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EFFECT OF TEMPERATURE AND PH ON THE ABSORPTION OF METHYLCELLULOSE HYDROGEL

Rocío Antonio Cruz
Tecnológico Nacional de México campus Villahermosa, Departamento de Ingeniería Química, Bioquímica y Ambiental.
Villahermosa, Tabasco, México
https://orcid.org/0000-0003-36388-5152

Nora Alicia Purata Pérez
Tecnológico Nacional de México campus Villahermosa, Departamento de Ingeniería Química, Bioquímica y Ambiental.
Villahermosa, Tabasco, México
https://orcid.org/0000-0002-6823-6912

Alicia Sosa Medina
Tecnológico Nacional de México campus Villahermosa, Departamento de Ingeniería Química, Bioquímica y Ambiental.
Villahermosa, Tabasco, México
https://orcid.org/0000-0003-1011-8021

María Berzabé Vázquez González
Tecnológico Nacional de México campus Villahermosa, Departamento de Ingeniería Química, Bioquímica y Ambiental.
Villahermosa, Tabasco, México
https://orcid.org/0000-003-2814-8819

José Luis Cáceres Javier
Tecnológico Nacional de México campus Villahermosa, Departamento de Ingeniería Química, Bioquímica y Ambiental.
Villahermosa, Tabasco, México
https://orcid.org/0000-0002-5455-5891

Abstract: The results presented in this work is the synthesis of methylcellulose (MC) gel using 0.0025 M glutaraldehyde as crosslinking agent and 0.01 M HCl as catalyst of the synthesis reaction. Subsequently, the MC hydrogel was evaluated at three temperatures (30, 40 and 50°C) and five pH values (2, 4, 7, 11 and 13), to determine the maximum absorption capacity and determine the pH and temperature. ideal of MC hydrogel. Hydrogel presented good absorption capacity at each temperature and pH evaluated and the results were favorable at 40°C and pH 4, presenting a maximum swelling of 890%. Therefore, the MC hydrogel can be used for the removal of heavy metals, especially lead (Pb) and copper (Cu). The atomic absorption analyzes showed a retention of 92% and 90% for Pb and Cu respectively.
Keywords: Hydrogel, Methylcellulose, Absorption, Heavy metals.

INTRODUCTION

For many years, surface waters such as rivers, streams, lakes, and estuaries were used as a vehicle for eliminate all kinds of waste and there was not enough knowledge about the impact that these pollutants could have on ecosystems and human health.

The Santiago River in the state of Jalisco, Mexico, is an example of the above and has generated a socio-environmental conflict because on the health and well-being of the surrounding population. Contamination is identified through the spectacular foamy and nauseating waterfall of the Santiago River, by the Salto de Juanacatlán. In it 2012, Greenpeace Mexico used that image as part of a campaign to denounce toxic rivers, when brave volunteers in protective gear waded into the river below the waterfall in inflatable canoes and almost surpassed by the white foam.

Another example is the pollution problem in the agricultural zone of the Barranca Biosphere Reserve of Metztitlán, Hidalgo, Mexico, is caused by the contribution of residual water that is made through the aquifers that irrigate the area, has generated that this site is exposed to a great risk of contamination by metals heavy, hydrocarbons and other contaminants, which remain bioavailable to plants and indirectly there is a high possibility of entering the animal food chain and finally the human being, with the risks that this would generate for the inhabitants and final consumers of the agricultural products that are generated there.

The most frequent contaminants in water are organic matter, microorganisms, hydrocarbons, industrial waste, heavy metals, pesticides, household chemicals and radioactive waste. Of these, heavy metals are considered among the most serious contaminants of aquatic ecosystems, since they are generally not removed by natural processes such as organic contaminants and these can enter the food chains through the processes of bioaccumulation, bioconcentration and biomagnification. The elements Toxics such as Hg, Cd, Cr, Cu and As, are accumulated in the sediment where it can be suspended in forms bioavailable chemicals producing acute or chronic poisoning. (Tejeda et al., 2011).

