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Water treatment: Chitosan associated with electrochemical methods

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Abstract. Pollution of water bodies due to the presence of toxic metals and organic compounds, bring out a series of environmental problems of public, government and social character. In addition, water pollution, has become the target and source of concern in many industrial sectors. Therefore, it is essential to develop technologies for treatment and purification of water. Chitosan is a natural product derived from chitin, extracted mainly from the shells of crustaceans. It is a low cost, renewable and biodegradable biopolymer of great socioeconomic and environmental importance. The classic treatment of wastewater containing metals involves physical chemistry processes of precipitation, ion exchange and electrochemistry. Electrochemical technology has been presented as the most promising methods for treating wastewater polluted with metals, colloids, dyes or oil in water emulsions; besides being used in removing organic compounds. Alternative methods like adsorption with biosorbents have been investigated. The great advantage of this latter over other techniques is the low generation of residues, easy recovery of metals and the possibility of reuse of the adsorbent. This article aimed to carry out an exploratory study, of bibliographical nature, on the use of chitosan in electrochemical methods for water treatment.

1. Introduction

Chitosan is a copolymer obtained by deacetylation of chitin, only differing in functional groups. It is a natural product of low cost, renewable, biodegradable and of great economic and environmental importance. Chitin, the main biopolymer used to extract chitosan, it is found in the exoskeletons of arthropods like crustaceans - crab, shrimp; and lobster; insects – ants, bees and butterflies; molluscs, as well as in the cell walls of fungus. Due to your wide range of use and application, technological feasibility has been increasingly studied [1-5].

There are those define chitosan as a linear chain polymer, cationic with protonation of the amino group (NH₃⁺) [6, 7]. It can be obtained by deacetylation of chitin, differentiating from this in terms of proportion of amino groups and the solubility. This characteristic of chitosan to provide free amino groups increases their ability to react with multiple molecules, making the biopolymer with increased availability of pendant groups, it can be employed as powder, beads or films [8].

There are a variety of studies on the properties, features and applications of chitosan, which is currently used in various fields such as medicine, agriculture, biotechnology, cosmetics industry



products, food and as adsorbents in removing dyes and metal species [9-15]. Due to the simplicity of obtaining a polymer in different physical forms, in various countries, the chitosan is produced on a large scale, with high industrial application [16].

Pollution of water bodies due to the presence of toxic metals and organic compounds, bring out a series of environmental problems of public, government and social character. In addition, water pollution, has become the target and source of concern in many industrial sectors. Due to population growth and the unsustainable use of water resources, water scarcity has become a major challenge in the world. Therefore, it is essential to develop efficient technologies for treatment and purification of water [17].

Electrochemical technology can be a powerful tool in addressing these challenges, because it has the following advantages: relative availability of electricity, reduced energy reaction conditions (cold processes), reproducible systems and easily controllable allowing the automatization and ease of assembly of relatively compact plants. The electrolytic process takes place when a potential is applied from an external current source causing a non-spontaneous chemical reaction in an aqueous medium. This process has been presented as the most promising methods for treating wastewater polluted with colloids, dyes or oil in water emulsions; besides being used in removing BTEX (benzene, toluene, ethylbenzene and xylene) [18].

A literature review on the subject and some of its various applications has been performed, since this is a source of renewable raw material, economically viable. It was possible to verify that there are very few studies using chitosan specifically in electrochemical methods for the treatment of effluent, confirming the importance of conducting studies in this area. This study is focused on the use of chitosan in electrochemical methods as a strategy for the treatment of effluent (water).

2. Theoretical foundations

Chitosan was industrially produced around 1971 in Japan and the US, leading countries of the world chitosan market. By 1993, Brazil also started marketing chitin and chitosan on a large scale. The chitosan is a biodegradable copolymer consisting of D-glucosamine units containing a free amino group [19]. The deacetylation of chitin leads to the production of copolymers with varying composition and molecular weight, depending on the conditions and extent of reaction.

Thus, the reproducibility of characteristics and properties is not always the case, even if similar reaction conditions are employed in the deacetylation of chitin, aiming at preparing chitosan. It is soluble in dilute acid, forming a cationic polymer by protonation of amino group (NH_3^+), which gives special properties different with respect to vegetable fibers, as cellulose [2].

Chitosan is a linear cationic polysaccharide, naturally occurring or can be obtained by deacetylation of chitin. While there is no definitive nomenclature for establishing a difference between chitin and chitosan, the term chitosan is generally copolymers of 2-amino-2-deoxy-D-glucose [8]. The deacetylation of chitin leads to chitosan obtained, its most important derivative whose primary structure is identical to that of chitin, but in chitosan predominate 2-amino-2-deoxy-D-glucopyranose units. The complete deacetylation of chitin is rarely performed, because many consecutive reactions are needed, which also favor the progressive depolymerization [8]. Thus, the term chitosan includes all polymers containing at least 50-60% of units of 2-amino-2-deoxy-D-glucopyranose. There are no well-defined limits in terms of content units of 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose for chitin and chitosan distinction, but due to their different compositions, polymers exhibit very different properties.

