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Title: Removal of aluminum (Al) and lead (Pb) in contaminated water using carboxymethylcellulose (CMC) gel polymer Line Research: Polymeric Materials

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Introduction

For many years, surface waters such as rivers, streams, lakes and estuaries were used as a vehicle to dispose of 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 fall and nauseating waterfall of the Santiago River, by the Juanacatlán Fall. In 2012, Greenpeace Mexico used that image as part of a campaign to denounce toxic rivers, when brave volunteers wearing protective gear entered the river below the waterfall in inflatable canoes and were almost overwhelmed by white foam.

The Santiago River receives municipal wastewater without treatment (or with low levels of treatment), especially discharges in the Guadalajara Metropolitan Area, in addition to industrial discharges, leachate from landfills located nearby, and agricultural runoff.

In addition to this, the problem of contamination in the agricultural area of the Barranca de Metztitlán Hidalgo Biosphere Reserve, 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 heavy metals, hydrocarbons and other contaminants, which remain bioavailable to plants and indirectly there is a high possibility of entering the food chain of animals and finally to humans, with the risks that this would generate for the inhabitants and final consumers of the agricultural products that are generated there.

Introduction

Bio-adsorption is a surface property by which certain solids (of biological origin) preferentially capture certain metals from a solution, concentrating them on their surface. For which many materials of biological origin have been studied as adsorbents to remove metal ions from water in industrial effluents (Bayramoglu et al., 2002).

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., 2002). One of the disadvantages of using this material is that in solutions with a low pH, chitosan suffers some dissolution. One way to avoid dissolution in an acid medium is by modifying it structurally and functionally through chemical crosslinking reactions.

Carboxymethylcellulose (CMC) is a water-soluble biopolymer derived from cellulose with anionic behavior. This colloid is a physiologically inert, rapidly soluble protector that can form films, as well as being able to thicken, suspend, stabilize and disperse. These properties give it a wide industrial application and a special interest in its application as bio-absorbent and/or coagulant-flocculant for water treatment.

This book chapter aims to synthesize a polymeric material from a cellulose derivative such as carboxymethylcellulose (CMC), which is a CMC gel that has the purpose of absorbing the metals aluminum (Al) and lead (Pb) of the water contaminated with these metals and thus recover the contaminated water and be able to reuse it in other processes.

Methodology

Synthesis of carboxymethylcellulose gel

In a batch-type glass reactor with a capacity of 500 ml, 10 g of CMC and distilled water were added until a 5% solution by weight was obtained and mixed for 1 hour, maintaining constant stirring and a controlled temperature of 80°C. Subsequently, 4 ml of glutaraldehyde were added as a crosslinking agent and 4 ml of hydrochloric acid as a catalyst for the synthesis reaction, and it was kept under constant stirring at 80°C for a reaction time of 2 hours. After this time, the mixture was poured into polycarbonate molds and placed in an oven at 60°C for 48 hours until a completely dry film of constant weight of the CMC gel was obtained. Finally, the films were removed from the molds and used in the recovery treatment of water contaminated by Al and Pb.

Swelling tests

This technique consisted of evaluating the absorption capacity of the CMC gel, maintaining constant temperature and pH. In this test approx. 200 mg of the gel with dimensions of 1 cm^2 and dried in an oven at 45 °C for 24 hours until constant weight was obtained. Subsequently, they were placed in vials with a capacity of 20 ml and 0.1 ml of distilled water was added every hour for 24 hours until the gel reached its maximum swelling.

Methodology

Infrared Spectroscopy (IR)

The IR characterization technique was carried out to identify the different characteristic groups of the CMC, which make up the gels, and it was also corroborated whether Al or Pb was found in the polymeric network of the gel. For this analysis, the Varian 640-IR model Fourier transform spectrophotometer was used, using the ATR technique with 12 scans and a frequency range of 4000 - 400 cm^{-1}. In this interval, the main functional groups of the CMC gel were observed, and it was verified if secondary reactions were present.

Preparation of Al and Pb solutions at laboratory level

The calculations were made to prepare the Al and Pb solutions that will have contact with the CMC gel called "substrate" and its function is to remove the two metals to be studied. The preparation consisted of the following: 11.8 mg of $AlK(SO_4)_2$ were weighed out and added to 1 l volumetric flask and deionized water was added. Subsequently, 11.8 mg of $Pb(NO_3)_2$ was weighed and added to another 1 l volumetric flask and deionized water was also added.

