Preparation of lanthanum functionalized adsorbents from a lignocellulosic biomass and their application in arsenic adsorption

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Introduction

Water pollution control is a relevant issue worldwide. In particular, the contents of arsenic (As) dissolved in the water extracted from the subsoil in several regions around the world, including Mexico, may exceed the concentration guidelines established by the World Health Organization (WHO). The natural presence of this geogenic pollutant becomes an environmental and public health problem. This situation implies that around of four million people have the risk to consump water polluted with arsenic concentrations higher than 10 µg/L. Under this perspective, the reduction of As concentrations in polluted effluents and water supply sources for human use and consumption constitutes one of the priority environmental challenges. An effective method for this purpose is the adsorption process. In particular, the preparation of adsorbents from waste materials is an alternative to improve the cost-effectiveness tradeoff of conventional removal methods. Lignocellulosic wastes have been successfully utilized as precursors to obtain adsorbents to remove different water pollutants due to their high carbon content, low cost and availability in nature. Therefore, this study has focused on the preparation of lanthanum-functionalized adsorbents to remove arsenic from aqueous solution using avocado seeds as precursor. Avocado seeds is an important lignocellulosic waste generated in Mexico and other countries by the food industry where this waste biomass is usually discarded. Carbon-based adsorbents were obtained via pyrolysis of this biomass and it was further functionalized with lanthanum using different experimental conditions. These adsorbents were characterized by X-ray diffraction and their arsenic uptakes were determined at batch conditions. Results of this study showed that the preparation of adsorbents for water treatment is a promising alternative to obtain add-value products from this waste biomass.

Methodology

A carbon-based adsorbent was obtained via the pyrolysis of avocado seed biomass at 800 °C for 2 h using a heating rate of 10 °C/min and a nitrogen flow of 100 mL/min. This adsorbent was functionalized with a lanthanum aqueous solution using a ratio of 5, 10 and 20 % w/w, respectively. The mixture adsorbent – lanthanum nitrate solution was stirred at 25 ° C for 1 h using a rotavapor. Then, a NaOH 1.5 M solution was added dropwise until a lanthanum hydroxide precipitate was obtained. After precipitation, the temperature was increased up to 70 °C and the system was stirred for 1 h. The suspension was filtered and the lanthanum functionalized adsorbent was rinsed with deionized water, dried at 105 °C for 24 h and calcined for 2 h at 800 °C using a nitrogen flow of 100 mL/min. Several adsorbents (La-MA) were obtained varying the lanthanum concentration and these materials were washed with deionized water. Raw and lanthanum-functionalized adsorbents were characterized by X-ray Diffraction (XRD) using an Empyrean Diffractometer (Malvern-Panalytical).

The arsenic adsorption capacities (q_{ads}, mg/g) of lanthanum-functionalized adsorbents were determined at 30 °C, pH 7, using batch conditions, 24 h of equilibrium time and agitation speed of 150 rpm. These adsorption experiments were performed with an adsorbent-adsorbate ratio of 2 g/L and an arsenic solution with initial concentration of 100 mg/L. All experiments were carried out in triplicate with a reproducibility of 5%. The adsorbent with the best performance was used to obtain kinetic and equilibrium data of arsenic adsorption. These experiments were done at same experimental conditions already described using initial concentrations from 20 to 200 mg/L.

Results and discussion

For illustration, Figure 1a reports the XRD patterns of all adsorbents, which showed the characteristic diffraction peaks of lanthanum hydroxide. This result confirmed the lanthanum functionalization of the carbon-based adsorbents. Arsenic adsorption capacities of lanthanum based adsorbents ranged from 2.5 to 4.9 mg/g. These adsorption capacities were higher than those obtained for the adsorbent without lanthanum. In fact, an increment of the arsenic removal up to 425 % was observed with the modified adsorbents, see Figure 1b. The presence of the lanthanum on the adsorbent surface favored the arsenic adsorption allowing an ionic exchange and electrostatic attraction forces that can be described by the next equations

$$\equiv\text{-COOH} + La(OH)_3 \leftrightarrows \equiv\text{-COO-}La(OH)_2 + H_2O \qquad [1]$$

$$\equiv\text{-COO-}La(OH)_x + xH_2AsO_4^- \leftrightarrows \equiv\text{-COO-}La(H_2AsO_4)_x + xOH^- \qquad [2]$$

Figure 1c shows the arsenic adsorption kinetic for the adsorbent La-MA 10%. The adsorption rate of arsenic ions initially increased with time where it was fast before 6 h and reached the equilibrium at 18 h. Adsorption kinetic profile corresponded to a single, smooth, and continuous curve leading to the adsorbent saturation. Finally, the adsorption isotherm for the adsorbent La-MA 10% is given in Figure 1d. This isotherm corresponds to the Langmuir type according with the Giles classification (Giles et al., 1960). The arsenic adsorption capacities ranged from 3.5 to 5.8 mg/g at pH 7 and 30 °C.

