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Evaluation of mercury (Hg^{2+}) adsorption capacity using exhausted coffee waste

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ABSTRACT

The adsorption capacity of mercury ion (Hg^{2+}) using exhausted coffee waste (ECW) was evaluated as a sustainable alternative for the treatment of water contaminated with this metallic ion. The Langmuir isotherm provided the best correlation for the adsorption of Hg^{2+} by the biomaterial, (31.75 mg g^{-1}). The kinetic studies showed that the adsorption of Hg^{2+} is fast, it can be adjusted to the pseudo second order model. It was determined that the ECW is an effective adsorbent for the elimination of Hg^{2+} and that it can be used as a valuable alternative in the treatment of water contaminated by this metal ion.

1. Introduction

The conventional methods for the removal of heavy metal ions from wastewater such as ion-exchange, reverse osmosis, electrodialysis, precipitation, coagulation-flocculation, nanofiltration and several electrochemical methods are the most frequently used (Dávila Guzmán, 2012; Plaza Cazón, 2012; Srivastava and Goyal, 2010); however, these methods have a disadvantage associated to their high cost of installation and maintenance, which makes it very difficult to implement in small and medium-sized enterprises or in economically disadvantaged communities in developing countries (Kamel, 2013; Kyzas et al., 2013; Tovar et al., 2012). Nowadays, the process of adsorption using biological materials (biosorption) has demonstrated to be a sustainable alternative for the treatment of different effluents of industrial origin (Kamel, 2013; Plaza Cazón, 2012; Tovar et al., 2012; Vizcaíno Mendoza and Fuentes Molina, 2015), because it is a clean, efficient and low-cost process. The use of natural biopolymers to remove metallic species present in aqueous solution involves physicochemical and biological phenomena where metal ions can be removed by traditional adsorption or by chelation due to the presence of organic groups on the surfaces (Federation and Association, 2005; Khan et al., 2005; Ramos Yánac, 2004; Roh et al., 2012). A large number of natural materials have a high affinity for heavy metals and other organic pollutants; therefore, there are many types of biomass potentially available for biosorption studies (Rubio et al., 2015).

Heavy metals pollution constitutes a very serious risk for the environment because these are substances with great chemical stability, high persistence, incorporation in the ecosystem which is associated with health problems and high rates of bioaccumulation in living beings (Riofrio Jumbo, 2016; Vergara Estupiñán and Rodríguez Africano, 2015). The presence of mercury in water resources has had a negative impact on the aquatic ecosystem and public health in general (Tejada-Tovar et al., 2015). When mercury ions: (Hg^{2+}, Hg_2^{+}) and methyl mercury are incorporated into the human body, they can alter the functions of the central nervous system (CNS) in people exposed to low levels of these pollutants producing neurophysiological sequelae (MADS, 2012; Pérez and Betancur, 2016; Tejada-Tovar et al., 2015).

The exhausted coffee waste (ECW) has been considered a domestic and very common type of waste that is getting attention due to its adsorbing properties for the removal of metals and dyes in aqueous matrices (Azouaou et al., 2010; Chou et al., 2012; Kyzas et al., 2013; Kyzas, 2012; Lafi and Hafiane, 2016; Pujol et al., 2013). This material has high availability and low cost, it is obtained after the elaboration of the drink and does not need a complex treatment. It can act as an adsorbent, which makes it ideal for its implementation as a promising system for removing harmful metallic ions from water. Its use for this purpose will provide added-value before its final disposal and will be in compliance with the principles of sustainability (environment, economy and society).

The exhausted coffee waste (ECW) has shown to have selectivity for removing cations of heavy metals such as Cd^{2+}, Cu^{2+}, Cr^{6+}, Pb^{2+}, Ni^{2+} y Zn^{2+} (Oliveira et al., 2008; Utomo and Hunter, 2006) at different pH and temperatures, it has chelation capacity due to the

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presence of carbonyl, carboxyl and sulfhydryl groups, and due to the high content of sodium and calcium it has cationic exchange capacity (Pujol et al., 2013; Seniunait et al., 2014). Additionally, there are studies related to the adsorption of Hg^{2+} using different biomaterials (Dawlet et al. 2013; Dula et al., 2014; Hanafiah et al., 2014; Hassan, 2016; Jafari and Cheraghi, 2014; Khoramzadeh et al., 2013; Kyzas et al., 2013; Kyzas, 2012; Lafi et al., 2014; Mondal et al., 2013; Nguyen et al., 2013; Peña-Rodríguez et al., 2013; David Pujol et al., 2013; Wang et al., 2013). However, the coffee residual capacities for mercury removal have not been used. In this study, the adsorption capacity of mercury ion (Hg^{2+}) using exhausted coffee waste (ECW), as a sustainable alternative for the treatment of water contaminated with this metallic ion, in environmental remediation processes, was evaluated to determinate if this waste is useful to removal this pollutant from environment.

2. Materials and methods

2.1. Determination of mercury concentration using diphenylthiocarbazone as a chelating agent

2.1.1. Reagents and equipment

In preparation of reagents, chemicals of analytical grade purity were used. All weighing was done using an analytical balance RADWAG model AS 220/C/2. UV–VIS spectral measurements were done on an UNICO model 1205 UV–VIS spectrophotometer and pH was determined by using an OAKTON model 2700.

