



Interactions between humin and potentially toxic metals: Prospects for its utilization as an environmental repair agent



Jonas Soares Jacundino^a, Oseas Silva Santos^b, Josué Carinhanha Caldas Santos^b,
Wander Gustavo Botero^b, Danielle Goveia^c, Janaina Braga do Carmo^d,
Luciana Camargo de Oliveira^{d,*}

^a Federal University of São Carlos, Sorocaba Campus, São Paulo 18052-780, Brazil

^b Federal University of Alagoas, Post-Graduate Program in Chemistry and Biotechnology, Alagoas 57309-005, Brazil

^c University State of São Paulo, Itapeva Campus, São Paulo 18409-010, Brazil

^d Federal University of São Carlos, Sorocaba Campus, Post-Graduate Program in Biotechnology and Environmental Monitoring, São Paulo 18052-780, Brazil

ARTICLE INFO

Article history:

Received 14 January 2015

Accepted 26 March 2015

Available online 3 April 2015

Keywords:

Humin

Peat

Metals

Application in situ

ABSTRACT

The disposal of potentially toxic metals in aquatic systems is an issue that mainly involves densely populated regions that dump these contaminants into the environment, either directly or indirectly. Substances that are able to interact with these metals and affect their disposal, transportation and bioavailability are of significant environmental interest. Humin, which represents a fraction of humic substances, exhibits important characteristics, being capable of affecting the bioavailability of potentially toxic metals in the environment. This study assessed the interaction between humin and potentially toxic metals with a view to humin's use as chelating resin in repairing contaminated matrices. To this end, humin samples were extracted from soils that were collected in different parts of Brazil (Southeast and Northeast). The structural characteristics of the humin samples extracted presented significant differences, including differences in their organic material content. The results of adsorption studies showed similar kinetic adsorption behavior (pseudo second order) for the different humin samples, exhibiting high adsorption for all the potentially toxic metals studied (Cu^{2+} , Cr^{3+} , Pb^{2+} , Cd^{2+} and Ni^{2+}). In situ application demonstrated that humin could be used as a chelating resin for matrices that had been contaminated by potentially toxic metals.

© 2015 Elsevier Ltd. All rights reserved.

Introduction

Economic development associated with the improvement of quality of life has resulted in a considerable increase in the amount of pollutants being released into the environment, compromising aquatic and land systems [1].

Among the various pollutants that are released, some of the most significant are metals, which belong to a particular class of compounds that have wide applicability and toxicity and which cannot be degraded either chemically or biologically [1]. Among metals, the term potentially toxic metal (PTM) has been used to refer to a group of metals and metalloids that are associated both with their essentiality as well with pollution and toxicity. The presence of high concentrations of PTM in the aquatic environment

can lead to the death of fish and photosynthetic organisms, thus altering the aquatic ecosystem [2–6]. The introduction of PTMs into the human organism via the food chain can result in numerous diseases, because they have a cumulative effect, and can even cause death [7,8].

Substances that are able to interact with these metals and influence their disposal, transportation and bioavailability are of significant environmental interest. Among the naturally occurring substances that have this characteristic and that are globally distributed in aquatic and land ecosystems, humic substances (HS) stand out [9–13].

HS can be fractionated based on their solubility into fulvic acids, the fraction of HS soluble at different pH levels; humic acids, which are insoluble at acidic pH and soluble at basic pH; and humin, which exhibits low solubility at different pH levels [13].

Humin is highly resistant to microbial degradation and is regarded as the last item produced in the humification process. This fraction of HS presents various functional groups: a series of

* Corresponding author. Tel.: +55 15 3229 5967; fax: +55 15 3229 5967.

E-mail address: lcamargo@ufscar.br (L. Camargo de Oliveira).

esters, methoxy alkanes and polar aromatic groups. In addition, humin is extremely porous, with a large surface area, making it a potential adsorbent [14].

Humin has aroused interest among the scientific community, and a number of studies have been carried out to evaluate the interaction between this fraction of the organic material and organic contaminants (herbicides, insecticides, fungicides, HPAs and PCBs) and metallic species [15–17].

The interaction of HS and humin with contaminants influences bioavailability and the toxicological effects of different substances in aquatic/land systems [12,15–18]. The complexes formed have different stabilities, which are highly dependent of the pH, ionic strength, HS concentration and redox conditions [19].

Unlike simple complexants and binding agents (Cl⁻, CO₃²⁻, amino acids), humic substances and their fractions contain various complexant sites per molecule, resulting in high thermodynamic stability of the complexes formed, considerably altering the chemical form (speciation) of the metal in solution [20]. The ability to form complexes with metals is mainly due to the high content of functional groups containing oxygen, which include carboxylics, phenols, enolics and alcoholics [9].

Thus, the aim of this study was to investigate, in the laboratory, the process of humin adsorption by PTMs and to correlate the observations with the structural characteristics of humin to optimize the adsorption conditions. The applicability of humin as a chelating resin for retaining PTMs in a contaminated system was then evaluated *in situ*.

