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Effective mercury(II) bioremoval from aqueous solution, and its electrochemical determination

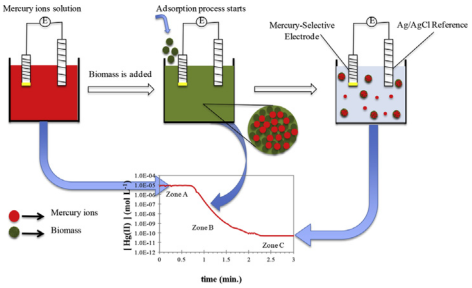
Patricia Balderas-Hernández [a], Gabriela Roa-Morales [a], María Teresa Ramírez-Silva [b], Mario Romero-Romo [c], Erika Rodríguez-Sevilla [d], Juan Marcos Esparza-Schulz [b], Jorge Juárez-Gómez [a, *]

[a] *Centro Conjunto de Investigación en Química Sustentable CCIQS, UAEM-UNAM, Universidad Autónoma del Estado de México, Carretera Toluca-Atlacomulco, km 14.5, C.P. 50200, Toluca, México*
[b] *Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Vicentina, Del. Iztapalapa, C.P. 09340, Ciudad de México, México*
[c] *Departamento de Materiales, Universidad Autónoma Metropolitana-Azcapotzalco, Av. San Pablo 180, Col. Reynosa-Tamaulipas, Del. Azcapotzalco, C.P. 02200, Ciudad de México, México*
[d] *Instituto de Física, Universidad Nacional Autónoma de México, Ciudad Universitaria, C.P. 04510, Ciudad de México, México*

HIGHLIGHTS

- A new methodology for mercury(II) bioelimination is proposed.
- Agricultural residues are used as adsorbent, and the biomass shows high density of strong mercury chelating.
- Biomass can also efficiently remove 99.4% mercury (II) within a few minutes.
- Mercury determination was carried out through potentiometry using an ISE built and optimized.
- Presents a new perspective for removing mercury(II) from contaminated water for environmental remediation.

GRAPHICAL ABSTRACT



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ABSTRACT

This work proposed mercury elimination using agricultural waste (*Allium Cepa L.*). The biomass removed 99.4% of mercury, following a pseudo-second order kinetics ($r^2 = 0.9999$). The Langmuir model was adequately fitted to the adsorption isotherm, thereby obtaining the maximum mercury adsorption capacity of 111.1 ± 0.3 mg g^{-1}. The biomass showed high density of strong mercury chelating groups, thus making it economically attractive. Also, the implementation of a mercury-selective electrode for continuous determination in real time is proposed; this electrode replaces techniques like atomic absorption spectroscopy, thus it can be applied to real time studies. This work therefore presents a new perspective for removing mercury(II) from contaminated water for environmental remediation.

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* Corresponding author.
E-mail address: el_inge85@hotmail.com (J. Juárez-Gómez).

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Isotherm
Breakthrough
ISE

1. Introduction

The toxicity of many metals has become a matter of deep, every day concern, due to environmental and human health deleterious effects. Unquestionably, mercury is known for its high toxicity, which for that matter has been closely regulated not only for residual but also potable waters (permissible limit 0.006 mg L^{-1}) (OMS, 2005). The World Health Organization has recommended, as integral part of a global strategy to improve the quality of the water distributed to the population, to develop affordable simple methods to analyze and dispose of this and other omnipresent contaminants from the environment. Further, all new methods proposed must be based on simple analytical techniques that could be easily implemented, and at the same time fully portable for *in situ* analyses outside the specialized laboratories, capable of working reliably in real time (OMS, 2005).