From a practical point of view, it is the solubility which allows simple and quick distinction, since chitosan is soluble in several dilute acidic aqueous solutions (the acid and hydrochloric acid solutions are the most commonly used), but chitin is not soluble in these media and it is dissolved in only a few solvent systems. According Campana-Filho (2007), deacetylation of chitin may be effected by chemical or enzymatic processes, but the latter are not employed on an industrial scale due to the high costs of deacetylases extraction, as well as low productivity [19]. The chemical processes of deacetylation of chitin can be achieved by the homogeneous route, which is made alkali-chitin, or heterogeneous, being the most extensively used and studied.

Generally, chitin is suspended in concentrated aqueous solutions of NaOH or KOH (40-60%) for varying times (0.5 to 24 h) and at relatively high temperatures (50-130 °C). The characteristics of the obtained chitosan are determined by the concentration of the alkaline solution and ratio chitin/alkaline solution, the particle size of chitin, temperature, time and atmosphere of the reaction. The most severe conditions are generally employed to favor the efficiency of deacetylation, but it results in marked depolymerization via alkaline hydrolysis.

Electrochemical methods have great potential in the treatment of industrial effluents because they are fast, low cost and can be used as a powerful tool in the identification, quantification and degradation of organic and inorganic substances present in these media.

A procedure widely used in electrochemical studies is the modification of the surface of the electrodes. The development and application of modified electrodes, has received great interest in science and technology, with application in various fields of research. The modification of the surface of an electrode can be performed through physical or chemical processes.

An example of physical surface modification is the construction of a partially blocked surface using an insulating resin that will render some areas of the electrode surface inactive while other areas will remain available for electrochemical reactions to occur. This type of procedure allows studies on the influence of parameters such as the diameter of the active sites, the active surface area and the density of active sites, on mass transport. Thus, allowing important information to be obtained from the kinetic point of view, which are applicable to the study of processes such as electrodisolution of metals, the mechanism of action of corrosion inhibitors and adsorption.

The chemical modification of the surface of an electrode is a means of controlling its properties because it allows the characteristics of interest of the modifier to be transferred to it. This procedure allows different conditions of selectivity and reactivity to be achieved in electrochemical systems. The manufacture of chemically modified electrodes depends on the ability to immobilize chemical species on the surface of the electrode.

In general, we can relate the following methods to accomplish this immobilization: Adsorption of the reagent on the surface of the electrode; Covalent bond formation between the electrode and the electroactive reagent; Coating the electrode with polymers.

Adsorption is an older and simpler technique for anchoring redox centers on the electrode surface. Although the first studies were carried out with platinum, most of the adsorption works were performed with pyrolytic graphite and vitreous carbon, directed to electrocatalytic applications, especially molecular oxygen reduction. This method is very simple. However, it is subject to interference from impurities that can adsorb more strongly than adsorbate. In addition, it does not allow you to create structures that are thicker than monolayers.

The first surface modification works employing covalent bonding were based on the use of silane reactants, which could react with hydroxyl groups found on metal oxide electrodes, to give species covalently bound via siloxane bonds. Tin oxide electrodes were initially used, which in analogy to the glass have hydroxyl groups reactive on the surface, with which the silanes could bind. However, it has been found that many metal electrodes, when oxidized in acidic media, are coated with a thin layer of oxide, which is reactive to silane reactants, thus allowing even the platinum to be modified with covalently bound silanes.

Although silane reactants offer the simplest means for covalent anchoring, other approaches are advantageous, including cyanuric chloride linkages and direct addition reactions to the graphite surface. The great interest in organic synthesis was responsible for the appearance of a line of modification of carbon surfaces with the use of pyrolytic graphite electrodes, vitreous carbon and carbon paste electrodes. The carbon paste electrodes present a particularity as to the modification process, since in this case the material of interest is incorporated into the pulp through a simple mixing process, which does not characterize a covalent attachment procedure. The advantage of this electrode is the ease of surface renewal.

Polymer-modified electrodes have a greatly enhanced signal when compared to those obtained with monolayer-modified electrodes. In this way, the realization of the measures is easier, besides having a greater stability. The preparation of the electrodes can be performed in different ways: (i) employing a preformed polymer containing the redox center; (ii) by binding a redox center to a previously prepared

polymer; (iii) by in-situ generation, by electropolymerization, of active redox monomers. This type of study has been carried out employing mainly voltammetric electrochemical techniques. More recently we have used impedance techniques for the kinetic study of modified electrodes [20-21].

The development and application of modified electrodes, has received great interest in science and technology, with application in various fields of research. The modified electrode is constructed by adding chemically active substances immobilized on the electrode substrate, in order to pre-establish and control the physical chemistry nature of the electrode/solution interface. The electrode modification usually gives the properties (reactivity, selectivity, etc.) of the modifier, thereby enabling the development of devices with adequate response for various purposes and applications [22, 23].

