



Improving lead sorption through chemical modification of de-oiled allspice husk by xanthate

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HIGHLIGHTS

- ▶ Mexican natural adsorbents have high adsorptive capacities for heavy metals.
- ▶ The removal kinetics was governed by the pseudo-second-order model.
- ▶ De-oiled allspice husk was used for removal of lead metal complexes after chemical modification.
- ▶ The resulting continuous adsorption process was a low-cost, efficient and eco-friendly.

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ABSTRACT

The de-oiled allspice husk in México has been converted into a cheap adsorbent that we aim to investigate for its ability to remove Pb^{2+} from aqueous solution after chemically modifying this material through a xanthate reaction. Batch tests were conducted to find out optimum pH and equilibrium isotherm. The adsorption process can attain equilibrium within 120 min and kinetics was found to be best-fit pseudo second-order equation at 25 °C, the best lead removal was 98% at pH 4, at 250 rpm. The maximum adsorption capacity of de-oiled allspice husk xanthate was found for a continuous process, removed 99.8%, the experimental results were appropriately fitted by the Thomas model, with 2.5 g of de-oiled allspice husk xanthate. The material was characterised using Fourier Transform Infrared Spectroscopy (FTIR), surface area measurement (BET) and Scanning Electron Microscope–Energy Dispersive Spectroscopy (SEM–EDS).

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1. Introduction

Lead is a hazardous metal that is risky for living systems; therefore, many environmental agencies throughout the world have set limits on the lead concentrations in potable water supplies and industrial effluent discharge [1,2]. Conventional methods for water treatment of hazardous metals include chemical precipitation, oxidation and ion exchange [3]. All these methods are inefficient and costly when the concentration of metals is low and when the sludge generation is high and their disposal is an environmental issue.

Recently, biosorption has been investigated as a promising technology for removal of hazardous metals. It has the potential to remove hazardous metal efficiently, faster and at lower cost

compared with other methods. Also, it has been demonstrated to possess the potential to replace conventional metal ion removal methods [4,5]. Many materials in nature and waste materials have contributed to the development of new adsorbents, bacteria, fungi, algae, industrial and agricultural wastes are examples of biomass-derived metal sorbents [6–12]. Previous studies indicate that natural sorbents containing cellulose, hemicellulose, pectin substances, chlorophyll pigments, and other low molecular weight compounds are efficient for hazardous metal uptake [13,14], the use of waste materials from agriculture and non-conventional adsorbents is being considered as a viable alternative for hazardous metal removal from wastewater. Studies in recent years provide information that shows an increase in adsorption capacity of biomass when it is chemically modified, explaining this phenomenon in terms of ion exchange and complexation mechanisms. These data show the feasibility of using biosorption systems at industrial liquid effluents consisting of diluted metal solutions.

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Among the absorbents used for the removal of hazardous metals, those containing sulphur-bearing groups have shown high affinity for heavy metals. Some sulphur-bearing compounds include sulphides, thiols, dithiocarbamates, dithiophosphates and xanthates [15]. According to the HSAB (hard and soft acids and bases) classification system, sulphur is considered a ligand group with a strong affinity for a number of metals, such as cadmium, copper, lead, and mercury, which are classified as soft acids [16]. Xanthates are formed by reacting an organic hydroxyl-containing substrate with carbon disulfide (Reaction scheme) under caustic conditions. Xanthates are easily prepared with relatively low-cost reagents and they are highly insoluble, the metal complexes formed with xanthates have a high stability constant [16]. Xanthation has been used previously on cellulose and sawdust [5], brown marine algae, and chitin [17]; in all cases, it increased the adsorption capacity. Allspice (*Pimenta dioica* L. Merrill) belongs to the Myrtaceae family. Mexico exports around 4500 tons per year and half the production is processed in the country. During the oil extraction processes either through steam distillation, hydro-distillation or supercritical extraction the berry oil yield ranges from 3.0% to 4.5% [18]. The residue of the oil extraction processes is at least 95.5% in weight, reaching annually 1500 tons in Mexico. Exhausted allspice is a fibrous material that contains 23.1% cellulose, 8.5% hemi-cellulose and 26.8% lignin. This paper deals with the preparation of a novel de-oiled allspice husk adsorbent by a xanthation process, along with the detailed investigation of the effect of various parameters including equilibrium pH, and contact time; a probable mechanism will be advanced on the adsorption of Pb^{2+} . The removals obtained with modified de-oiled allspice husk were also compared with the results obtained with non-modified allspice husk, under the same conditions.

