Chapter 5 Removal of aluminium (Al) and lead (Pb) in contaminated water using carboxymethylcellulose (CMC) gel polymer

Capítulo 5 Eliminación de aluminio (Al) y plomo (Pb) en agua contaminada utilizando un polímero de gel de carboximetilcelulosa (CMC)

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Abstract

Water is a renewable resource, very important for living beings and essential for various activities. However, when it is contaminated, it becomes a non-renewable resource and it is necessary to investigate and know how to preserve it. Nowadays, water is a highly polluted resource, mainly due to human and industrial activities, due to this, a treatment is sought to solve one of the problems, such as the presence of heavy metals such as: lead, cadmium, arsenic and mercury, which are very toxic and accumulate by the organisms that absorb them, which in turn are a source of contamination of food chains that, when ingested by man, cause blindness, amnesia, rickets, myasthenia or even death (Covarrubias and Peña, 2017). On the other hand, aluminum has a wide application in the food, pharmaceutical, paper and construction industries and in the treatment of drinking water and wastewater. However, the possible damage to health caused by the consumption of this element has not been emphasized. One of the diseases that has been associated with the intake of this element is Alzheimer's and there is a risk of developing other conditions (Trejo *et al*., 2004). Currently, the use of clean technologies is being promoted, which are products, tools or processes that seek to reduce environmental pollution. An example are gels, these are cross-linked hydrophilic polymers capable of expanding their volumes due to their high expansion in water and are widely used in wastewater purification. There are different types of absorbent materials such as activated carbon, minerals, zeolites, ion exchange resins, biosorbents (biomasses) and cross-linked polymers. In this research work, a polymer (carboxymethylcellulose gel) was synthesized, using glutaraldehyde (GA) as a binding agent. crosslinking and hydrochloric acid (HCl) as reaction catalyst. The carboxymethylcellulose (CMC) gel was in contact with the contaminated water containing Al and Pb ions, these were retained by the absorption process within the cross-linked network of the CMC gel, and by atomic absorption (AA) analysis. the amount of Al and Pb ions removed from the contaminated water was determined.

Aluminum, Lead, Gels, Carboxymethylcellulose

Resumen

El agua es un recurso renovable, muy importante para los seres vivos y fundamental para diversas actividades. Sin embargo, cuando se encuentra contaminada se convierten en un recurso no renovable y, es necesario investigar y conocer la manera de preservarla. Hoy en día el agua es un recurso muy contaminado principalmente por las actividades humanas e industriales, debido a eso, se busca un tratamiento para resolver uno de los problemas como son, la presencia de metales pesado como: plomo, cadmio, arsénico y mercurio, los cuales son muy tóxicos y acumulables por los organismos que lo absorben, los cuales a su vez son fuente de contaminación de las cadenas alimenticias que al ser ingeridos por el hombre provocan, ceguera, amnesia, raquitismo, miastenia o hasta la muerte (Covarrubias y Peña, 2017). Por otro lado, el aluminio tiene una amplia aplicación en la industria alimenticia, farmacéutica, del papel, de la construcción y en el tratamiento de agua para beber y agua residual. Sin embargo, no se ha dado énfasis a los posibles daños a la salud originados por el consumo de este elemento. Una de las enfermedades que ha sido asociada a la ingesta de este elemento es el Alzheimer y se corre el riesgo de desarrollar otros padecimientos (Trejo *et al*., 2004). En la actualidad se está fomentando el uso de tecnologías limpias que son productos, herramientas o procesos que buscan reducir la contaminación del medio ambiental. Un ejemplo, son los geles, estos son polímeros hidrófilos reticulados capaces de ampliar sus volúmenes debido a su alta expansión en el agua y son ampliamente utilizados en la purificación de aguas residuales. Existen diferentes tipos de materiales absorbentes como carbón activado, minerales, zeolitas, resinas de intercambio iónico, biosorbentes (biomasas) y polímeros entrecruzados, en este trabajo de investigación se sintetizó un polímero (gel de carboximetilcelulosa), utilizando glutaraldehído (GA) como agente de entrecruzamiento y ácido clorhídrico (HCl) como catalizador de la reacción. El gel de carboximetilcelulosa (CMC) estuvo en contacto con el agua contaminada que contiene iones de Al y Pb, estos fueron retenidos mediante el proceso de absorción dentro de la red entrecruzada del gel de CMC, y mediante el análisis de absorción atómica (AA) se determinó la cantidad de iones de Al y Pb eliminados del agua contaminada.

Aluminio, Plomo, Geles, Carboximetilcelulosa

5.1 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.

The most frequent contaminants in water are organic matter, microorganisms, hydrocarbons, industrial waste, heavy metals, pesticides, household chemicals and radioactive waste. These, heavy metals are considered among the most serious pollutants in aquatic ecosystems, since they are generally not removed by natural processes like organic pollutants and they can enter food chains through bioaccumulation, bioconcentration and biomagnification processes. Toxic elements such as Hg, Cd, Cr, Cu and As are accumulated in the sediment where it can be suspended in bioavailable chemical forms 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. For this reason, it is necessary to prevent the entry of toxic metals into aquatic environments and, above all, for industries to reduce their concentration to levels that do not generate toxicity problems. Consequently, controlling the discharge of heavy metals and their removal from the water has become a challenge for this new century.