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

Methodology

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.

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

$$q(mg/g) = \frac{V(C_o - C_f)}{m} \quad (2)$$

Where:

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

V = volume of metal solution, l

Co = Initial concentration, mg/l

Cf = Final concentration, mg/l

m = mass of substrate (CMC gel) on a dry basis, g

Results

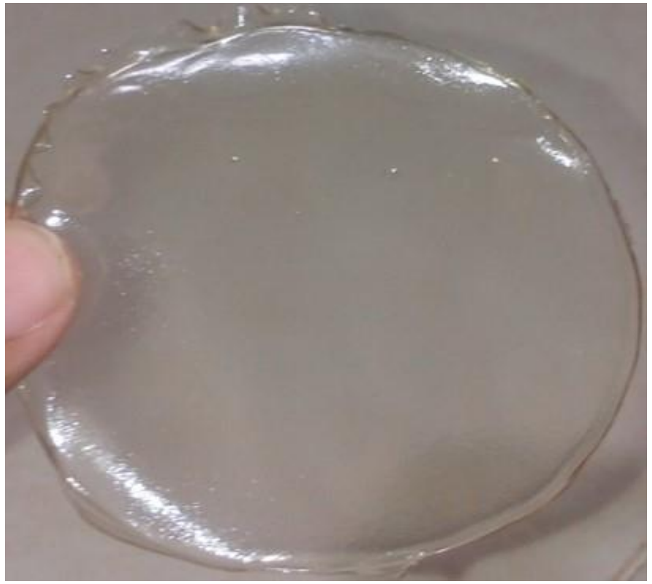

Figure 1. Carboxymethylcellulose gel film

Source: self-made

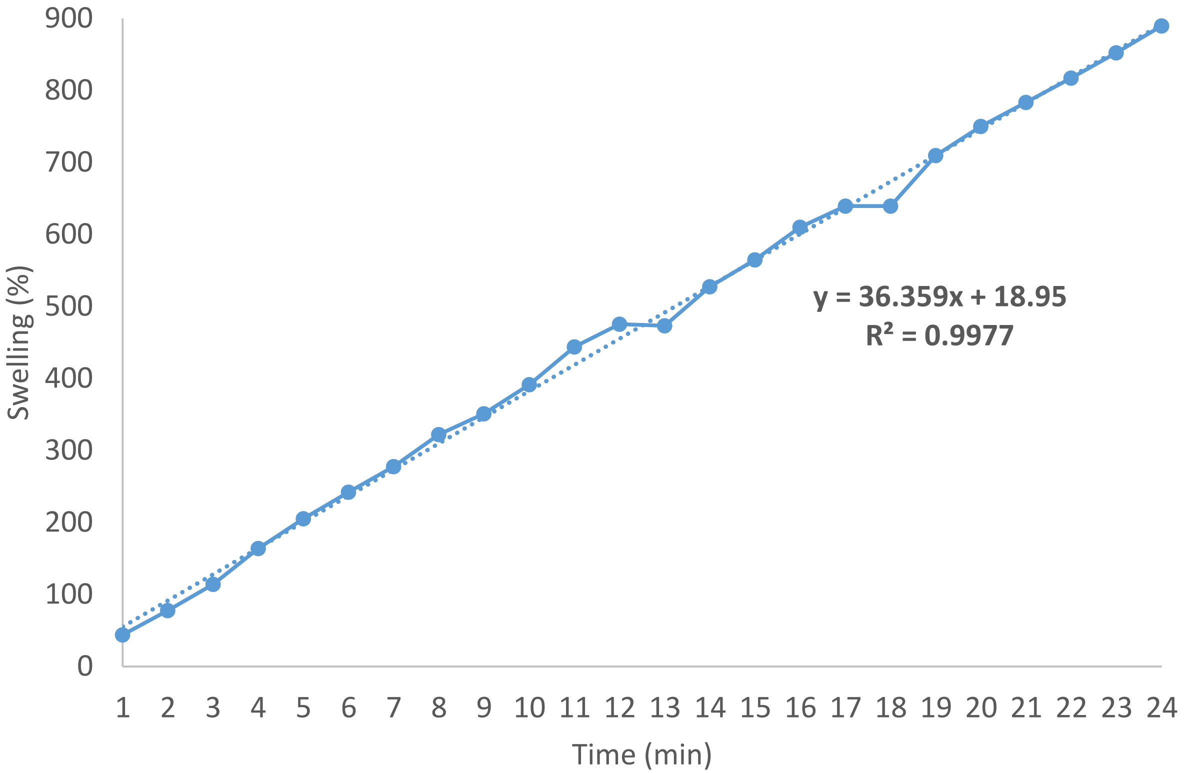

Figure 2. Percentage of swelling of carboxymethylcellulose gel

