Bulgarian Chemical Communications, Volume 51, Special Issue B (pp. 124– 127) 2019 DOI:10.34049/bcc.51.B.009

Avocado seeds valorization as adsorbents of priority pollutants from water

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Received: July 10, 2019; revised:, 2019

This study has focused on the synthesis of lanthanum-, cerium- and calcium-functionalized adsorbents to remove heavy metal ions from aqueous solutions. Avocado seeds were used as a feedstock to obtain carbon-based adsorbents via pyrolysis and these adsorbents were further functionalized with lanthanum, cerium and calcium species using different experimental conditions to improve its adsorption properties. These adsorbents were utilized for the adsorption of heavy metals from aqueous solutions. At tested experimental conditions, the raw adsorbent showed an adsorption capacity of 7.04, 10.91, 11.41 and 6.38 mg/g for cadmium, nickel, copper and zinc, respectively. These adsorption capacities increased up to 70 % after adsorbent surface functionalization. These results suggested that the adsorption capacity of avocado-based adsorbents appeared to be dependent of the adsorbate properties.

Key words: Adsorption, heavy metals, lignocellulosic waste, water purification, avocado seed.

INTRODUCTION

Agroindustrial wastes generated by agricultural, forestry and industrial activities including by-products of agrifood industry are generated in high amounts every year. Specifically, it has been estimated that around 1550 million of tons are generated annually [1] where 80 % of this biomass is burning (for heating, cooking, charcoal production, and the generation of steam for mechanical and electric power applications), 15 % is used as animal feed, 4.5 % is reincorporated to the ground without previous decomposition and the remaining 0.5 % is used as raw material in industrial processes [2,3]. These wastes are considered as renewable organic materials with high content in cellulose, hemicellulose, lignin and starch [4].

Lignocellulosic wastes have been used in different industrial activities including the fermentation for the biofuel production [3], the biotransformation for edible fungi [5], the development of sustainable construction materials [6] and others environmental applications such as the preparation of adsorbents for the removal of priority pollutants [7]. The last option has resulted as one of the most attractive and viable alternatives for the utilization of these wastes since the lignocellulosic biomasses offer several advantages such as wide diversity, availability in high amounts and renewability [8]. Note that the synthesis of adsorbents from this feedstock is simple due to the high reactivity of lignocellulosic materials. Besides the disposal costs and the environmental impact of waste management can be reduced with this application [9]. These biomasses have been used as adsorbents (in its raw form or chemically modified) or as precursors of carbon-based adsorbents [10,11]. However, the modification of the surface chemistry of these adsorbents can be improved significantly and, consequently, they are more stable from the chemical point of view [7,10,12].

This study focuses on the preparation of lanthanum-, cerium- and calcium-functionalized adsorbents to remove heavy metals from aqueous solutions. These adsorbents have been obtained using avocado seeds as feedstock. The fruit of the avocado is substantially consumed in the food industry (i.e., the annual production of avocado worldwide in 2017 was 6048508 tons). However, its seed that represents the 10-13 % of the fruit can be considered as an agricultural waste, which is discarded without further applications [13]. Several alternative uses have been proposed for this organic waste including its use as an adsorbent and as a precursor for the synthesis of carbon-based adsorbents for the removal of priority pollutants from water [8,13-16]. Herein, it is important to remark that the number of studies related to the heavy metal removal using this biomass is limited. Therefore, this paper aims to contribute with the valorization of such residue as a feedstock for the preparation of an adsorbent for the removal of metallic species. This type of adsorbent could be also an alternative product to be obtained in a biorefinery context.