Recently and in response to this problem, procedures have been developed to try to counteract pollution in water bodies. Conventional methods for the treatment of effluents with heavy metals include precipitation, oxidation, reduction, ion exchange, filtration, electrochemical treatment and membrane technologies, or chemical processes that have the drawbacks of high costs, low efficiency for dilute solutions and in some cases the production of sludge that is difficult to manage or dispose of (Tenorio-Rivas, 2006). One of the new developments for metal removal in recent years is the use of bio-absorption.

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.

The techniques that were used for the development of this research work were: (1) Swelling tests, where the optimal absorption time was determined, (2) Infrared spectroscopy (IR) showed the functional groups of the CMC gel before and after being in contact with water contaminated with Al and Pb, (3) Scanning Electron Microscopy (SEM) presented the morphological surface of the CMC gel before and after being exposed to water contaminated with Al and Pb and (4) Absorption Atomic (AA) allowed to quantify the amount of metal eliminated in the water contaminated by the metals under study.

5.2 Background

The increase in recent years of industrial production activities in our country has brought with it environmental problems such as contamination of national waters by heavy and non-heavy metals from extractive and manufacturing companies.

A clear example of the above is the case of the Upper Course of the Lerma River (CARL), which is part of the Lerma-Chapala-Santiago hydrological system, which is a very active industrial area with very important agricultural production and accelerated urban growth. and industrial, which has caused an overexploitation of its aquifers, as well as the contamination of its residual water bodies and agricultural runoff. Much of the wastewater generated is treated in several treatment plants and is later discharged directly into the Lerma River, thus this body has become a collector of industrial and domestic waste that channels, and streams drag. Due to this contamination, the quality of the river's water and sediments have seriously deteriorated, causing in turn an alteration of the trophic chains and the disappearance of fish and other aquatic organisms, surviving in some areas, only those organisms that are highly resistant such as the water lily (Eichhornia crassipies), some species of nematodes and plankton, among others (Government of the State of Mexico, 2005).

Recent research works on the evaluation of the water quality of the Lerma river during a hydrological cycle (Tejeda et al., 2006) show the presence and distribution of heavy metals such as Cr, Mn, Fe, Cu, Zn and Pb in the matter. suspended, with Fe being the element found in the highest concentration (average 4244 mg/kg), Cr and Cu with a measurement of 34 mg/kg, and Zn with an average value of 158 mg/kg; Mn and Pb present an average of 172 mg/kg respectively.

The World Health Organization in 2010, published that Lead is a toxic chemical element with the characteristic of accumulating and affecting numerous parts of the body, such as the neurological, hematological, gastrointestinal, cardiovascular and renal systems. Children are vulnerable to the neurotoxic effects of lead, which even at low levels of exposure to said metal can cause serious neurological damage and in some cases irreversible, there is no level of exposure to lead that is safe for health.

They also published that Cadmium has toxic effects on the kidney and on the bone and respiratory systems and is also classified as carcinogenic to humans. Arsenic in its inorganic form is soluble and highly toxic, the alterations it causes can take years to appear, this is in relation to the level of exposure; The toxic effects of arsenic are the generation of skin lesions, peripheral neuropathy, gastrointestinal symptoms, diabetes, kidney problems, cardiovascular diseases and cancer.

Finally, Mercury is a metal that is toxic to human health and a threat to the proper development of the fetus in the womb. This substance can be presented in various forms: elemental (or metallic); inorganic (for example mercuric chloride) and organic (for example methyl and ethylmercury), each form in which mercury occurs generates different toxic effects, in general mercury affects the nervous, digestive and immune systems, as well as the lungs, kidneys, skin, and eyes.

Heavy metal contamination of water resources is of great interest due to the toxic effects to humans and other animals and plants in the environment. The sources of heavy and non-heavy metals as pollutants are usually industries such as mining, electrolytic finishing, manufacturing of electrical products, among others. For example, Salas et al., in 2019 published that lead is a metal that has had a great impact on environmental contamination. It is found naturally in the soil, air, water, and fresh and processed foods of plant origin. The presence of this metal has caused numerous health problems and death in individuals.

They also reported that irrigation water contaminated by industrial waste or fertilizer remains is one of the main factors of lead contamination, while in industry contamination can occur in different areas such as: glass, plastic, combustion anti-knocks, batteries. (accumulators), etc. In addition, lead is a metal present in the environment and highly harmful to human health, its contamination has spread to fresh, processed foods and even kitchen utensils, causing serious health problems and affecting the quality of life of individuals.