3. State of the art

Different methodologies and strategies for applications of chitosan have been proposed in the literature. The majority of studies showed the chitosan applications in the coating of edible films [24-27]; effluent treatment due to the interaction of this with metal ions [28-30] and fat reduction [2]. Worry and concern with environmental issues have increased over the decades. Scientists around the world are developing research studies to assess and reduce pollution impacts on the biosphere, and to develop clean technologies that generate less waste. Among the many pollutants, metals have received special attention because some are very toxic to a wide variety of organisms, even at extremely low concentrations [29].

The classic treatment of wastewater containing metals involves physical chemistry processes of precipitation, ion exchange and electrochemistry. However, these traditional techniques are unsuitable for decontamination of large volumes of wastewater containing metals in low concentrations due to low operational efficiency and high costs of this process. Therefore, alternative methods have been investigated as, for example, electrodialysis, reverse osmosis, ultrafiltration and adsorption with biosorbents. The great advantage of this latter over other techniques is the low generation of residues, easy recovery of metals and the possibility of reuse of the adsorbent [29].

Among the natural materials, chitosan, the plus abundant and low cost is a good adsorbent for heavy metals, since it has the ability to form complexes with transition metal ions in aqueous solution and cause the neutralization of acidic solutions. Chitosan can be physically modified, one of the most interesting advantages being its great versatility in being prepared in different forms, such as powders, flakes, microspheres, nanoparticles, membranes, sponges, hives, fibers and hollow fibers [9, 17].

The versatility of chitosan is attributed to free amino groups, which are exposed after the deacetylation of chitin [31, 32]. The preparation of chitosan microspheres is a strategy for increasing their adsorption capacity, once the microspheres have a surface area greater than the chitosan flake. Moreover, microspheres have faster absorption kinetics and greater ease of handling and operation [2].

Several recent studies show that chitosan can be used as microspheres for different purposes. Laus et al. (2006) proposed a method using chitosan microspheres crosslinked with tripolyphosphates used for removal of acidity, Fe^{3+} and Mn^{2+} water contaminated with coal mining [30]. Among the environmental impacts related to the mining of coal, the most aggravating is the pollution of water sources in the regions close to the mines, where the mineral is exploited.

Water pollution, observed in mining, is due to the generation of acid effluents from mines and coal wastes. This characteristic of acidic mining waste is given mainly by the presence of pyrite (FeS_2), a very common sulfide mineral in the Brazilian coals. Pyrite is rapidly oxidized and dissociated when exposed to air and water, releasing Fe^{2+} . In this study, chitosan crosslinked with tripolyphosphate were used in the form of microspheres used in remediation of contaminated water by coal mining, being shown

The dissolution of sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) in a chitosan solution induces an ionic crosslinking among the ions tripolyphosphate (TPP) and the protonated amino group of chitosan. Crosslinking of chitosan prevents the polymer is dissolved in an acidic medium and introduces phosphate groups, which have basic sites that might interact with H_3O^+ and metal ions in aqueous solution can increase its remediation capacity of aquatic environments contaminated by coal mining.

According to Ma (2016), due to population growth and the unsustainable use of water resources, water scarcity has become a major challenge in the world. Therefore, it is necessary to construct new technological alternatives for treatment and purification of water [33].

Carbon materials such as activated carbon and carbon nanotubes have been used electrochemically modified for the treatment of water and industrial effluents. The adsorption process is recognized as an effective method for the removal of environmental contaminants from aqueous solutions. Researchers have studied the use of carbon nanotubes to remove electrochemically pollutants. The adsorption capacity of carbon nanotubes can be significantly improved by electrochemical methods [34-37].

The electrosorption process, which is an adsorption induced by the potential of undesirable ions and contaminants on the surface of charged electrodes, has attracted much attention due to its compatibility with the environment and its low energy consumption [38]. The development of analytical and electroanalytical techniques to determine low concentrations of metals in natural water and wastewaters have been of extreme interest. Janegitz et al. (2007) developed a carbon paste electrode modified with chitosan, for the determination of Cu^{2+} in wastewater by voltammetry [31, 32].

The use of chitosan as a modifying agent for metal ions sensors has been little explored, despite the high affinity of this material by metal cations. In this experiment, they used a system with three electrodes, wherein the working electrode is a chemically modified electrode with chitosan, the reference electrode, an Ag/AgCl electrode and the auxiliary a platinum electrode.

In the treatment of industrial effluents the modified electrodes are increasingly being used to detect trace metals. However, electrodes modified with chitosan nanotubes are still little explored. Martínez-Huitle et al. (2010) developed a research modifying vitreous carbon electrode with chitosan [39]. According to the proposed study, it was used to determine trace metals (Cu, Pb, Cd, Co, As and Pt) in aqueous solutions. The modified surface of the electrode exhibited an affinity with metal ions in solution, forming complexes.

4. Conclusion

Among the natural materials, chitosan, the plus abundant and low cost, is a good adsorbent for heavy metals, since it has the ability to form complexes with transition metal ions in aqueous solution and cause the neutralization of acidic solutions. The application of electrochemical techniques to determine and remediate low concentrations of metals in natural water and wastewaters it is an advantageous and cost-effective alternative. The use of chitosan as a modifying agent for metal ions sensors has been little explored, despite the high affinity of this material by metal cation, therefore it appears as a promising alternative for the treatment of wastewater.

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