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EXPERIMENTAL

A carbon-based adsorbent was obtained via the pyrolysis of avocado seeds with a mean particle size of 0.50 - 0.85 mm, at 800 °C for 2 h with a heating rate of 10 °C/min and a nitrogen flow of 100 mL/min. This adsorbent was functionalized with aqueous solutions of lanthanum, cerium and calcium using a ratio of 5, 10 and 20 % w/w, respectively. These solutions were prepared using lanthanum (III) nitrate hexahydrate, ammonium cerium (IV) nitrate and calcium nitrate tetrahydrate salts plus deionized water. The mixture adsorbent – (lanthanum, cerium or calcium) 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, cerium or calcium hydroxide precipitate was obtained. After precipitation, the temperature was increased until 70 °C and the system was stirred for 1 h. The suspension was filtered and the functionalized adsorbent was rinsed with deionized water, dried at 105 °C for 24 h and calcined during 2 h at 800 °C for the case of lanthanum- and cerium-impregnated samples, and at 900 °C for calcium-functionalized adsorbents using a nitrogen flow of 100 mL/min in all cases. Several adsorbents (M-La, M-Ce or M-Ca) were obtained varying the lanthanum, cerium and calcium concentrations and these materials were washed with deionized water.

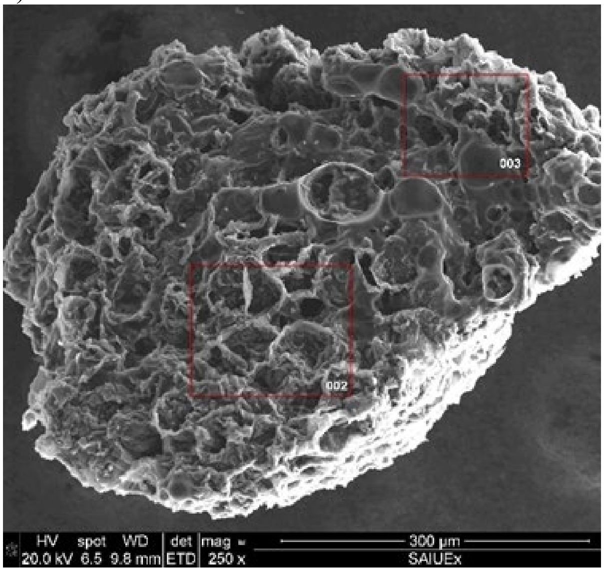
The morphology and elemental composition of raw adsorbent was characterized by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) using a FEI Quanta 3D FEG equipment. The functionalized adsorbents were characterized by X-ray Diffraction (XRD) where XRD patterns were obtained at 40 kV and 45 mA with an Empyrean Diffractometer (Malvern-Panalytical) in the Bragg-Brentano geometry from 10 to 150 °2θ and using Cu-Kα radiation.

The heavy metals adsorption capacities (q_{ads}, mg/g) of lanthanum-, cerium- and calcium-functionalized adsorbents were determined using agitated tanks at 30 °C, pH 5, 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 heavy metal solutions with an initial concentration of 250 mg/L. All experiments were carried out in triplicate obtaining a reproducibility of 5%.

RESULTS AND DISCUSSION

SEM micrographs of the avocado-based adsorbent are reported in Figure 1. It showed a regular, rough and porous structure. EDX results indicated that the relevant elements of the adsorbent were carbon (92.7%) and oxygen (6.3%) and it also contained trace elements such as Mg, Al, Si and P.

a)



b)

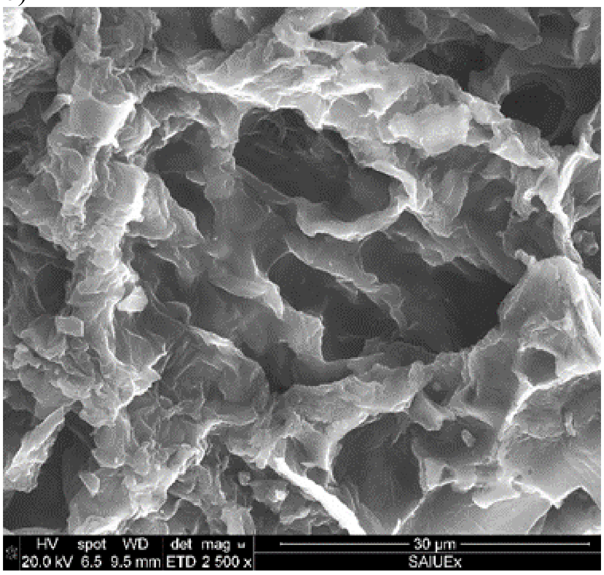


Fig. 1. SEM images of raw avocado seed-based adsorbent at a magnification of a) 250x and b)2500x.