On the other hand, the high concentrations of fluorides in the drinking water of states such as Aguascalientes, San Luis Potosí, Durango, Zacatecas, Jalisco, Hidalgo, Chihuahua, Guanajuato and others, and the fact that aluminum compounds are present in the purification processes of the water with unknown concentrations, there is a risk not yet evaluated, due to exposure of the population to alumina fluoride compounds whose effects occur in the long term, and most of the human intake of aluminum comes from food, through different sources and In the pharmaceutical industry, aluminum is used as the main compound of medicines used to counteract heartburn, diarrhea and other gastrointestinal problems. (Trejo and Hernandez, 2004).

Therefore, it is important to detect measures to prevent contamination, which can help reduce the risk of contamination by these metals (Al and Pb). Currently, research work is in search of clean technologies and every day it grows very rapidly. Given this scenario, research centers, organizations or institutions seek alternatives to develop new or better products or procedures that allow the elimination or reduction of metals present in contaminated water.

5.3 Theoretical framework

Removal of metals in wastewater

Environmental contamination with heavy metals represents one of the biggest problems in the world. Cleanup methodologies are based on energy-intensive engineering processes, which are complicated and expensive. Within these technologies are chemical precipitation, electrodeposition, ion exchange, membranes and adsorption. Of these methods, chemical precipitation, for example with OH^- or S^{-2}, has the lowest operating cost, but is inefficient for dilute solutions. Furthermore, the biggest drawback is the formation of sludge which must be subject to restrictions.

Ion exchange and reverse osmosis are generally effective but have high operation and maintenance costs and are subject to scaling. Adsorption is a promising alternative for this purpose, especially using low-cost adsorbents such as clays, agricultural residues, and shellfish processing residues (Bailey *et al*., 2008).

On the other hand, biopolymers are a potential tool that provides ample opportunity for chemical reactions with metals, soil particles, and other biopolymers. In addition, they may have the ability to create interpenetrating cross-linking networks that manage to encapsulate contaminants (Etemadi *et al*., 2008).

One of these polymeric materials of great interest in recent research for the removal of heavy metal ions present in wastewater has been chitosan [poly (β-1-4)-2-amino-2-deoxy-D-glucopyranose] a derivative of the N-deacetylation of chitin, a natural biopolymer from crustaceans or the biomass of fungi capable of removing ions such as mercury, lead, cadmium, etc. by physical or chemical adsorption. This material has the advantage of adsorption at very low concentrations of the ion, in addition to being widely available and friendly to the environment (Li and Bai, 2009).

Adsorption of metals in aqueous solution

Adsorption is the adherence or retention of a thin layer of molecules of a gas or liquid mixture in contact with a solid surface, because of force fields on that surface. Due to the fact that the surface can present different affinities to the various components of the fluid, causing the composition of the adsorbed layer to be different from the composition of the fluid, this phenomenon is an excellent means of removing contaminants, since the unwanted components of a fluid mixture, in addition to the fact that the amounts removed can be very high compared to other methods (Ruthven, 2003).

In general, there are three stages involved in the sorption of contaminants within the solid sorbent: (1) transport of the contaminant from solution to the sorbent surface (2) adsorption on the particle surface; (3) transport within the sorbent particle (Crini, 2010).

Due to the complexity of the materials used and the specific characteristics (such as the presence of complex chemical groups, small surface area, poor porosity), the sorption mechanism in polysaccharide-based materials is different from other conventional adsorbents. These mechanisms are, in general, complicated because they imply the presence of different interactions. Furthermore, a wide range of chemical structures, pH, salt concentrations, and the presence of bonds often complicate the process (Kumar *et al*., 2009).

Some of the interactions reported for the contaminant adsorption process with polysaccharide-based materials are: ion exchange, complex formation, coordination/chelation, electrostatic, acid-base, hydrophobic, hydrogen bond, physical adsorption and precipitation interactions (Crini, 2010).

On the other hand, for the selection of the best adsorbent, the surface area, the type of solute and the solvent that act in the process must be considered, as well as the possible associations that are established between the adsorbent and the adsorbate. Recognizing the type of association, the process can be classified as chemical or physical adsorption, also called chemisorption or physisorption, respectively (Maron and Pruton, 1978).

If the Van der Waals forces justify the association of the adsorbate on the surface, this process is of the physical adsorption type. In this case, the process releases an amount of heat known as heat of adsorption. It is known that the amount of adsorbed matter, in the case of physical adsorption, increases with decreasing temperature. The process is interpreted as the accumulation of multiple layers of adsorbate on the adsorbent (Tryebal, 2005).

Chemical adsorption is justified by the sharing of electrons between the adsorbate and the adsorbent. With this, the formation of a bond justified by the release of energy known as heat of reaction is proposed. This process is known to restrict adsorption to monolayer formations. The amount of adsorbate fixed in this type of process is greater with increasing temperature (Mc Cabe *et al*., 1998).

Bioadsorption

Bioadsorption is a physicochemical process that includes the phenomena of adsorption and absorption of molecules and ions. This unconventional method mainly seeks the removal of heavy metals in wastewater from the industrial sector, using different materials of biological origin (alive or dead) as sorbent, such as: algae, fungi, bacteria, fruit peels, agricultural products and some types of biopolymers. These materials are inexpensive and are found in great abundance in nature, and their transformation to biosorbent is not an expensive process.

