Arsenic removal from water of the Peruvian rivers using low cost carbon base adsorbents produced from agro industry waste

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ABSTRACT: Microporous-mesoporous activated carbons or biochar were produced from sawdust from Peruvian forestry species and agro-industrial wastes as potential materials for application in water and wastewater treatment. The used sawdust samples were from *Cedrelinga catenaeformis* Ducke and *Colicodendron scabrida* and the agro-industrial wastes were cocoa pod husk, corncob, red mombin seed, internal and external part of the mango pit, and coffee husk. Hybrid materials based on activated carbons with chitosan or ZnO nanoparticles were produced in order to add an antibacterial capacity or photocatalytic properties. The impregnated samples showed adsorption capacity of Arsenic from Tumbes River water with removal capacities between 80–100% at first 5 min of experiments. Besides, the antibacterial properties against *E. coli* and *Shigella flexneri* were evident.

1 INTRODUCTION

Arsenic contamination of water can occur naturally or as a consequence of human activities such as mining. Natural sources of arsenic in Peru are mainly enargite-bearing copper, zinc and lead deposits. In the South of Peru (Arequipa, Tacna and Moquegua) the groundwater has dangerous levels of arsenic. Peru is a mining country and represents around 60% of its exports, primarily gold, copper, and zinc. In South America the most water-stressed country is Peru and every year mining and metallurgy release over 13 billion m³ of effluents into Peru's bodies of water (Bebbington and Williams, 2008).

Connections between mining and water risks are many. Méndez performed a study in the Rímac river basin and showed that mine tailings resulted in elevated arsenic, copper and lead concentrations in the river and its tributaries. C. de Meyer *et al.* (2017) have detected health-threatening concentrations of arsenic, manganese, and aluminum in almost half of the groundwater resources investigated from the Peruvian Western Amazonia.

In Peru, the current national regulatory standards for arsenic in drinking water are based on WHO's recommended limit; however, little is known about the extent of arsenic contamination of the drinking water and about its health implications in the country. George *et al.* (2014) have found that in several districts of Peru, drinking water shows widespread arsenic contamination, exceeding the WHO arsenic guideline. This poses a public health threat requiring further investigation and action especially in the rural areas where there is not water treatment.

Peru is a mainly agricultural country with a high level of production of fruits, cereals, and different

vegetables for internal and external markets. The environmental problems related to the management of the residual agricultural biomass have become alarming to social and governmental entities. The inadequate disposal and open field burning of these materials produce different pollutants, affecting mainly the air and soil quality and the surrounding population.

The search for new renewable precursors for production of activated carbons (AC) with highly microporous-mesoporous structure and adsorption capacities comparable with those of commercial adsorbents remains an important issue for industrial application in water treatment.

2 EXPERIMENTAL

To produce activated carbons, raw materials were collected in the agricultural areas in Piura and Tumbes in Peru. The raw materials were washed with potable water and then dried at 80°C until constant weight was reached. The dried raw materials were ground and sieved to obtain 0.5–1 mm particle-size.

Raw materials were mixed with ZnCl₂ in a proportion 1/1 (raw material/chemical reagent) and then put in a ceramic reactor in a horizontal oven. The activation and carbonization were carried out in a single step in presence of N₂ flow (150 mL min⁻¹), heated up in the oven until 600°C was reached. The carbonization time was 2 h and then the material was cooled by keeping in the inert atmosphere. Finally, the carbonized materials were washed with a 0.15 M hydrochloride acid solution then with distilled water (Cruz *et al.*, 2015).

Prepared activated carbons were codified as follows: RMS-AC, red mombin seed activated carbon; GS-AC, ice-cream bean activated carbon; CPH-AC,

cocoa pod husk activated carbon; CH-AC, coffee husk activated carbon; MSEP-AC, mango seed external part activated carbon; MSIP-AC mango seed internal part activated carbon; and CC-AC, corncob activated carbon (Cruz *et al.*, 2017).

Chitosan was impregnated onto the bare activated carbons using the wet impregnation method. A mixture of 50 mL of chitosan solution and 1 g of activated carbon was stirred and heated at 100°C during 1 h in a closed steel reactor. The pressure was increased until 239.2 kPa and kept during the impregnation. The samples code for activated carbons from corncob and red mombim seed impregnated with chitosan were CC-Ch and RMS-Ch, respectively.

For the production of activated carbons impregnated with ZnO nanoparticles, both precursors were mixed with zinc chloride (ZnCl_2) as the chemical activator and zinc acetate ($\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$) dissolved in distilled water as the ZnO nanoparticles precursor in a proportion 1/1/0.5, respectively. The mixture was dried overnight at 80°C and then put in a ceramic tube to be carbonized into a metallic reactor to be introduced in a horizontal oven and heated to 600°C. This temperature was kept during 2 h under nitrogen atmosphere. The material was cooled and then washed repeatedly. These samples were codified as: CCmod and RMSmod, respectively.

Kinetic experiments were performed with real polluted water to test the As adsorption capacity of the activated carbons with and without impregnation.

A sample of polluted river water was taken from Tumbes River in Peru and preserved with concentrated nitric acid. At the laboratory, the water sample was filtered and the pH of the samples was re-adjusted to pH around 6 before the adsorption experiments. Different aliquots were taken at the beginning and at different times between 5 and 300 min with a 10 mL syringe. Aliquots were filtered to retain activated carbon particles with a 0.2 μm filter, removing the first 1 mL to avoid the effect of the filter in the concentration of heavy metals. Then, 10 mL sample was acidified with nitric acid p.a. to be sure that the pH of the sample was reduced at level less than 3 and then storage at 4°C until the analysis.

3 RESULTS AND DISCUSSION

Since the adsorption of As and Pb was very fast by the samples and the adsorption equilibrium was reached in the earlier stages of the experiments, only the adsorption data of the first 90 min was used in the evaluation. The initial concentration of heavy metals was 1750 $\mu\text{g L}^{-1}$ of Al, 56.7 $\mu\text{g L}^{-1}$ of As, 2920 $\mu\text{g L}^{-1}$ of Fe, 224 $\mu\text{g L}^{-1}$ of Pb and 272 $\mu\text{g L}^{-1}$ of Zn.

The Figure 1 shows that both bare activated carbons exhibit high removal capacity of As from the polluted river water, reaching removal levels close to 100% within the first five min. Almost similar behavior presents the samples impregnated with chitosan and the samples impregnated with ZnO. All

Figure 1. Arsenic removal kinetics of RMS-Ch and CC-Ch.

adsorbents impregnated or not had the ability to eliminate *Escherichia coli* and *Shigella flexneri*.

4 CONCLUSIONS

The produced activated carbons impregnated with chitosan or ZnO are promising materials for application in removal of arsenic from contaminated water.

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