Heavy metals in high concentrations are harmful to humans, aquatic and terrestrial flora and fauna. The harmful capacity of metals is mainly since most of them are non-biodegradable. By For this reason, it is necessary to prevent the entry of toxic metals into aquatic environments and, above all, that industries reduce the concentration to levels that do not generate toxicity problems. Consequently, control Heavy metal discharges and their removal from the water have become a challenge for this new century.

Recently, and in response to this problem, procedures have been developed to try to counteract the pollution in water bodies. Conventional methods for treating effluents with heavy metals include precipitation, oxidation, reduction, ion exchange, filtration, electrochemical treatment and membrane technologies, or chemical processes that have as drawbacks high costs, low efficiency for diluted solutions and in some cases the production of sludge that is difficult to handle or dispose of (Tenorio-Rivas, 2009).

One of the new developments for metal removal in recent years is the use of biosorption. The Bioadsorption is a surface property by which certain solids (of biological origin) absorb with Preference certain metals from a solution by concentrating them on its surface. For which many materials of biological origin have been studied as adsorbents to remove metal ions from water in effluents industrial (Bayramoglu et al., 2009).

Chitosan is a biomaterial that has been used for the adsorption of heavy metals such as Cu(II), Cd(II), Zn(II), Pb (II), Fe (II), Mn (II), Ag (II), this fact is due to the ability of this polymer to undergo chelation reactions (Rhaza et al., 2007). One of the disadvantages of using this material is that at low pH solutions the chitosan suffers some dissolution. One way to avoid dissolution in an acid medium is by modifying it structurally and functionally through chemical cross-linking reactions.

Methylcellulose (MC) is a commonly used excipient in the pharmaceutical and cosmetic industry due to its great versatility, which allows it to be incorporated in low concentrations in a wide range of formulations: solid, liquid and semisolid. This versatility is due to the important functional properties it possesses: rheological control, film former, adhesive power, binding power and the property of reversible thermal gelation (Greminger, 1979).

Therefore, this research synthesized a polymeric material (MC hydrogel) in the form of a film, with the purpose of achieving the adsorption of Lead (Pb) and Copper (Cu) ions. The general objective is the recovery of water contaminated using MC hydrogel for the removal of metals (Pb and Cu).

MATERIALS AND METHODS

SYNTHESIS OF THE METHYLCELLULOSE HYDROGEL

The method of Rivas et al. (2010), in a batch type glass reactor with a capacity of 500 ml, 10 g of MC and distilled water were added until a 2% by weight solution and mixed for 1 hour maintaining constant stirring and controlled temperature at 60°C, subsequently, 4 ml of glutaraldehyde was added as a crosslinking agent and 4 ml of acid hydrochloric acid as a catalyst for the synthesis reaction, and was kept under constant stirring at 60°C for a period of 2 hour reaction.

After that time, the mixture was poured into polycarbonate molds and placed in an oven at 50°C for 48 hours until obtaining a completely dry film and a constant weight of the MC hydrogel. Finally, the movies were removed from the molds and used in the recovery treatment of water contaminated by Pb and Cu.

SWELLING TESTS

This technique consisted in evaluating the absorption capacity of the MC hydrogel, MC hydrogel, which were cut with an area of approximately 1 cm^2 to be placed in glass vials with a capacity of 20 ml., to carry out the swelling tests and determine the absorption capacity. The vials were labeled for each pH with its corresponding duplicate and it was brought to constant weight and 200 mg of 1 cm^2 films were placed and again it was brought to constant weight and dried in an oven at 45 °C. The constant weights of the vials and the films were recorded, to obtain the initial weight of the dried MC gel.

Once the 5 pH samples were obtained in duplicate, a micropipette was used adjusting it to 0.1 ml and 5 nozzles (one for each pH to avoid contamination) were used to add the pH to the vials with MC films and it was adjusted to a temperature of 30°C (first value to be evaluated), later it was evaluated at 40°C and finally at 50°C. The analysis time was 12 h. following the method of Ortiz et al., 2006. The test consisted of adding 0.1 ml of the pH to be evaluated in duplicate, to the MC gel contained in each vial and its weight in g was recorded on an analytical balance, until complete 12 h.