The bioadsorption process involves a solid phase (biomass) and a liquid phase (water) containing dissolved substances of interest to be adsorbed (in this case, metal ions). For the bioadsorption process to be carried out successfully, there must be a great affinity between the functional groups of the biomass and the contaminant, since the latter must be attracted to the solid and bound by different mechanisms.

The phenomenon of bioadsorption of metal ions, using biological materials as adsorbents, can be carried out through various physicochemical and metabolic mechanisms in which the process of capturing heavy metals can differ, and there are two methods:

1. Bioaccumulation: It is the adsorption of metallic species by means of accumulation mechanisms inside living biomass cells.

2. Bioadsorption: It is the adsorption of ions on the cell surface. This occurs by ion exchange, precipitation, complexation, or electrostatic attraction.

The bioaccumulation process involves a first stage that is bioadsorption, however, it is followed by other stages that allow the transport of contaminants through an active transport system that provides energy consumption inside the cell.

Due to the above, it is established that bioadsorption can be considered as the best alternative for the elimination of metallic ions present in wastewater, since it does not use living organisms as biosorbent materials; since these can be affected by the high concentrations of said contaminants, interrupting the adsorption process due to their death. Therefore, by using dead biomass, the rapid deterioration of the biosorbent material can be avoided, and certain variables can even be adjusted to increase the efficiency of the process.

Carboxymethylcellulose

Carboxymethylcellulose (CMC) is a derivative of cellulose with carboxymethyl groups ($-CH_2-COOH$) well known for its superabsorbent properties. It is a water-soluble anionic polymer that is produced by reacting cellulosic alkali with an esterifying agent known as sodium monochloroacetate. Its production is simpler than that of cellulose ethers because all the reagents are solid or liquid and allow working at atmospheric pressure. It is soluble in water and is very useful for its super absorbent characteristic.

All grades of CMC are white, odorless and non-toxic. Its dispersion and aqueous dissolution are not complicated, however, since it is a polymer it tends to agglomerate and form lumps when it is moistened, for which it is necessary to disperse and dissolve it in water, adding it very slowly and with vigorous stirring.

Among the most important physical properties are its hydrophilic character, high viscosity in diluted solutions, ability to form films, innocuousness, ability to act as a water-retaining agent, null toxicity, biocompatibility and excellent behavior as a colloid, protector and adhesive, make that CMC can be widely used in the pharmaceutical industry for tablet coatings (because it is insoluble in the acidic environment of the stomach but soluble in the basic medium of the intestine), as a drug-carrying gel former, tablet disintegrator and stabilizer for suspensions, emulsions, aerosols and bioadhesives in tablets that adhere internally to the mucus of some part of the body, in agriculture in pesticides and water-based sprays, CMC acts as a suspending agent. Also, it works as a glue after application to bind the insecticide to plant leaves. On some occasions, CMC is used as an aid in the degradation of some highly polluting fertilizers, among others.

Gels

A gel is a three-dimensional network made up of flexible polymer chains that absorb considerable amounts of water. These polymers have well-known characteristics, such as being hydrophilic, soft, elastic and insoluble in water, in addition to swelling in its presence, increasing their volume appreciably while maintaining their shape until reaching physical-chemical equilibrium. Additionally, they can have great mechanical resistance depending on the method with which they are obtained. Its three-dimensional conformation occurs in concentrated aqueous solutions when the initial polymer is capable of gelling with the consequent formation of non-covalent spatial networks. The hydrophilic character is due to the presence of hydrophilic functional groups such as: OH, COOH, CONH, among others. (Arredondo *et al*., 2009).

Since gels are very brittle, it is necessary to improve their mechanical properties in the swollen state. Due to the above, research has been carried out on hydrogels of semi-interpenetrated polymeric networks based on cross-linked polyacrylamide (PAAm) and having poly N-isopropylacrylamine (PNIPAAm) inside, presenting qualitatively good mechanical properties, even in a swollen state (Muñoz y Zuluaga, 2009).

Polymeric materials can undergo temporary deformations when a stress is applied to them. This behavior is called elasticity and is related to the molecular flexibility of polymers when the material is cross-linked (either through chemical or physical bonds) forming a mesh and can withstand much greater stresses without losing its original shape, since intermolecular bonds prevent the displacement of some chains with respect to others.

Some derivatives of natural polymers such as xanthan gum or cellulose (methylcellulose, ethylhydroxyethylcellulose, hydroxypropylmethylcellulose) and certain synthetic copolymers, gelation occurs because of a change in temperature. Cellulose derivatives can chemically cross-link forming a three-dimensional hydrophilic network through intermolecular covalent bonds between polymer molecules. Methylcellulose (MC) has been chemically crosslinked with a di-aldehyde (GA) in the presence of a strong acid (HCl) to generate a hydrogel (Park *et al*., 2001).

Due to their wide field of applications, gels have great technological and economic importance. The presence of water is beneficial for the biocompatibility of hydrogels, but it causes a decrease in the mechanical properties, which is why it is necessary to develop them with a high absorption capacity, while maintaining good mechanical properties.