2. Materials and methods

2.1. Materials

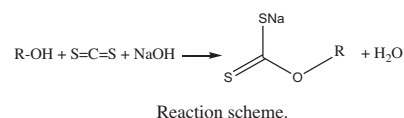
The crushed de-oiled residue of allspice was obtained as a product from the hydro-distillation process. This waste was first washed with an ethanol–water solution (40–60% v/v), in order to eliminate colored and remaining substances, later on, it was dried at 70 °C for 24 h. Once the adsorbent was cooled, it was sieved through a No. 8 mesh, obtaining particles sized 2.36 mm (Grinder Arthur H. Thomas CO., Scientific Apparatus, Philadelphia, PA, USA Series 113c925A83), and stored in desiccators. This particle size was chosen because smaller particle sizes generated flooding in the column when operating in a continuous regime. The product obtained was a residue dried pepper labelled MPS for further adsorption studies. An atomic absorption spectrophotometer (Perkin–Elmer 2380) was used for total Pb(II) analysis for the batch and continuous process. The material was characterised by Fourier Transform Infrared (FT-IR), thus the spectrometer (FTIR Nicolet AVATAR 360) spectra of non-adsorbed (MPS), modified-adsorbed (MPX) and adsorbed de-oiled residue of allspice (MPXPb) were obtained. All calibrations and procedures were carried out in accordance with American Water Works Association (AWWA) standards.

2.2. Bromatological analysis

The de-oiled allspice husk was analyzed for cellulose, hemicellulose, lignin, fibre content and moisture in accordance with food standard methods analysis [19].

2.3. Xanthation of de-oiled allspice husk

The xanthation process was carried out as follows: about 50 g of MPS dried product was placed in a 200 ml Erlenmeyer flask and mixed with 200 ml of a NaOH 4 N solution during 3 h with continuous stirring at room temperature; stirring continued for another 3 h after the addition of 10 mL of carbon disulfide (CS_2). Excess alkali was removed by washing with double distilled water and dried at 70 °C in a stove. Reaction scheme shows the xanthation reaction. This product is abbreviated as MPX or modified material by reaction of xanthation.



2.4. Chemicals and metal solutions

Solutions of Pb(II) were prepared using lead nitrate (Merck, 99.5%) in deionized water. Diluting was done daily adding deionized water as per requirements. All pH adjustments were carried out with 1 M HNO_3 and 1 M NaOH analytical grade.

2.5. Adsorption experiments

Batch experiments were carried out with synthetic solutions in polypropylene tubes at 250 rpm of orbital stirring into MPS and MPX, at room temperature. To prevent metal contamination during the experiments, the following cleaning procedure was used. Test tubes were soaked with 10% (w/v) HCl overnight. Then, they were washed and rinsed with deionized water. The residual solution was filtered with Whatman No. 42 filter paper. The sorbent product obtained was labelled as MPXPb or modified material by reaction of xanthation on contact by metal. Unless otherwise stated the parameters with synthetic water were: sample volume 10 ml, sorbent dose 10 mg L^{-1} , initial metal ion concentration 25 mg L^{-1} , pH 4, equilibration time 3 h. For pH studies this was varied from 2 to 6 keeping the other conditions the same. Experiments were not conducted at higher pH due to precipitation of lead hydroxide [20,21]. Using this information, the chemical species distribution diagrams was calculated using the MEDUSA program [22]. For kinetic studies the sample volume was maintained at 10 mL and at every 50 min sample was withdrawn for analysis. For equilibrium studies the adsorbent dose was maintained at 10 mg L^{-1} and 25 mL varying the initial Pb^{2+} concentrations from 5 to 700 mg L^{-1} .

2.6. Continuous sorption process

Continuous fixed bed column studies were performed in order to examine the Pb(II) uptake by MPX, using 0.025 L min^{-1} volumetric flow rate at 25 °C. Solutions lead(II) concentration was 60 mg L^{-1} at pH 4. The column consisted of a glass tube with an inside diameter of 0.0178 m, a bed depth of 0.05 m with 2.5 g of MPX (mesh 8). The column was preconditioned to pH 4 by eluting deionized water. Solution at a known concentration and flow rate was passed continuously through the stationary sorbent bed. Samples were taken from the effluent at timed intervals, in the beginning each 5 min and then the samples were taken at longer periods. The effluent samples were analyzed using atomic absorption spectrometry. The exhausted sorbent was labelled as MPXPb.

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