ABSORPTION CALCULATIONS

To determine the absorption capacity of the MC gel, records of the swelling tests were needed every hour for 12 h. and the equation 1 of Zumaya et al., 2009 was used, obtaining the percentage at different temperatures and pH evaluated. On the other hand, the speed of adsorption of the MC gel was evaluated using equation 2 of the authors López and Calixto, 2015. The results are expressed in g of adsorbed water/min.

$$W = \frac{(Wh - Ws)}{Ws} \, x \, 100\% \qquad (1)$$

Where:

W_h is the weight of the swollen sample and

W_s is the weight of the sample in the dry state

$$adsorption\ speed = \frac{g\ of\ adsorbed\ water}{t} \qquad (2)$$

Where:

g of adsorbed water is the amount of liquid that the MC hydrogel adsorbs and t is the time it adsorbs it Figure 1 shows the samples after 12 h. in contact with the medium (pH), the data recorded at each hour were used to determine the swelling percentage and the adsorption speed, and to compare them with each other to determine the ideal temperature and pH.

PREPARATION OF AL AND PB SOLUTIONS AT LABORATORY LEVEL

Calculations were made to prepare the Pb and Cu solutions that will have contact with the MC hydrogel called "substrate" and its function is to remove the two metals to be studied. The preparation consisted of the following: 0.4 g of $Pb(NO_3)_2$ were weighed and added to a 250 ml volumetric flask and deionized water was added. Subsequently, 1.183 g of $CuSO_4$ was weighed and added to another 250 ml volumetric flask and deionized water was also added.

15 ml of the Pb solution was added in a 20 ml capacity vial, which contains the substrate (MC hydrogel), this was done in triplicate. The same procedure was carried out for the Cu solution. Subsequently, the 6 vials were placed in a bath with controlled temperature and stirring, and the optimal contact time was found to remove the two metals. In addition, the amount of metal absorbed by the substrate was determined using the atomic absorption technique.

ATOMIC ABSORPTION

In analytical chemistry, atomic absorption spectrometry is a technique for determining the concentration of a given metallic element in a sample and is used to analyze the concentration of more than 62 different metals in a solution. The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample.

In this analysis, the amount of lead (Pb) and copper (Cu) ions present in the water solutions was determined, before and after being in contact with the MC hydrogel using the atomic absorption equipment, model AA 240Z, and PSD 120, VARIAN brand, using an acetylene/air gas ratio and a lead and copper detection lamp. Once the initial (mother solution) and final concentration were determined, the amount of Pb and Cu was calculated absorbed per gram dry base of the MC hydrogel, q (mg/g) using equation 3.

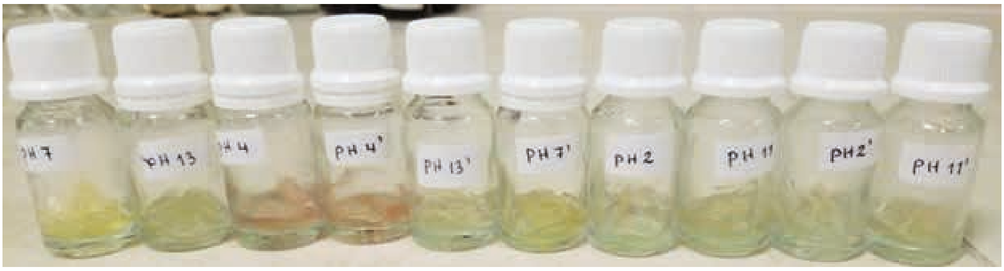

Figure 1. Swelling of the MC gel at different pH.


Figure 2. Methylcellulose hydrogel in film form

Temperature (°C)	pH				
	2	4	7	11	13
30	0.493	1.104	0.534	0.505	0.472
40	0.597	0.614	0.567	0.613	0.530
50	0.572	0.649	0.578	0.633	0.688

Table 1. MC hydrogel adsorption rate in g/min

$$q\left({}^{mg}/_{g}\right) = \left(\frac{V\,x\,(C_o - C_f)}{m}\right) \qquad (3)$$

Where:

q = Amount of metal absorbed per gram of substrate, mg/g

V = volume of the metal solution, l

C_o = Initial concentration, mg/l

C_f = Final concentration, mg/l

m = mass of the substrate (MC hydrogel) on a dry basis, g

RESULTS AND DISCUSSION

Figure 2 shows the film obtained from the synthesis of methylcellulose hydrogel, with a transparent and flexible appearance to the touch, presenting an adequate homogeneity to be used in metal (Pb and Cu) absorption and elimination tests.