Figure 2 reports the XRD patterns of all adsorbents, which showed the characteristic diffraction peaks of lanthanum hydroxide, cerium oxide and calcium oxide, respectively. This result confirmed the surface functionalization of the carbon-based adsorbents with the different elements. The crystallinity of adsorbent samples increased as the percentage of the functionalized specie increased. Note that the XRD patterns exhibited the characteristic diffraction peaks of graphitic structures at ~23 and 43 °2θ [17].

Adsorption capacities of tested adsorbents were: 2.02 - 7.05 mg/g for cadmium, 1.97 - 10.24 mg/g for zinc, 0 - 15.30 mg/g for copper and 4.14 - 18.75 mg/g for nickel, see Figure 3. In general, the adsorption capacities of nickel and zinc were higher than those obtained for the adsorbent without lanthanum, cerium and calcium, while the removal of cadmium and copper was not improved. An increment of the nickel uptake up to 70 % was obtained for the adsorbent modified with a calcium solution at 10 % (see Figure 3a). However, the adsorbents modified with the lanthanum salt showed the best performance for the nickel removal. Zinc adsorption increased up to 60 % with the surface chemistry modification using both lanthanum and cerium, see Figure 3b. Results showed that the best functionalization conditions corresponded to M-La 10% and M-Ce 20%. These findings indicated that the heavy metal properties played an important role in the adsorption process. Similar trends have been reported in previous studies for the adsorption of heavy metal ions [8,12].