In general, polymeric gels are capable of being polymerized in long linear chains that chemically or physically intersect to form a three-dimensional network. In the case of chemical gels, using bifunctional monomers in small amounts, crosslinking of the chains is achieved, while in physical gels this crosslinking is due to non-covalent secondary interactions (Muñoz y Zuluaga, 2009).

The two possible states of a gel are: the collapsed state and the swollen state, in the dry state it is called xerogel, but when a solvent is added it swells until it reaches the swelling equilibrium, so that the solvent is retained inside. (Sáez *et al*., 2003).

Aluminum

Aluminum is the third most abundant element in the earth's crust. Even when its toxicity has been demonstrated, geochemical control maintains its bioavailability within harmless parameters. However, natural modifications and anthropogenic interventions contribute to its release, increasing the incidence of diseases in the population and generating harmful accumulations in the environment. The most important sources of non-occupational exposure to aluminum are food, water, certain medications and cosmetics, as well as the containers and utensils used for food preparation (Torrellas, 2013).

Aluminum is found in the natural environment in the form of the ionic species Al^{+3}. In soils it is combined in minerals and rocks of aluminosilicates (feldspars, imogolite, kaolinite), phosphates (variscite), sulfates (jurbanite) and hydroxides (gibbsite) (Soon, 1993).

From a chemical point of view, this ion with a small ionic radius (0.50 Å) and a strong charge produces an intense electric field that attracts electrons. Aqueous solutions of aluminum salts are acidic due to hydrolysis of the Al^{+3} species (Cotton, 1989).

The concentration of the Al^{+3} ion in water is much higher than that of other biologically important cations such as Mg^{+2}, Fe^{+3} or Zn^{+2}. Aluminum is not an essential element for living organisms in ecosystems and has been found to be a toxic agent (Bondy, 2010; Lewis, 1989). The main reason why this toxic ionic species does not affect organisms in their natural environment is because aluminum readily reacts with silicon, the most abundant element on the planet, thereby forming aluminosilicates and bauxite with oxygen. Thus, geochemical control maintains the bioavailability of aluminum within harmless parameters. However, interventions in the environment are increasing its bioavailability and, consequently, causing impacts (Gustafsson, 2001).

Lead

Lead is a heavy metal whose density is 11.34 $g \cdot cm^{-3}$ at 20°C and its atomic mass is 207.19 $g \cdot mol^{-1}$. This metal can be found naturally in the environment, more specifically in the earth's crust. Its proportion in the earth's crust is approximately 15 $mg \cdot kg^{-1}$, whose total amount is estimated at $3.8 \cdot 10^{14}$ tons. Also, it can be found anthropogenicly due to human activities such as the burning of fossil fuels and mining. (Jacobs y Belaire, 2017).

Lead exposure can occur through ingestion of contaminated food and drinking water, and through inadvertent ingestion such as lead paint or dust particles from soil. Furthermore, 95% of inorganic lead is absorbed by inhalation.

This chemical element is toxic, dense and cumulative, which affects both living organisms and humans, and can enter food chains. Currently, the intake of this metal is reduced due to the controls established by regulations at the industrial level, leading to a lower risk of exposure (Londoño *et al.*, 2016).

Lead is used as a metal in 40%, and of that percentage, 25% is used for applications in alloys and 35% is used as chemical compounds of both organic and inorganic origin. Some of the main applications are lead oxide in the production of paints and car battery components (Ubillus, 2003).

5.4 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.

These swelling tests were carried out at a temperature of 40 °C and agitation at 120 rpm in a bath with agitation and controlled temperature. The amount of water absorbed by the gels was determined using equation 1, expressed as a percentage (Rivas et al., 2010).

$$H = \frac{(W - W_o)}{W_o} x\ 100\% \qquad (1)$$

Where:

H = Swelling, %

W = Weight of swollen gel, g (at different contact times)

W_o = Initial dry gel weight, g

Infrared Spectroscopy (IR)

Infrared spectroscopy has the potential to determine a myriad of substances by virtue of almost any species absorbing in this region, it allows identifying and establishing the structure of organic, inorganic and biochemical species.

The infrared (IR) region of the electromagnetic spectrum covers the upper visible range (7.8×10^{-7} m), but only medium absorption (from 4000 cm^{-1} - 400 cm^{-1}) is used for organic chemical compounds. IR radiation energy levels range from 48 kJ/mol to 4.88 kJ/mol (11.5 to 1.15 kcal/mol). This tool is mainly used in organic chemistry to detect functional groups, identify compounds, and analyze mixtures (McMurry, 2009).

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.

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. It is largely based on the Beer-Lambert law. In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals for an instant by absorbing an amount of energy (i.e. light of a certain wavelength). This amount of energy (or wavelength) specifically refers to one electron transition in an element, and in general, each wavelength corresponds to a single element.

Since the amount of energy that is put into the flame is known, and the amount remaining on the other side (the detector) can be measured, it is possible, from the Beer-Lambert law, to calculate how many of these transitions take place, and thus obtain a signal that is proportional to the concentration of the element being measured.