Source: self-made

Results

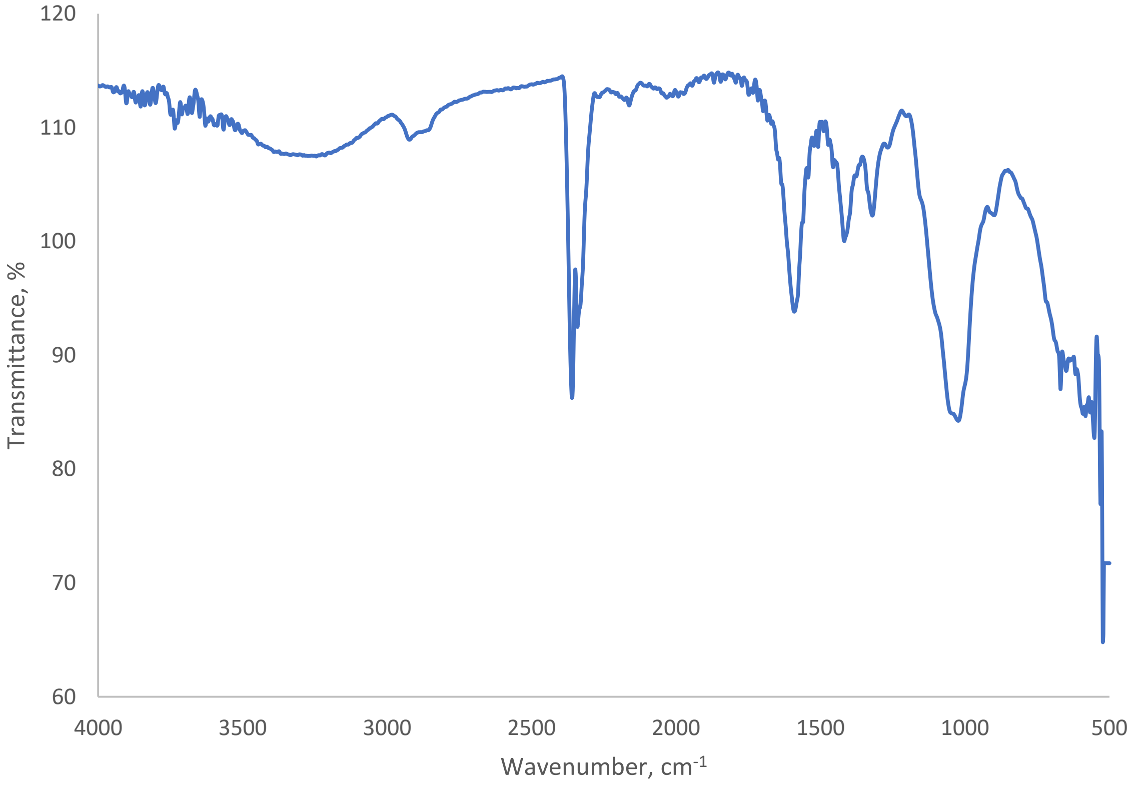

Figure 3. IR spectrum of carboxymethylcellulose gel
Source: self-made

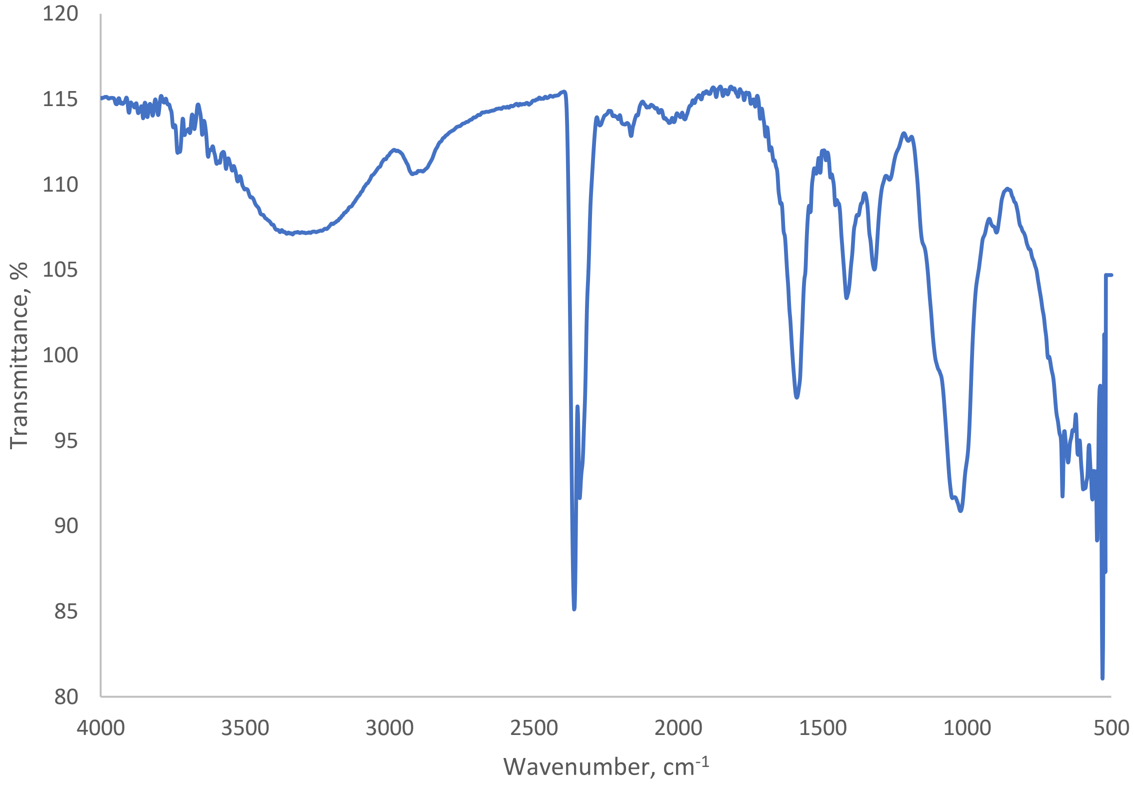

Figure 4. IR spectrum of carboxymethylcellulose gel after exposure to water contaminated with Al metal
Source: self-made

