN et al, 2015). Although all values of are within the range, it is observed that the PCA membrane presents greater , besides presenting the curve with more linear profile, that is the mass of adsorbate retained per unit mass of the adsorbent is proportional to of the adsorbate. The difference between the adsorption processes of PVA and the PSSA membrane can be justified.

In this case, the adsorption is of the physical type and there is no chemical interaction between the adsorbed fluid and the adsorbent solid, a fact that is evident in the value of calculated after the linearization of the curve by the Langmuir method. In the case of the crosslinked membranes, the value of confirms the type of adsorption curve obtained, characterizing the occurrence of chemical adsorption. In this sense, the constant value for the reticulated membranes was within the considered favorable. It is also worth noting that the result of the separation factor of the isotherm of the CA crosslinked membranes, in addition to being closer to the unit, was within the range of values obtained for Cu adsorption in other studies. In the case of membranes containing SSA, there is a trend of behavior close to the irreversible, with value of very close to zero, as well as that of PVA.

3.1 Kinetic control of Cu adsorption in samples of PCA and PSSA membranes.

The evaluation of the Cu element adsorption kinetics in PVA membranes crosslinked with SSA and CA having different values of ionic concentrations were analyzed at different times, such way it was possible to evaluate the predominant isotherm type according to the previous analysis, as well as the ion adsorption speed control step by the different membranes. Figure 4 shows the percentages of adsorption of Cu²⁺ ions in samples from different membranes (PCA and PSSA).

Figure 4 - Percentages of adsorption of Cu²⁺ ions in samples of different polymeric membranes PCA and PSSA.

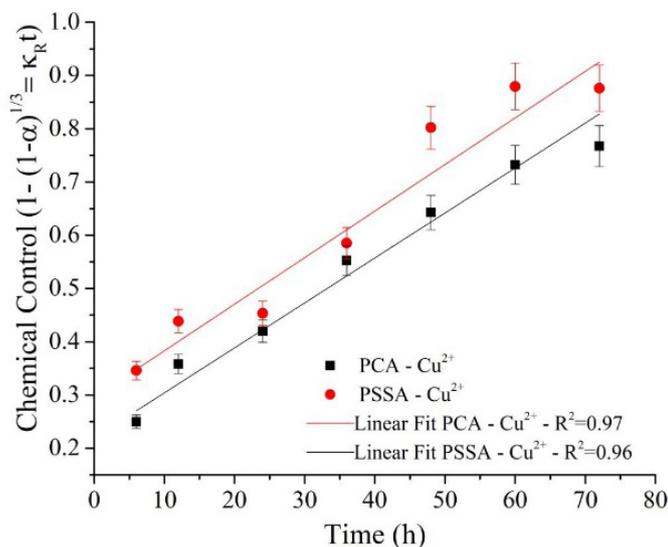


Source: Authors (2021)

It was observed in Figure 4 that in values of times close to 50 minutes there is an increase in value the adsorption of ions Cu²⁺ of the PSSA and PCA membranes. It was observed of the PCA membrane having the highest adsorption values of Cu²⁺ ions. Figure 5 presents the evaluation of the chemical control step for adsorption kinetics of the Cu²⁺ element in the PSSA and PCA membranes.

It was observed in Figure 1 the rare related to C=O stretching and out-of-plane stretch of CA hydroxyls, respectively. In the PSSA membranes, the hydroxyl groups is less intense due to the reduction of free O-H by the more effective cross-linking compared to the membranes of the CA group. Fact confirmed by figure 2 where the hydrophilic character of the CA since it has a higher number of hydroxyls, so the water is more retained by the structure of the polymer due to the hydrogen bonds. So it is a fact that such groups are characterized by their effective tendency to ion exchange with 2+ charge ions demonstrated also by an increase in value the adsorption of ions Cu²⁺ of the PSSA and PCA membranes.

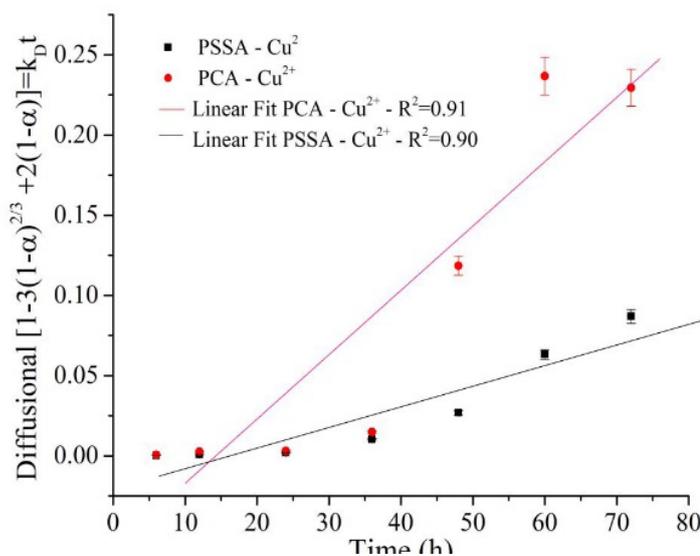
Figure 5- Evaluation of the chemical control step for Cu^{2+} adsorption kinetics.



Source: Authors (2021)

In figure 3 it was demonstrated that the adsorption is of the physical type and there is no chemical interaction between the adsorbed fluid and the adsorbent solid fo Ca and SSA membranes. Going against the previous statement Figure 5 shows the correlation coefficient of PSSA/ Cu^{2+} 0.97; PCA / Cu^{2+} 0.91; thus indicating a possible tendency to the adsorption speed stage controlled by the surface adsorption of Cu^{2+} ions by the crosslinked membranes.

Figure 6 - Evaluation of the diffusional control step for adsorption kinetics of the Cu^{2+} element by PSSA membranes; PCA.



Source: Authors (2021)

Figure 6, the evaluation of the diffusional control step for Cu²⁺ adsorption kinetics was presented, making it possible to observe the PSSA/Cu²⁺ 0.90 correlation coefficient value; PCA/Cu²⁺ 0.91; indicating a possible tendency towards the adsorption speed step controlled by the diffusional adsorption of ions by the crosslinked membranes. Going against the previous statement Figure 3 in the case of membranes containing SSA, there is a trend of behavior close to the irreversible, with value of β very close to zero Langmuir adsorption isotherms.

4 CONCLUSION

With the objective of evaluating the adsorption profile of Cu²⁺ elements by the PCA and PSSA members, an isothermal and kinetic evaluation was elaborated in function of the chemical and diffusional control steps in samples of different polymeric membranes in contact with Cu²⁺ ions. Thus we have the following conclusions.

The value of β confirms the type of adsorption curve obtained, characterizing the occurrence of chemical adsorption. In this sense, the constant value for the reticulated membranes was within the considered favorable. It is also worth noting that the result of the separation factor of the isotherm of the PCA, in addition to being closer to the unit, was within the range of values obtained for Cu²⁺ adsorption in other studies. In the case of PSSA membrane, there is a trend of behavior close to the irreversible, with value of β very close to zero.

Through the values of correlational coefficients demonstrated by the reduction rate of Cu²⁺ ions in the initial solutions in contact with the different reticulated membranes, it was possible to observe the predominance of the diffusional and chemical control stages, thus featuring the equilibrium stage characterized by adsorption on the surface and inside the PSSA and PCA membranes in contact with Cu²⁺ ions.

Through all the results presented, it was possible to indicate possible applications for the polyvinyl alcohol membrane, all of them as reinforcement in effluent treatment equipment. However, the most important application occurs as a reinforcement component for landfill and industrial landfill.

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