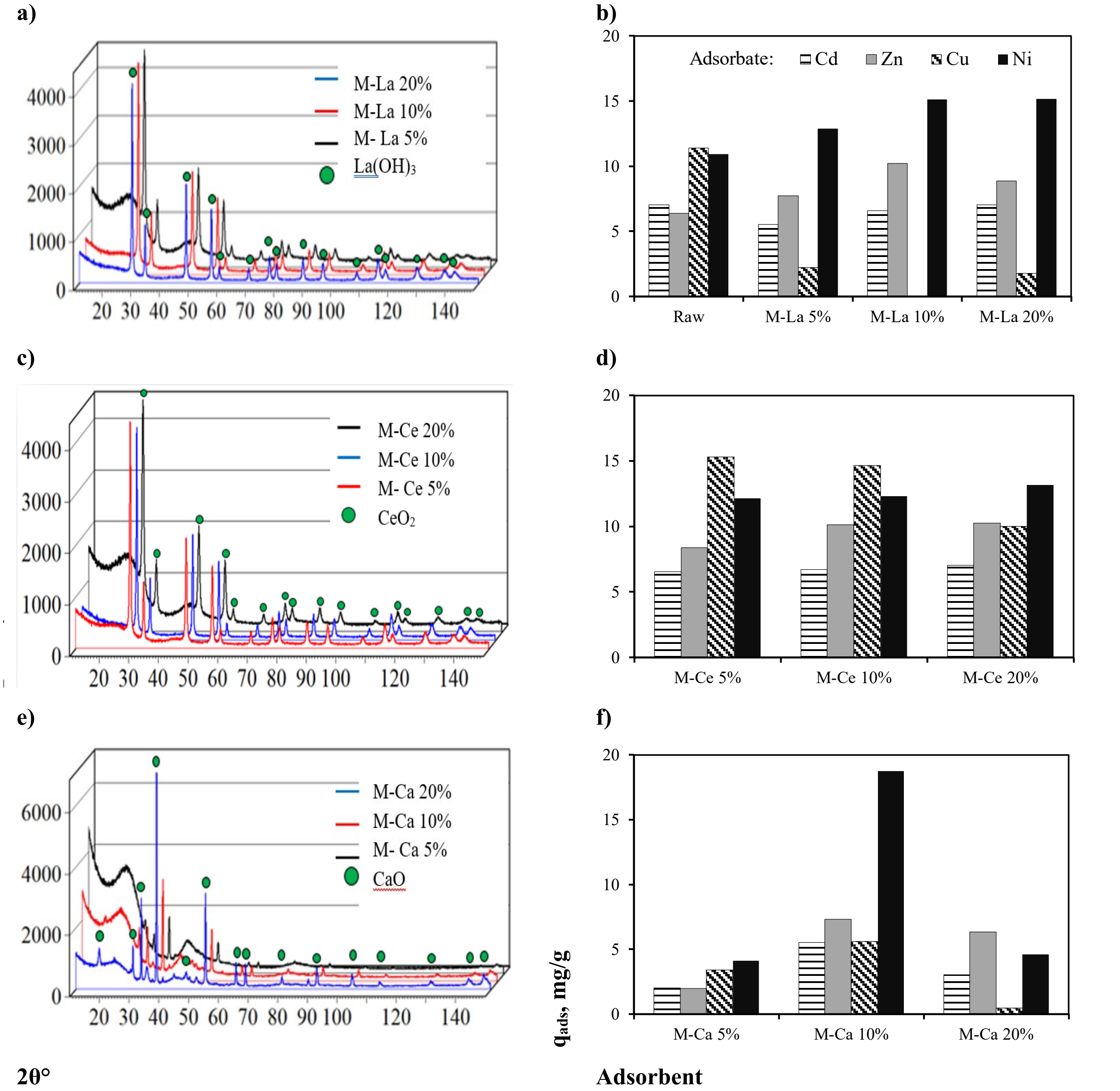


Fig. 2. XRD patterns of a) M-La, c) M-Ce, e) M-Ca and adsorption capacities of cadmium, zinc, copper and nickel using b) M-La, d) M-Ce and f) M-Ca adsorbents.

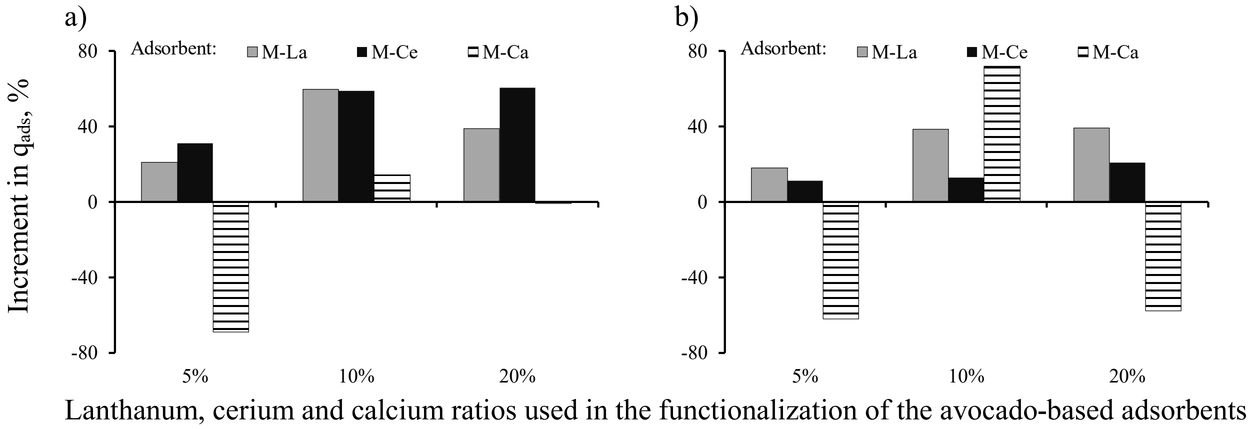


Fig. 3. Improvement in the adsorption of a) zinc and b) nickel using M-La, M-Ce and M-Ca modified adsorbents.

