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Research paper

Adsorption of metals by crosslinked chitosan beads in sugarcane contaminated streams

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ABSTRACT

Streams situated in areas of sugarcane cultivation receive high concentrations of metal ions from the adjacent areas, causing accumulation of metals in the aquatic sediment. Several adsorbents have been used to remove metal from water. Activated carbons clays and biopolymers are among the common adsorbents utilized. Chitosan beads, an alternative biopolymer that exhibits a high affinity for metal ions, are easy to prepare under laboratory conditions, have low overall cost and can be indicated for the removal of metals from aquatic sediments. This work studied, for the first time, the possible use of Chitosan beads in the adsorption of metals from sediments of streams located in areas adjacent to sugarcane cultivation. The sediments were collected from four streams historically impacted by sugarcane; one of them is located in a preserved area, used as the control site. The sediments were evaluated for adsorption of Cr, Cu, Zn, Mn and Mg. The results showed that the maximum adsorption of metals in chitosan beads (containing only 5.5% of chitosan) were obtained in São João Stream, such as: 0.65 mg kg^{-1} for Cr^{6+}, 2.85 mg kg^{-1} for Cu^{2+}, 2.5 mg kg^{-1} for Mg^{2+} and 0.85 mg kg^{-1} for Zn^{2+}. For manganese, the maximum adsorption was 0.84 mg kg^{-1}, obtained for the Agua Sumida Stream. The adsorption had high affinity for Cu, Zn and Cr and low affinity for Mg and Mn. Chitosan presented potential and viability for use in the remediation of the impacts of metals on aquatic sediment systems, with high adsorption and capacity to be applied "*in loco*".

1. Introduction

Sediments act as carriers and sinks for contaminants in aquatic environments, where metal ions are the most common environmental pollutants [1] that can exert a deleterious impact on freshwater fauna [2–4]. Sediments contaminated by metals are potential sources of natural water pollution, because they are confined to sediments by adsorption, and can be released into water with pH alteration [5]. The oxidative process of organic matter of contaminated sediments causes a decrease in pH and is correlated to the release of metals in solution [6].

Brazil is the main sugarcane producer in the world, followed by India, China, Pakistan, Mexico, Colombia, the Phillipines, Australia, Indonesia and the United States according to FAOSTAT [7]. The projection for 2016/2017 is that Brazil will reach 6.8×10^8 tons of sugarcane production [8]. In the southeast region of Brazil, specifically in the state of São Paulo, sugarcane culture has an annual production of about 3.7×10^8 tons covering an area of 4.5×10^6 ha [8]. In Brazil, sugarcane is the main source of sugar and alcohol production, through a fermentative sugarcane process [9].

There is a considerable increase in the use of fertilizers and pesticides due to sugarcane expansion in Brazil [10]. Fertilizers, used in sugarcane crops, contain different concentrations of metal ions, such as lead, cooper, nickel, chromium, cadmium, aluminum and zinc [11,12] and fertigation, a fertilizer that consists of the application of stillage onto the soil, is also an adopted practice in Brazil [13] that also contains such metals.In addition, the deforestation of riparian vegetation can increase impacts on the water resources of the areas adjacent to sugarcane crops, leading to contamination of the aquatic sediments [2,14,15], causing serious damage [16]. Sediments can contribute expressively to the metal concentration in aquatic macroinvertebrates, either by absorption/adsorption from interstitial water or ingestion. The accumulation of metals in sediments and the contamination of the

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aquatic invertebrates represent a dangerous association in the transferal of metals to high trophic levels, such as fishes and birds. Every year, applications of fertilizers on sugarcane are repeated. This process has caused damage to aquatic communities [17].

Many techniques can be adopted to treat contaminated environments, such as: precipitation, ion exchange, adsorption, and co-precipitation/adsorption [18]. Among various treatment methods, adsorption is generally considered the most appropriate, since it can remove both organic and inorganic pollutants [19]. As pointed out by Ngah et al. [20], many adsorbents have been used to remove metal ions from wastewater particularly those that are damaging to humans. For example, activated carbons, plant or lignocellulosic wastes, clays and biopolymers are among the common adsorbents utilized.

Chitin and chitosan-derivatives have also gained wide attention as effective biosorbents due to their low cost and high content of amino and hydroxyl functional groups which show significant adsorption potential for the removal of various aquatic pollutants [21]. Chitosan is a very interesting biopolymer to be applied in natural environments, due to its non-toxicity for aquatic organisms [20]. Chitosan is a biopolymer extracted from crustacean shells or from fungal biomass [22] and is considered to be one of the most promising and applicable materials in adsorption applications [23], which characterizes it as a low-cost adsorbent [24]. The fact that chitin is as an effective material for sutures essentially because of its biocompatibility, biodegradability and non-toxicity together with its antimicrobial activity and low immunogenicity, points to immense potential for future development [25] [26]. This biopolymer is able to bind strongly to metal ions by chelation on amine groups of chitosan in near neutral solutions [27]. The application of chitosan as an adsorbent in contaminated soils demonstrated that it is indicated to be used for remediation "*in situ*" [28]. As pointed out by Kyzas et al. (2017) [29], numerous papers have been published regarding the use of chitosan as an adsorbent for the decontamination of wastewater (or effluents, seawater, drinking samples) from various pollutants, either organic (dyes, phenolic and pharmaceutical compounds, herbicides, pesticides, drugs) or inorganic species (metals, ions). A study conducted by Muzzarelli (2011) [30] also analyzed the potential of chitin/chitosan-bearing materials for uranium recovery. In the review conducted by Kyzas et al. (2017) [29], the researchers also made an extensive search on modified chitosans for metals/ions adsorption, especially from aqueous solutions.