Recently, diverse sorbent materials have been used to eliminate various polluting metals, although among them those obtained from organic residues have attracted significant attention (biomass). The bioadsorption methods exhibit advantages over other methods used for toxic metals elimination, like chemical precipitation, oxidation or ion exchange: the former is a low cost, easily implementable method, where the biomass can be regenerated and the pH and temperature conditions are normally manipulated for the required optimizations (Vijayaraghavan and Yeoung-Sang, 2008). One inconvenient is the selectivity of the method, although improvements could be attained by chemically improving the biomass (Vijayaraghavan and Yeoung-Sang, 2008; Wang and Chen, 2009; Torres-Blancas et al., 2013). Several highly toxic metals have been effectively eliminated through using adsorbent biomaterials. It is apparent that for mercury removal, a wide variety of inorganic and organic materials have been proposed. Among the latter, some have been synthesized, for example López-Munoz et al. (2016), reported the synthesis and adsorption of mercury on titanate nanotubes with a maximum adsorption capacity of 140 mg g^{-1}, Alijani et al. (2015), reported a maximum mercury adsorption capacity of 200 mg g^{-1} when using carbon nanotubes and Duan et al. (2016), reported 90% of Hg(II) removed during the first 5 contact minutes with pyrite particles. As for the organic materials, the sea lettuce or green algae (*Ulva lactuca*) has been specifically used for mercury, with 149.25 mg mercury adsorbed per gram of algae (Zeroual et al., 2003), fern (*Filicopsida*) contained 49 mg mercury adsorbed per gram (Carro et al., 2010), the fungi (*Phanerochaete chrysosporium*) with a maximum adsorption of 61 mg g^{-1} (Saglam et al., 1999), *Microcistis aeroginosa* that has also been used in column to eliminate mercury at 90% efficiency (Jian-Zhong et al., 2005) and also reported the use of functionalized thymine with a maximum adsorption of 51.27 mg g^{-1} following a pseudo-second order model (Luo et al., 2016).

Allium Cepa L. is here proposed as matrix to adsorb Hg(II) ions, as it contains cysteine-derived molecules, an aminoacid comprising sulphur-donor groups (Imai et al., 2002; Eady et al., 2008) involving significant affinity toward mercury atoms. Also, it is proposed to implement a mercury ion selective electrode, ISE, for continuous real time monitoring of the metal concentration variation. The kinetic study was conducted in batch and its application to continuous flow presented.

2. Materials and methods

All reactants were analytical grade. EDTA, NaOH, $Na_2C_2O_2$, dithizone, chloroform, $KMnO_4$, H_2SO_4 and HNO_3 were from Merck. The supporting electrolyte was $HClO_4$ (J.T. Baker) together with $Hg(NO_3)_2 \cdot H_2O$ (Merck) that were used to prepare the metal-bearing and all other solutions, in 18 MΩ resistivity deionized water obtained from a Milli-Q Millipore equipment. 2,2′−Bisphenol, Toluene, 2−Propanol anhydrous, Phosphorous pentasulphide and 1-Bromopenthane all were from Sigma Aldrich. NMR spectra were obtained from a Bruker DMX500 instrument, UV−Vis spectra were obtained from a Perkin Elmer UV/Vis Spectrometer Lambda 20, IR spectra were obtained from an IR Affinity-1 Shimadzu, SEM images were obtained from a JSM-7800F Schottky Field Emission Scanning Electron Microscope.

2.1. Biomass preparation

The *Allium Cepa L.* crushed residue was obtained as a by-product of the hydro-distillation process. This biomass was first washed with an ethanol−water solution (40−60% v/v), in order to eliminate colored and remaining substances: subsequently, it was dried at 70 °C for 24 h, and sieved to retain the 0.841 mm sized particles. The biosorbent was subsequently washed with deionized water through a continuous flow column at 1.8 mL min^{-1} for 24 h to eliminate residues, and then the biosorbent was desiccated at 60 °C and finally stored for 24 h at ambient temperature until used.

2.2. Construction of ion-selective electrodes and electrochemical system

250 mg of Araldite M resin were mixed with 100 mg of hardener HY 5162 (Ciba-Geigy) in a small glass container, together with 350 mg of graphite and 20 mg of O,O′-(2,2′-biphenylen)dithiophosphate pentyl (PenDTF) ligand; the ionophore was synthesized and characterized in agreement with Pérez-García et al. (2010). After mixing thoroughly all constituents until a homogeneous paste, a small portion was pressed into a 7 mm OD PVC tube, containing a copper contact bar wholly immersed in the compacted paste, to provide effective electrical connection. Subsequently, the device hereinafter termed Hg(II)-ISE-PenDTF, was left to rest for 24 h at 40 °C. After, the resulting electrode was immersed-conditioned in 1.0×10^{-3} mol L^{-1} $Hg(NO_3)_2$ for 5 min prior running each test. The construction, evaluation and optimization of the Hg(II)-ISE-PenDTF sensor was done in agreement with Juárez-Gómez et al. (2013).

The Hg(II) analyses were undertaken by means of chronopotentiometry at the null current potential using a potentiostat/galvanostat μAutoLab Type III. A two-electrode set-up was used where the working electrode was that obtained after mixing in the ligand PenDTF while a saturated Ag/AgCl worked as reference. All experiments were carried out with the aid of a conventional glass electrochemical cell.

2.3. Mercury determination through UV−Vis spectroscopy

The UV−vis spectroscopy determination of mercury was done through a modified mercury complexation method with dithizone.