2.1.2. Preparation of solution of bis(diphenylthiocarbazone) of mercury using Triton x-100 as surfactant

The reagents were mixed in a 10 mL graduated flask in the following order: a standard solution of $HgCl_2$, 1 mL of H_2SO_4 (4.39 mol L^{-1}), 1 mL of saturated solution of diphenylthiocarbazone in absolute ethanol (5.19×10^{-4} mol L^{-1}). This mixture was allowed to react for 2 min until the complete formation of the compound bis(diphenylthiocarbazone) of mercury: [Hg (DTZ) $_2$] (Ahmed and Alam, 2003; Association, 2012; Khan et al., 2005). Then, 5 mL of Triton x-100 (0.084 mol L^{-1}) were added, and the solution was completed using type II water. After 212.60 min, the absorbance was read at 501 nm by UV–VIS spectrophotometer. The entire procedure was performed in the absence of light and at a room temperature.

2.2. Adsorbent preparation

2.2.1. Exhausted coffee waste treatment

The ECW (Arabica species) was collected from different coffee shops and homes. The collected material was washed using potable water at boiling temperature to remove excess color and then washed with water type II with a pH between 6 and 7 with an average temperature of 90–100 °C. The material was dried in an oven at 105 °C for 24 h (Kyzas et al., 2013).

2.2.2. Sieving of the material

Once the ECW was dry, it was manually sieved sequentially using number 80, 120 and 270 mesh sieves in order to obtain a particle size of the material lower than 53 μm. The sifted material was dried again at 105 °C for 24 h and kept in a desiccator until further use.

2.3. Surface analysis

Scanning electron microscopy (SEM) observations of the prepared particles were carried out using a JEOL JSM 6490LV scanning microscope equipped with an energy-dispersive X-ray (EDX).

The surface area was also determined with a Micromeritics BET (Brunauer, Emmett and Teller) surface area analyzer, model T-flex, using ultra pure nitrogen.

Table 1
Coding levels to factors used in the compose central design.

Factor	Parameters	Units	Coding level				
			-2	-1	0	1	2
A	pH	–	3.0	4.0	5.0	6.0	7.0
B	Concentration Hg^{2+}	mg L^{-1}	27.5	85.0	142.5	200.0	257.5
C	Adsorption time	M	15.0	90.0	165.0	240.0	315.0
D	Temperature	°C	17.5	25.0	32.5	40.0	47.5

2.4. Fourier transform infrared (FTIR) spectroscopy analysis

FTIR spectrum (Tracer-100 Shimadzu) was used to identify the main chemical functional groups presents in the surface of the material and to analyze if there was a change in the bands of the unloaded and metal-loaded biomaterial in the region of 400–3500 cm^{-1}. The samples were prepared using KBr for FTIR measurement.

2.5. Adsorption experiments

Each adsorption experiment was prepared using polystyrene beakers.

100 mL of Hg^{2+} solution (with the different concentrations indicated in Table 1) were added into a beaker, controlling the pH with hydrochloric acid (0.5; 0.1 and 0.01 mol L^{-1}) and sodium hydroxide (0.50; 0.10 and 0.01 mol L^{-1}); once the operating temperature according to the statistic model was reached (in thermostatic bath), 0.40 g of the sieved ECW were added. The beaker was covered with foil and stirred at 375 rpm in a multi-shaking plate for the operation time fixed in Table 1. Then, the content was filtered with quantitative filter paper (1.23 mm), the pH of the final solution was determined by using a potentiometer and the Hg^{2+} content was determined by UV–VIS spectrophotometry according to the method described at 2.1.2.

2.5.1. Optimal conditions of adsorption

A central design composed of star points was made and 5 levels were defined for each factor. These values were coded and presented in Table 1. Data were analyzed using Statgraphics Centurion XV software (Version 15.2.00 for MS Windows; Statpoint, Inc., VA, USA)

2.6. Adsorption isotherms

The experiments were carried out for different concentrations of Hg^{2+} (50, 60, 70, 80, 90, 100 and 110 mg L^{-1}) using the optimal parameters from the star point design.

2.7. Adsorption kinetics

For the kinetic study, aliquots (700 μL) of the solution were taken at fixed time intervals (0, 10, 20, 30, 40, 70, 100, 130, 160, 190 and 220 min). Adsorption kinetics was studied by first and second order kinetic models.

2.8. Adsorbent regeneration

2.8.1. Preparation of desorption experiments

Two desorption agents were evaluated: HNO_3 (0.5 mol L^{-1}) and HCl (0.5 mol L^{-1}). The desorption experiments were carried out by mixing 0.40 g of ECW with Hg^{2+} (the amount of Hg^{2+} ions loaded in the adsorbent is 76.40 mg g^{-1}) with 100 mL of desorption agent. The suspension was stirred at 375 rpm at a temperature of 33.00 °C. Aliquots (700 μL) of the solution were taken at fixed time intervals (0, 15, 30, 45, 60, 90, 120, 150, 180 and 210 min).