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 equation 2.

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

Where:

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

V = volume of metal solution, l

C_o = Initial concentration, mg/l

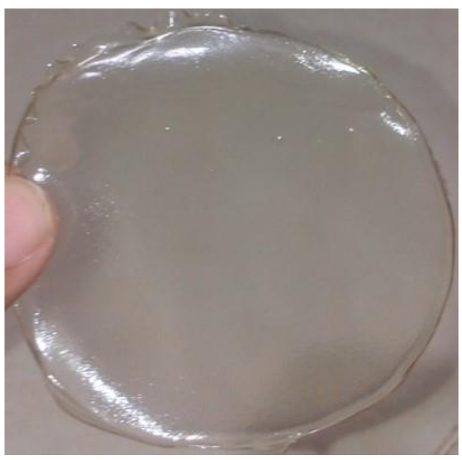
C_f = Final concentration, mg/l

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

5.5 Results

Figure 5.1 shows the film obtained from the synthesis of the carboxymethylcellulose gel, with a transparent appearance and flexible to the touch, presenting an adequate homogeneity to be used in the tests of absorption and elimination of metals (Al and Pb).

Figure 5.1 Carboxymethylcellulose gel film



Source: Own elaboration

200 mg of film cut into vials approximately 1 cm^2 was added and placed in an oven at 45°C until a constant weight was obtained, proceeding with the swelling tests and determining the maximum degree of absorption. Table 5.1 shows the results of the weights obtained in the swelling tests, to determine the absorption capacity of the CMC gel with a degree of substitution (DS) of 0.7 at 25°C for 24 h.

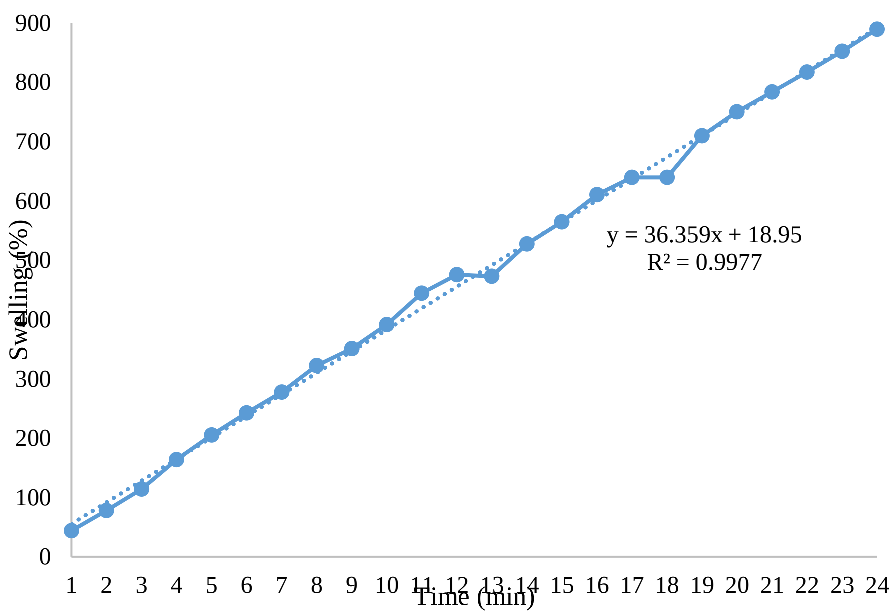
Table 5.1 Increase in swelling with respect to time

Time (min)	Swelling (%)
1	43.8212
2	77.7491
3	113.8293
4	163.7598
5	204.9231
6	242.2268
7	277.4690
8	322.0128
9	350.8397
10	391.3876
11	444.0103
12	475.2322
13	473.0119
14	527.1385
15	564.5464
16	610.1092
17	639.4191
18	639.4191
19	709.4710
20	749.9724
21	783.37298
22	816.9908
23	852.2581
24	889.5588

Source: Own elaboration

The data obtained were plotted in figure 5.2 using Excel to observe the behavior of the CMC gel with respect to time, maintaining the temperature and controlled agitation of 40°C and 120 rpm, respectively, showing that the gel absorbs around 889. 5% in a period of 24 hours.