Results

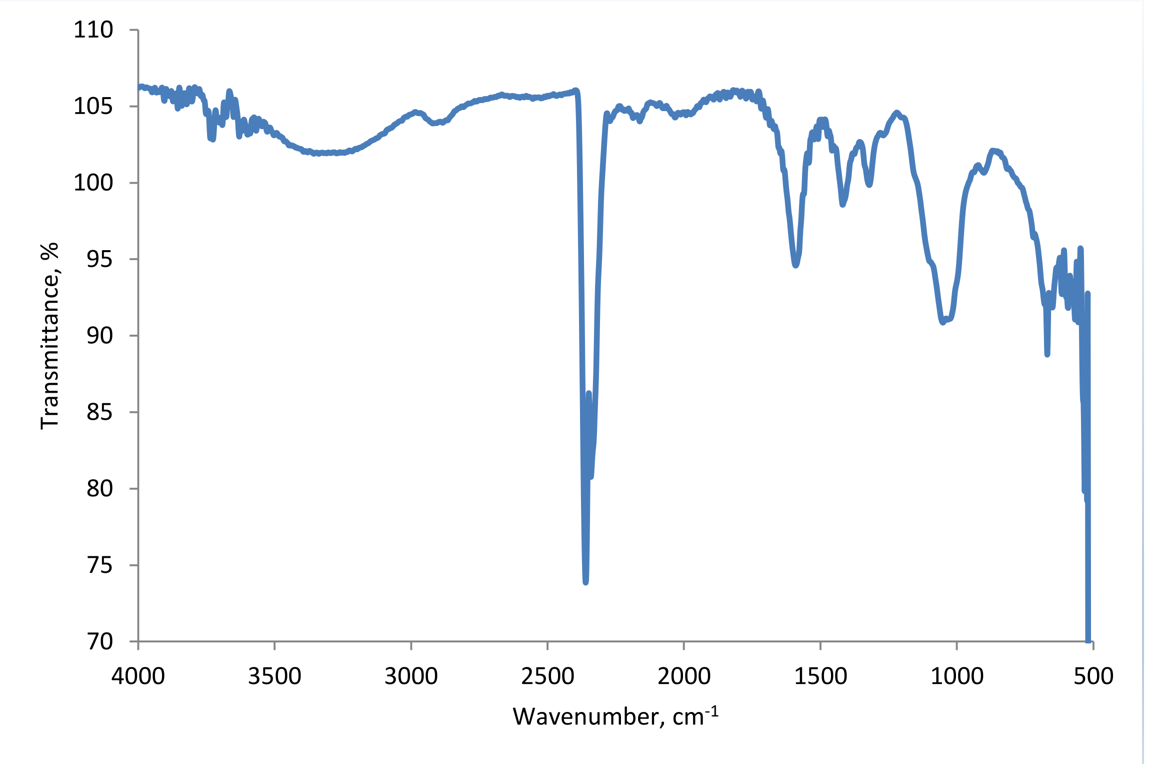

Figure 5. IR spectrum of carboxymethylcellulose gel after exposure to water contaminated with the Pb metal
Source: self-made

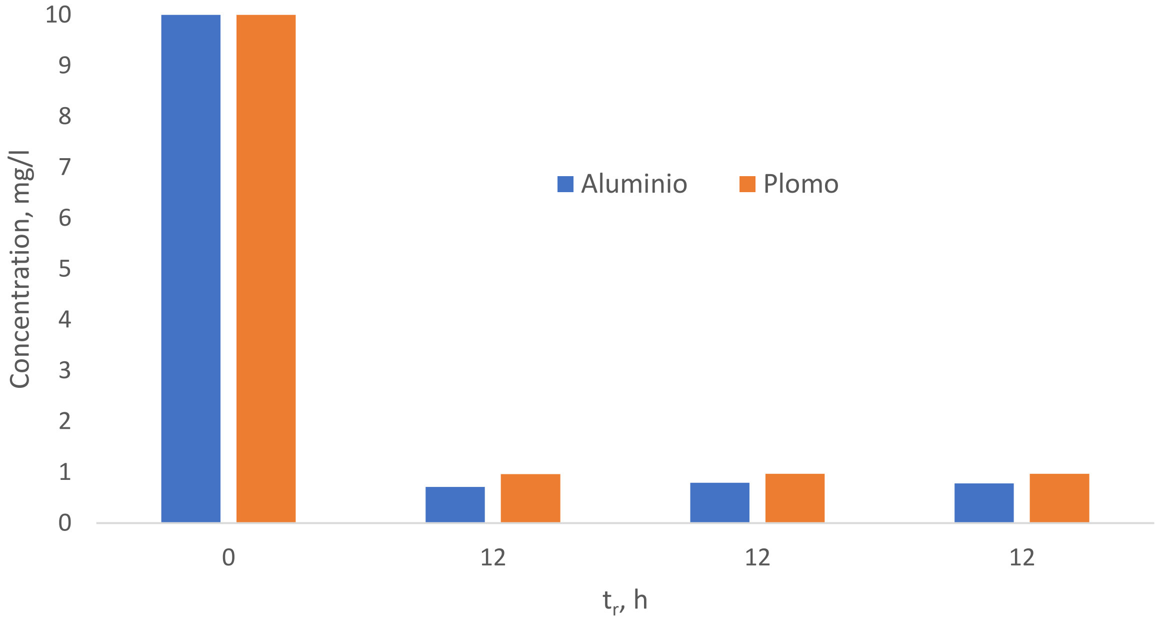

Figure 6. Concentration of Al and Pb after being exposed with the carboxymethylcellulose gel
Source: self-made

Conclusions

The CMC gel was obtained according to the conditions described in the methodology, presenting favorable characteristics 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 that time. the gel collapses and its structure are no longer cross-linked, that is, the material cannot capture or retain more liquid.

By means of FTIR, the hydroxyl, carboxyl and carbonyl functional groups that are part of the structure of carboxymethylcellulose were observed and the Atomic Absorption analysis showed a retention of Al and Pb of 92% and 90%, respectively. In addition, it was shown that when using 1 g of substrate (CMC gel) around 9 mg of metal is retained per gram of substrate, which is advantageous for treating water contaminated by these metals

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