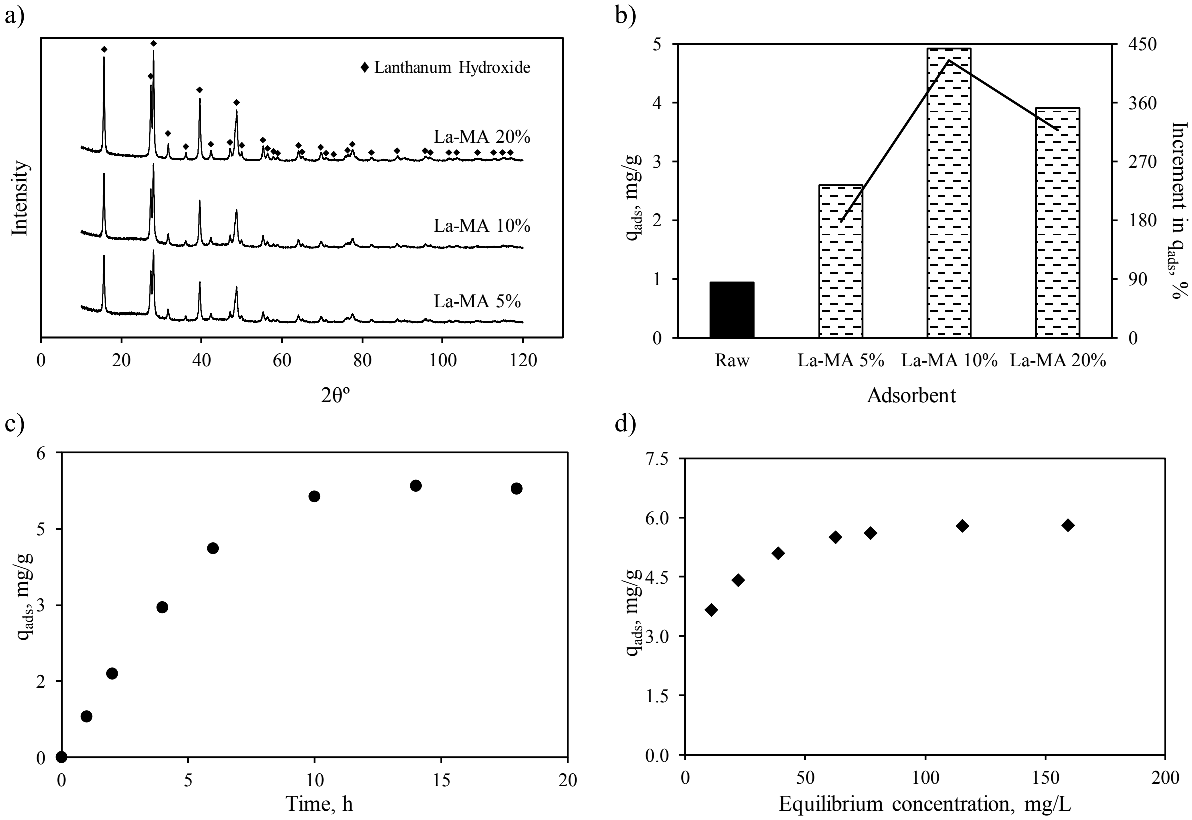

Figure 1. a) XRD patterns of La-MA, b) adsorption capacities and increment in the removal of arsenic using La-MA, c) adsorption kinetic of La-MA 10% and d) adsorption isotherm of La-MA 10%, respectively.

Conclusions

Avocado seed biomass can be used in the preparation of novel adsorbents for water treatment and purification. In particular, the incorporation of lanthanum functionalities is an alternative to tailor the surface chemistry of the carbon-based adsorbents obtained from this biomass to remove priority pollutants such as arsenic from water. This type of adsorbents can show a competitive performance for the removal of geogenic pollutants in water treatment and purification.

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