Here, we report for the first time, the possible use of chitosan beads in the adsorption of metals in stream sediments contaminated by sugarcane cultivation.

2. Material and methods

2.1. Study sites

The four streams were located in the Jacaré-Guaçu River Basin, in the State of São Paulo, Brazil (Table 1; Fig. 1). All streams are of low order, have low water velocity ($< 1\ m\ s^{-1}$), low depth ($< 1.5\ m$), low width ($< 2\ m$) and are located at an altitude of 500–700 m. Values of dissolved oxygen varied from 5.32 to 8.13 $mg\ L^{-1}$ and pH varied from 5.28 to 6.92. The streams analyzed are located in the areas of Brazilian Cerrado and for that reason, have predominantly sandy substrates (fine and coarse) (80% of the total), a small percentage of silt (10%), clay (10%) and low organic matter contents [4]. The average annual precipitation in the Jacaré-Guaçu River basin is about 1400 mm [31].

Table 1
General characteristics of the four sampling sites, showing the land use types, city and geographic coordinates.

Legend	Stream	City	Land use	Coordinates
S1	Água Sumida	Araraquara	Sugarcane	21º56' (S) 48º16' (W)
S2	São João	Guarapiranga	Sugarcane	21º96′(S) 48º26′(W)
S3	Bela Vista	Araraquara	Sugarcane	21º90′(S) 48º22′(W)
S4	Espraiado	São Carlos	Riparian vegetation	21º98' (S) 47º87' (W)

The wet season occurs between October and March, while the dry season occurs from April to September. Sites S1 to S3 are located in extensive areas with sugarcane cultivation, without riparian vegetation. Site S4 is located in a preserved area. All streams are free from other anthropic impacts such as industrial, domestic or mining activities [4].

2.2. Sediment sampling and storage

Sediments were sampled, in triplicate, from the sites using a standard Ekman-Birge grab with a sampling area of 255 cm^2. Samples were taken twice at each site, from March to April 2016. Sediments were stored at 4 °C until testing. An aliquot of the sediment was separated for the organic matter and granulometric analysis.

The determination of the granulometric composition was carried out according to Callisto and Esteves [32] by the sieving methodology, where an aliquot of 100 g was dried in an oven (60 °C per 72h), and stirred in sieves (16.00, 4.00, 2.00, 1.00, 0.50, 0.25, 0.125 and 0.062 mm). The organic matter contents were determined by the gravimetric method, where aliquots (0.3 + 0.1 g) were calcined (550 °C for 4h), and the difference between the initial weight of the sample and the weight after calcination provided the percentage of the organic content of sediment samples [32].

2.3. Chitosan

Commercial chitosan were acquired from Chengyue Planting Co. Ltd., China, and it was used as it was received.

The average degree of acetylation ($\overline{DA}$) of chitosan was determined according to Hirai et al. [33] from its ^{1}HNMR spectrum. The polymer (8 mg) was dissolved in D_2O/HCl (1 g/5 μL) and the spectrum was acquired at 25 ± 1 °C by using a Bruker AVANCE III spectrometer (ν = 400 MHz). The viscosity average molecular weight ($\overline{M_v}$) of chitosan was determined from the corresponding intrinsic viscosity by using the Mark-Houwink-Sakurada parameters (K' and α) according to the polymer nature, solvent and temperature [34].

The chitosan used in this work is characterized by $\overline{DA} \approx$ 5.5% and molecular weight ($M_v \approx 85{,}000\ g\ mol^{-1}$).

2.4. Chitosan beads

For the chitosan beads preparation, we used the methodology adapted from Goy [35], with 1.5 g of chitosan solubilized in diluted acetic acid at 5% (w/v). The viscous solution was coagulated in alkali medium, when it was dripped into an NaOH 2.5 $mol\ L^{-1}$ solution using a Titronic Universal Schott automatic titrator. The speed was 3 $mL\ min^{-1}$ and coupled to a needle 18 galge diameter to standardize the size of the beads, under environment temperature (25 °C ± 2). The beads were kept under constant stirring for 16 h and then they were thoroughly washed with deionized water to remove the excess of NaOH and salts [35].

Aiming to avoid the solubilization of chitosan beads in acid conditions, the beads were subjected to crosslinking reaction. This reaction was carried out by adding 4.9 mL of epichlorohydrin per 10 g of chitosan beads in 50 °C (for 1 h). Subsequently, 70 mL of aqueous NaOH (0.1 $mol\ L^{-1}$) were added under heating (90 °C) for 2 h. Chitosan was washed exhaustively with deionized water for pH stabilization and removal of the excess of the crosslinking agent [36].

The percentage of chitosan on beads was measured by mass quotient. Ten beads were weighed in triplicate, and the samples were then placed in an oven at 60 °C for 24h for water evaporation. The samples