Table 1 shows the influence of temperature in each medium (pH) evaluated to determine the speed of adsorption, indicating that the maximum speed is for a pH of 4 at a temperature of 30°C. Therefore, the incorporation of the MC hydrogel will be carried out under these conditions.

Figure 3 shows the effect caused by the temperature of 30°C for each pH evaluated, during 12 h, showing a considerable increase every hour, until reaching the maximum swelling. While figure 4 presented less swelling compared to figure 3, since the temperature was increased to 40°C, causing a decrease in the absorption capacity of the CMC gel. On the other hand, figure 5 showed swelling at 50°C greater than figure 4, but less than figure 3, and its behavior is very similar to the tests carried out at 30°C and 40°C.

A study of the effect of the substrate (MC hydrogel) was carried out in each of the solutions prepared of Pb and Cu, by triplicate for each solution, keeping the temperature constant at 40°C, stirring at 120 rpm and contact time at After 12 h, after that time, the amount of Pb and Cu that was removed from the contaminated water was determined, using the Atomic Absorption technique.

Figure 6 shows the data obtained by atomic absorption (AA) analysis, where observe the results for the removal of the metal (Pb and Cu), obtaining a reduction of 92.4% and 90.33% for Pb and Cu, respectively.

The initial concentration (Co) of the Pb and Cu solutions that were prepared was 10 mg/l; and added 15 ml of solution to 0.2 g of MC hydrogel contained in 20 ml vials and kept in contact for 12 h, and then the AA analysis was performed, reaching the final concentrations of Pb and Cu of 0.76 mg/l and 0.97 mg/ml, respectively. Subsequently, equation 3 was used to determine the amount of metal absorbed per gram of substrate, obtaining 9.24 mg/g for Pb and 9.03 mg/g for Cu.

CONCLUSION

The MC hydrogel was obtained according to the conditions described in the methodology presenting characteristics favorable for the swelling tests, these were performed in triplicate and the values were averaged obtaining a maximum absorption value of 889.5% in 24 h, after which time the hydrogel collapsed and its structure stopped be crosslinked, that is, the material cannot capture or retain more liquid.

The Atomic Absorption analyzes showed a retention of Pb and Cu of 92% and 90%, respectively. Also, I know showed that when using 1 g of substrate (MC hydrogel) about 9 mg of the metal is retained per gram of substrate, which It presents an advantage for treating water contaminated by these metals.

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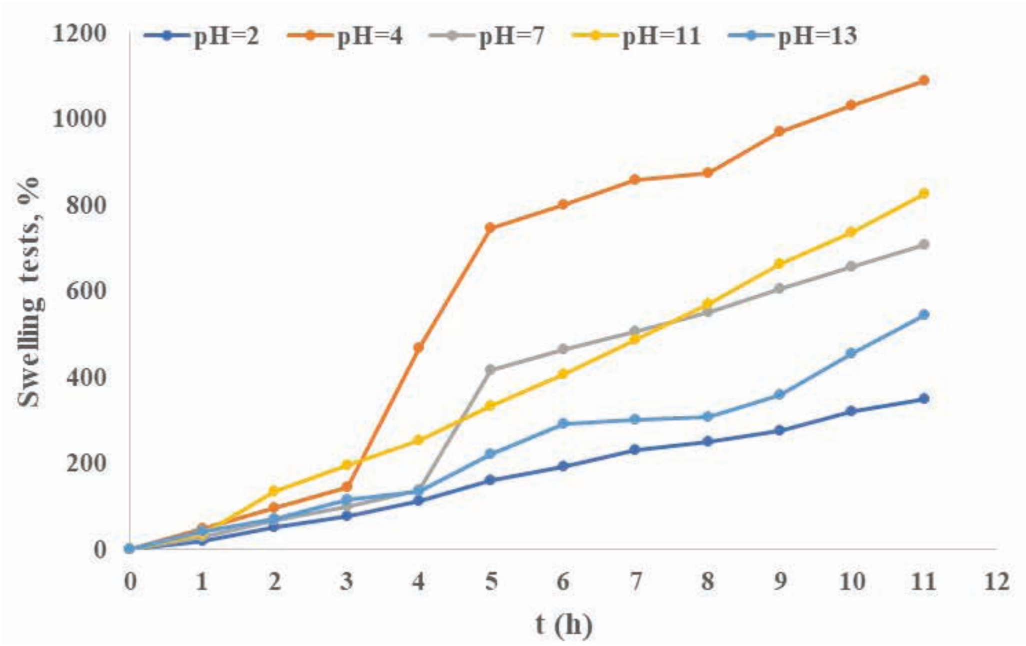