CONCLUSION

The incorporation of lanthanum, cerium and calcium functionalities is an alternative to tailor the surface chemistry of avocado-based adsorbents to remove priority pollutants such as nickel, copper and zinc from aqueous solutions. The preparation of adsorbents or other materials useful for environmental applications contributes to the alternatives to reuse, minimize and valorize wastes generated by the food industry and, in turn, to face the water and wastewater treatment.

Acknowledgements: *The authors acknowledge the funding received from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 778168.*

REFERENCES

1. M. Ramírez-Carmona, O. Muñoz-Blandón, *Rev. Mex. Ing. Quim.,* **5**(1), 23 (2016).
2. F.O. Obi, B.O. Ugwuishiwu, J.N. Nwakaire, *Niger. J. Technol.,* **35**(4), 957 (2016).
3. P.K. Sadh, S. Duhan, J.S. Duhan, *Bioresour. Bioprocess.*, **5**(1), 1 (2018).
4. R. Singh, V. Kapoor, V. Kumar, *Braz. J. Microbiol.*, **43**(4), 1545 (2012).
5. G.M.O Arias-Carbajal, G. Bueno García, D. Betancourt Rodríguez, I. Álvarez, A.L. González, *Rev. CENIC Cienc. Biol.*, **36**, 1 (2005).
6. S. Mucahit, A. Sedat, *Ceram. Int.*, **35**, 2625 (2009).
7. A. Abdolali, W.S. Guo, H.H. Ngo, S.S. Chen, N.C. Nguyen, T.L. Tung, *Bioresour. Technol.*, **160**, 57 (2014).
8. L.L. Díaz-Muñoz, A. Bonilla-Petriciolet, H.E. Reynel-Ávila, D.I. Mendoza-Castillo, *J. Mol. Liq.*, **215**, 555 (2016).
9. F. López, T. Centeno, I. García-Díaz, F. Alguacil, *J. Anal. Appl. Pyrol.*, **104**, 551 (2013).
10. M. Bilal, J.A. Shah, T. Ashfaq, S.M.H. Gardazi, A.A. Tahir, A. Pervez, H. Haroon, Q. Mahmood, **263**, 322 (2013).
11. L.H. Velazquez-Jimenez, E. Vences-Alvarez, J.F. Flores-Arciniega, H. Flores-Zuñiga, J.R. Rangel-Mendez, *Sep. Purif. Technol.*, **150**, 292 (2015).
12. H. Treviño-Cordero, L.G. Juárez-Aguilar, D.I. Mendoza-Castillo, V. Hernández-Montoya, A. Bonilla-Petriciolet, M.A. Montes-Morán. *Ind. Crops Prod.*, **42**, 315 (2013).
13. M.P. Elizalde-González, J. Mattusch, A.A. Peláez-Cid, R. Wennrich, *J. Anal. Appl. Pyrol.,* **78**, 185 (2007).
14. L. Alvares-Rodrigues, M. Caetano-Pinto da Silva, M. Alvarez-Mendes, *Chem. Eng. J.*, **174**, 49 (2011).
15. M. Bhaumik, H. Choi, M. Seopela, R. McCrindle, A. Mayti, *Ind. Eng. Chem. Res*., **88**, 1214 (2014).
16. M. Salomón-Negrete, H.E. Reynel-Ávila, D.I. Mendoza-Castillo, A. Bonilla-Petriciolet, C. Duran-Valle, *J. Mol. Liq*., **254**, 188 (2018).
17. P. González-García, *Renew. Sust. Energ. Rev*., **82**, 1393 (2018).