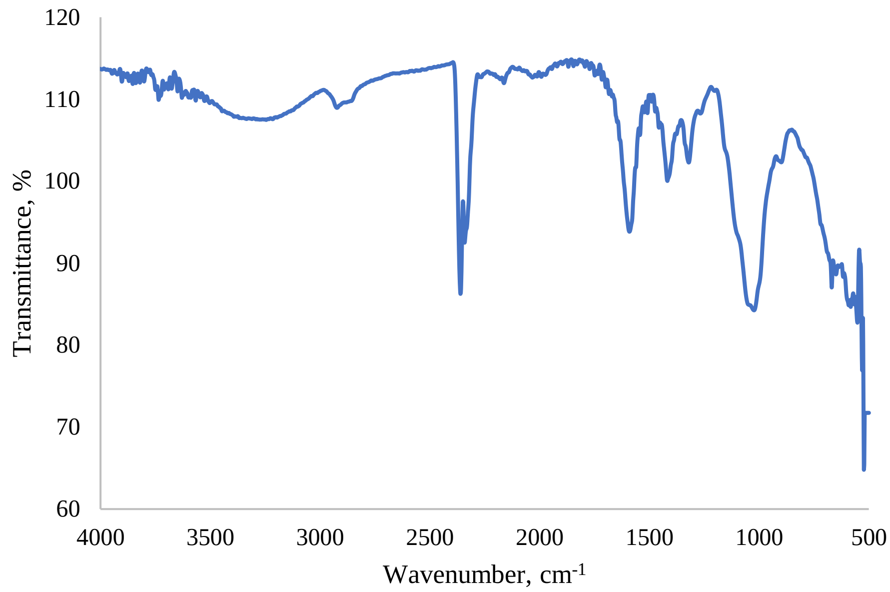
Figure 5.2 Percentage of swelling of carboxymethylcellulose gel



Source: Own elaboration

Figure 5.3 shows the infrared spectrum of CMC gel before being incorporated into water contaminated with Al and Pb, showing the characteristic functional groups, at a wavelength of 3271 cm^{-1} the characteristic –OH group of CMC is observed. the structure of carboxymethylcellulose, while at 2904 cm^{-1} the CH_2 group was found, at 1591 cm^{-1} and at 1417 cm^{-1} there is a stretch band due to the carbonyl and carboxyl groups, respectively. On the other hand, the bending by the $-CH_2-$ groups at 1323 cm^{-1} are shown and finally in the region of 1038 cm^{-1} we find the C-C bonds, characteristic of cellulose.

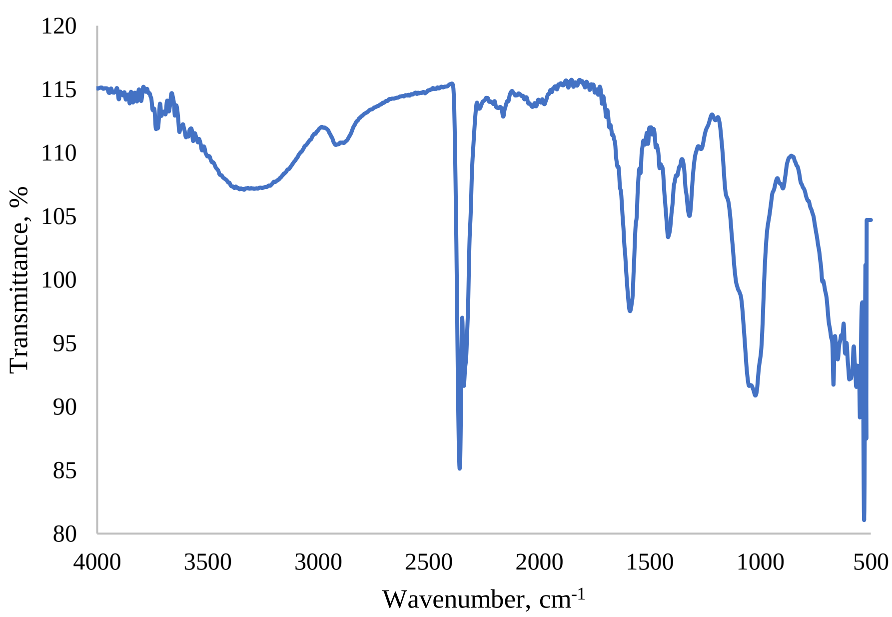
Figure 5.3 IR spectrum of carboxymethylcellulose gel



Source: Own elaboration

Figure 5.4 shows the IR spectrum of the carboxymethylcellulose gel after being in contact for 12 h in an Al solution and using 200 mg of substrate (CMC gel), showing a broad band at 3253 cm^{-1} of the group - OH characteristic of the CMC structure, at 2904 cm^{-1} a weak signal of the CH2 group is present, at 1597 cm-1 and 1417 cm^{-1} a stretching of the carbonyl and carboxyl group is shown, respectively. On the other hand, at 1319 cm^{-1} a bending of the -CH^{2}- group is observed and in the region of 1026 cm^{-1} the C-C bond, characteristic of cellulose, was present.