Figure 3. Swelling of the MC hydrogel at 30 °C

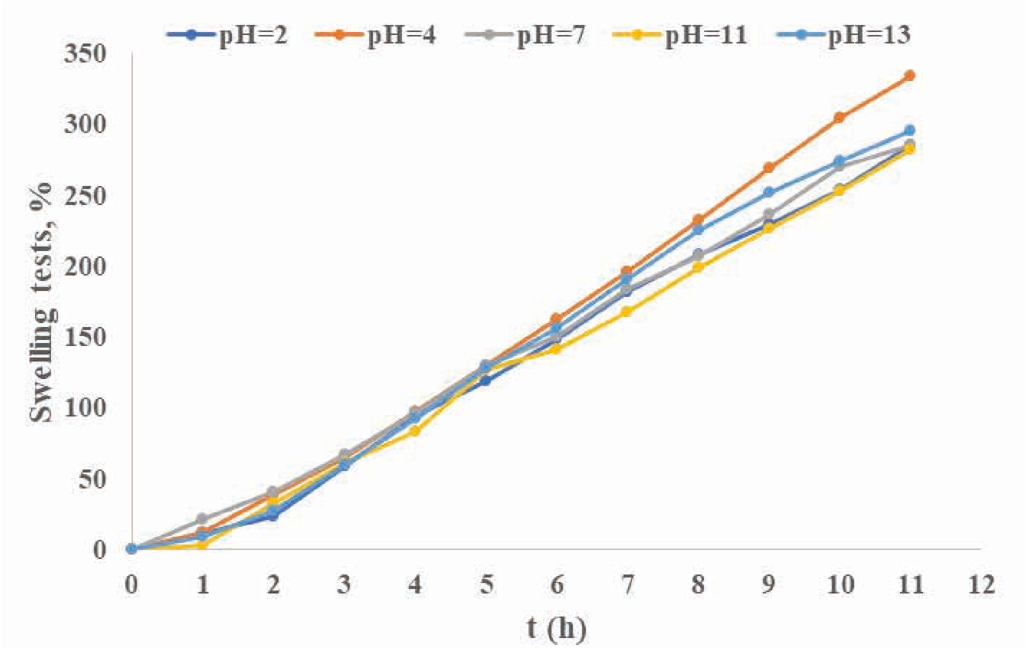

Figure 4. Swelling of the MC hydrogel at 40 °C

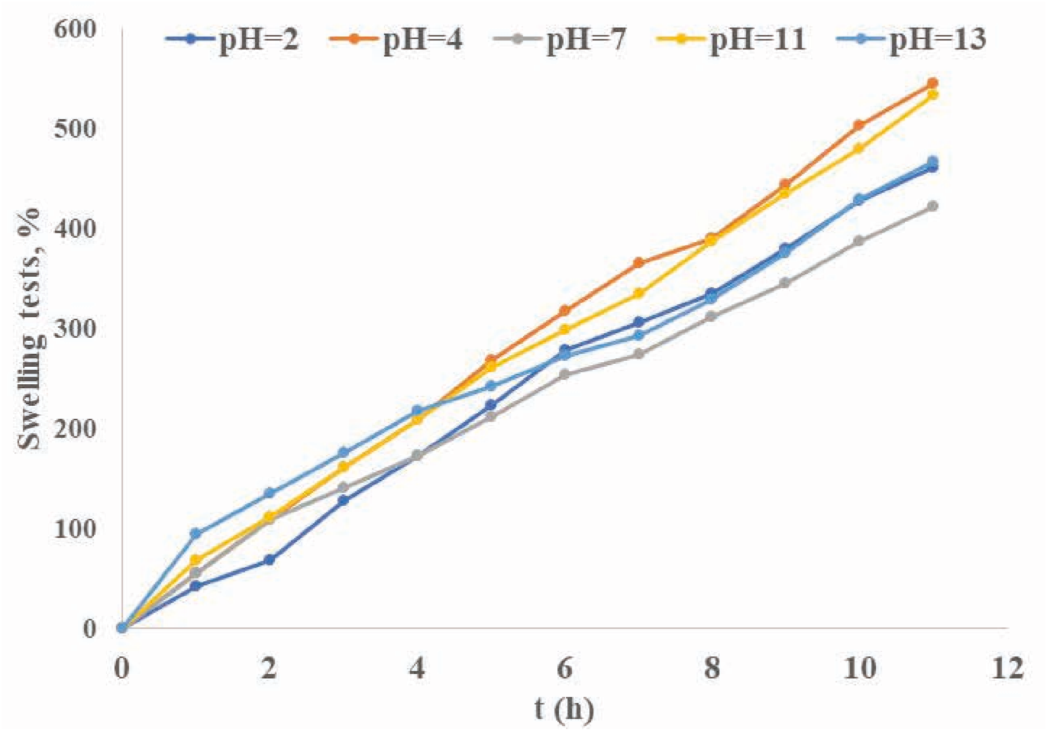