Material and methods

Soil samples preparation and collection

Soil samples were collected in the Taquaral district, located in the municipality of Ribeirão Preto, Sao Paulo State (Brazil's Southeast Region), and in the municipality of Floriano Peixoto, Alagoas State (Brazil's Northeast Region), close to the Pratagi River as shown in the sample schematic in Fig. 1. The compound samples were transferred to wooden trays and, after being air-dried until they reached a constant mass, were placed in plastic sieves with 2 mm openings.

Humin extraction

The humic substances were extracted by alkaline extraction using NaOH, the methodology most widely used by researchers in this area, according to the International Humic Substances Society (IHSS). Specifically, HS were extracted using 0.1 mol L⁻¹ NaOH for 4 h, with a soil/extractant ratio of 1:10, under a nitrogen atmosphere. The low-solubility extract is called humin and was separated by centrifugation [18] and thoroughly washed with deionized water.

Humin characterization

Determination of the organic material content

The determination of the organic material (OM) content present in the humin samples was done in triplicate by gravimetry, burning 10.0 g of sample for 4 h at a temperature of 650 °C [21].

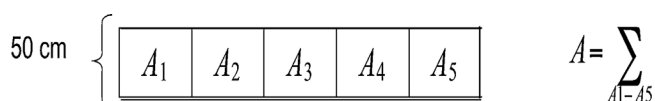


Fig. 1. Schematic illustration of the procedure used in the collection of the soil samples.

Spectroscopy in the infrared region

The FTIR spectra of the humin samples were obtained using KBr pellets (sample – KBr ratio of 1:100) (Varian 640 IR spectrometer) [22].

UV–vis spectroscopy: determination of the E₄/E₆ ratio

The E₄/E₆ ratio was ascertained by measuring approximately 2.0 mg of humin in 10 mL of a NaHCO₃ 0.05 mol L⁻¹ solution and later reading the absorbance at 465 and 665 nm on a DR 3900 spectrometer [13,22].

Nuclear magnetic resonance of carbon ¹³C(NMR ¹³C)

The samples were characterized by NMR ¹³C with crossed polarization (CP) and magic angle spinning (MAS) in a Bruker spectrometer, Avance III 400 MHz, with a rotation of 5 kHz, contact time of 2 ms, relaxation waiting time of 5 s and 11,000 scans [21].

Studies of the adsorption between PTM and humin: pH effect

The adsorption process depends on the relationship between the masses of metallic species and of the material that can adsorb or complex with the metallic species, as well as on the volume of the solution [23]. Initially solutions of copper (Cu²⁺), chromium (Cr³⁺), lead (Pb²⁺), cadmium (Cd²⁺) and nickel (Ni²⁺) were prepared in a concentration of 16.0 mg L⁻¹. For these studies, three different pH levels (4, 6 and 8) and different contact times between the humin and the solution of the metallic species (10, 30, 60, 120, 240, 1440 and 2880 min) were applied. Therefore, 50 mL aliquots of the solutions of prepared metals at different pH levels were added to falcon-type tubes containing 100.00 mg of humin samples. The tubes were kept in a mechanical shaker at a temperature of 25 ± 3 °C. After reaching the contact times, the solutions were filtered using a system equipped with membrane filters with a pore size of 0.45 μm, and the potentially toxic metals were determined by inductively coupled argon plasma atomic emission spectroscopy (ICP-OES) [24]. The Cu²⁺, Cr³⁺, Pb²⁺, Cd²⁺ and Ni²⁺ concentrations adsorbed in the humin were then calculated based on the difference between the initial and final concentrations of the solution, using Eq. (1).

$$Q_{\text{eq}} = \frac{(C_0 - C)V}{m} \quad (1)$$

In this case, Q_{eq} is the adsorption capacity of the metallic species in mg g⁻¹ of humin, C₀ is the initial concentration of the metallic ions in mg L⁻¹, C is the final concentration of the metallic ions in mg L⁻¹, V is the volume of the solution in L, and m is the mass of the adsorbent humin in mg.

Application of humin in metal retention *in situ*

In situ experiments were carried out at the Mundau–Manguaba lagoon complex in the State of Alagoas, Brazil, in an area reported to have high concentrations of potentially toxic metals due to man-made activities [25]. The *in situ* studies were carried out using the procedure described by Rosa et al. [26]. The masses used for the *in situ* application were 200, 300 and 500 mg of humin, and the contact time varied from 30 to 480 min. The experiments were carried out in triplicate at the same point in the lagoon complex, with a point distant from the effects of man-made activities used for reference. Metal elution was carried out using HNO₃ 1 mol L⁻¹ [26].

Results and discussion

Humin is the fraction of organic material that is closely linked to inorganic colloids in soil and is therefore the most stable form of

Download English Version:

<https://daneshyari.com/en/article/222293>

Download Persian Version:

<https://daneshyari.com/article/222293>

[Daneshyari.com](https://daneshyari.com)