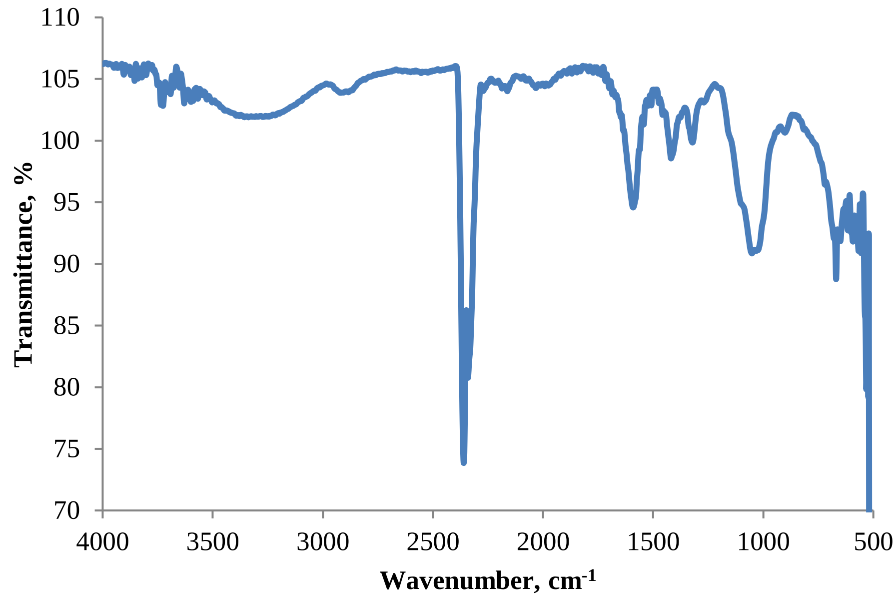
Figure 5.4 IR spectrum of carboxymethylcellulose gel after exposure to water contaminated with Al metal



Source: Own elaboration

Figure 5.5 shows the IR spectrum of the carboxymethylcellulose gel after being in contact for 12 h in a Pb solution and using 200 mg of substrate (CMC gel), showing a broad band at 3298 cm^{-1} of the group -OH characteristic of the CMC structure, at 2910 cm^{-1} a weak signal of the CH_2 group is present, at 1587 cm^{-1} and 1419 cm^{-1} a stretching of the carbonyl and carboxyl group is shown, respectively. On the other hand, at 1325 cm^{-1} a bending of the -CH_2- group is observed and in the region of 1049 cm^{-1} the C-C bond, characteristic of cellulose, was present. In addition, at 895 cm-1 a peak appears due to out-of-plane twisting of the carboxyl group dimer.

Figure 3.5 IR spectrum of carboxymethylcellulose gel after exposure to water contaminated with the Pb metal

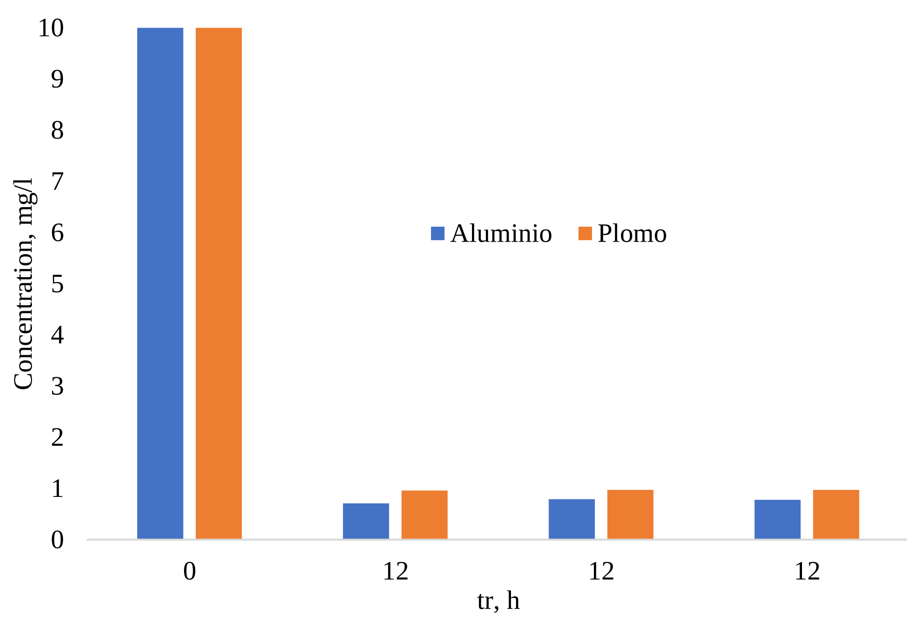


Source: Own elaboration

The effect of the substrate (CMC gel) was studied in each of the prepared solutions of Al and Pb, and it was carried out in triplicate for each solution, keeping the temperature constant at 25°C, agitation at 120 rpm and contact time at 12 h, after that time, the amount of Al and Pb that was removed from the contaminated water was determined, using the Atomic Absorption technique.

Figure 6.6 shows the data obtained by atomic absorption analysis (AA), where the results for metal removal (Al and Pb) are observed, obtaining a reduction of 92.4% and 90.33% for Al and Pb, respectively.

Figure 6.6 Concentration of Al and Pb after being exposed with the carboxymethylcellulose gel



Source: Own elaboration

The initial concentration (Co) of the Al and Pb solutions that were prepared was 10 mg/l; and 15 ml of solution was added to 0.2 g of CMC gel contained in 20 ml vials and kept in contact for 12 h, and then the AA analysis was performed, reaching the final concentrations of Al and Pb of 0.76 mg/ l and 0.97 mg/ml, respectively. Subsequently, equation 2 was used to determine the amount of metal absorbed per gram of substrate, obtaining 9.24 mg/g for Al and 9.03 mg/g for Pb.

5.6 Acknowledgement

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5.7 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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