Figure 5. Swelling of the MC hydrogel at 50 °C

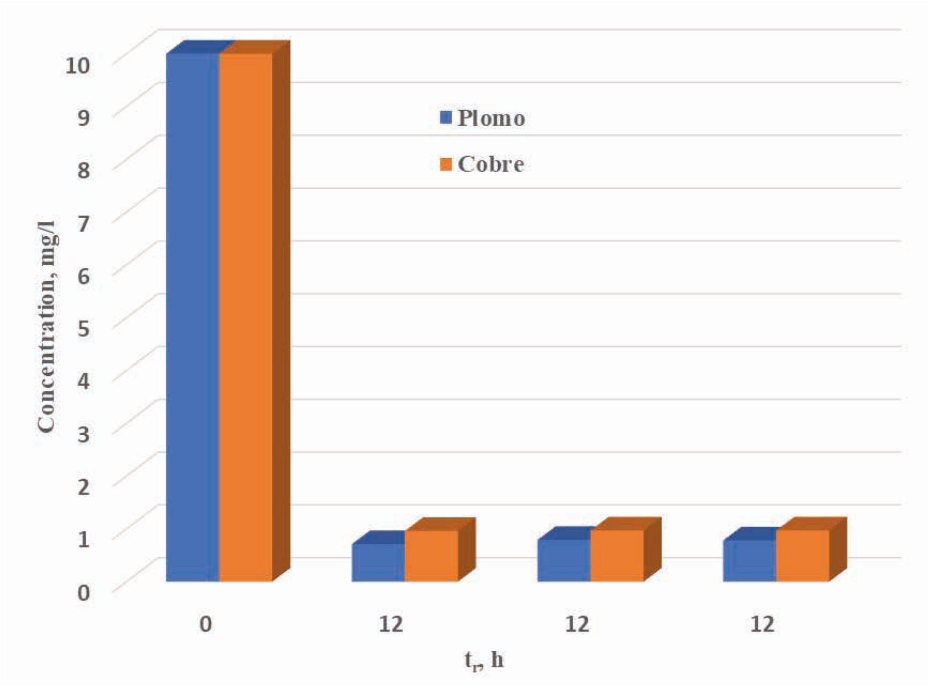

Figure 6. Pb and Cu concentration after being in contact with the MC hydrogel

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