

Valorisation of Olive Pomace for the Production of Bio-Composite Adsorbents Applied in as Removal from Drinking Waters

Pietro Altimari^a, Fabrizio Di Caprio^a, Ilario Falcone^b, Jacopo Coletta^c, Emanuela Moscardini^c, Maria Luisa Astolfi^a, Antonio Brasiello^d, Francesca Pagnanelli^a

^a Department of Chemistry, Sapienza University, Piazzale A. Moro 5, 00185, Rome, Italy

^b Technosind S.r.l., Viale P. Togliatti 1639, 00155 Roma, Italy

^c Eco Recycling Srl, Via Francesco Siacci, 4, 00197 Rome, Italy

^d Department of Chemical Engineering, Materials, Environment, Sapienza University, via Eudossiana 18, 00184 Rome, Italy
pietro.altimari@uniroma1.it

Arsenic is a toxic metalloid representing a serious threat to human health, reaching a concentration in drinking water above the limit of 10 µg/L in many regions of the world. Although adsorption technologies are available today to remove arsenic from water, the employed adsorbents are expensive, which severely hinders the possibility of water treatment in marginal and rural areas.

In this study, a two-stage process is investigated in which an adsorbent for the removal of arsenic from water is produced by hydrothermal carbonization (HTC) of olive pomace followed by iron precipitation. In the first part of the study, the kinetics of solid mass variation during the HTC process were analyzed to derive indications about the mechanisms driving the thermochemical conversion of olive pomace to hydrochar. It was thus verified that a satisfactory hydrochar yield could be attained after 30 min through the polymerization of hydrolysis products released during the early stages of HTC. Adsorption isotherms were determined for the Fe-hydrochar and the Fe-biochar produced by iron precipitation onto the hydrochar and the pyrolyzed olive pomace (biochar). Fe-hydrochar showed higher adsorption capacity ($q_{\max}=8.7$ mg/g) compared to the Fe-biochar ($q_{\max}=5.3$ mg/g). Fe-hydrochar was finally tested in a fixed-bed adsorption column for As removal, evidencing the ability to maintain the arsenic concentration below the 10 µg/L limit when employed in the configuration conventionally adopted for water treatment. However, in this configuration, the apparent adsorption capacity was reduced, indicating the need for an optimization of the fixed bed-column design.

1. Introduction

Arsenic is a toxic metalloid found in natural systems and, if ingested through drinking water, can severely harm human health, causing vascular diseases, neurological disorders, and skin alteration even at concentrations much lower than 1 ppm (IARC, 2012). In consideration of this risk, the limit currently recommended by the World Health Organization for the arsenic concentration in drinking water is 10 ppb. However, arsenic concentrations above this limit are detected in drinking water over wide geographic areas, including several Italian regions, making the application of arsenic removal technologies necessary.

The treatment technology most commonly adopted is the adsorption onto granulated ferric oxide or hydroxide (GFO or GFH) (Carneiro, 2021). However, GFO and GFH are expensive (5–10 €/kg), which hinders the application of arsenic treatment plants, especially in rural and marginal areas (Driehaus, 2002).

To overcome this limitation, the synthesis of adsorption materials from inexpensive biomasses was investigated. The application of uncarbonized biomass treated with acid or alkali was proposed by some authors. However, this strategy can hardly be implemented owing to the limited stability of the employed biomasses. A thermal treatment is therefore needed to fix carbon and enforce the long-term chemical stability of the produced adsorbent (Jain et al., 2016).

In this framework, biochar produced by pyrolysis has been traditionally employed (Li et al., 2018). To ensure arsenic adsorption, the biochar surface is functionalized with iron oxides or hydroxides by co-precipitation at an alkaline pH (Fe-biochar). However, pyrolysis requires the drying of the biomass before carbonization, then another suspension in water to carry out Fe precipitation, and finally a second drying phase. This, along with the energy consumption by biomass pyrolysis, contributes to increasing the cost and the environmental impact of the process.

An alternative technology is hydrothermal carbonization (HTC), whereby a wet biomass is converted to a solid carbonaceous material (hydrochar) in closed reactors by employing biomasses whose moisture content is > 50% at 150–250 °C under an autogenously generated pressure (Khan et al., 2021).

For the production of arsenic adsorbents, the main advantage of HTC with respect to pyrolysis is the possibility to exclude the preliminary biomass drying and to work in a water suspension in which Fe precipitation can be directly carried out (Mourao et al. 2022). Furthermore, unlike biomass pyrolysis, which is an endothermic process, HTC is moderately exothermic (Pecchi et al., 2022), and the reaction heat can thus reduce the energy demand of the process.

Previous studies evidenced that pH plays a pivotal role in determining the yield and the composition of the hydrochar delivered by the HTC: acidic pH values enhance the carbonization, improving chemical stability, but they do not allow effective Fe precipitation (Capobianco et al., 2020). Therefore, a two-stage process was proposed, including an HTC stage at acidic pH values, followed by the precipitation of iron oxide or hydrogen oxide at alkaline pH in a second reaction stage (Di Caprio et al., 2022) to obtain a Fe-hydrochar adsorbent. However, so far, Fe-hydrochar has been tested only in batch tests for arsenic removal and not compared directly with Fe-biochar.

In this article, the implementation of the two-stage process to produce an arsenic adsorbent from olive pomace, an inexpensive by-product of olive oil production, is analysed. The reported experimental study was performed within the BioAS project, a EU project funded under the LIFE program (www.lifebioas.eu). We compare the Fe-hydrochar and the Fe-biochar obtained from the same biomass, by determining arsenic adsorption isotherms. The performances of the produced Fe-hydrochar are then assessed by analysing the results of arsenic adsorption experiments in packed bed columns.

2. Materials and methods

2.1 Materials

Olive pomace (OP) was collected from a continuous two-phase olive oil mill plant at Roccasecca dei Volsci (LT, Italy) and successively treated in a second plant to remove residual oil and nuts. Before its utilization, nut- and oil-free OP was dried at 60 °C, manually ground in an agate mortar, and finally sieved to remove particles larger than 1 mm. The biochar was obtained by heating OP at 10 °C/min to 600 °C and then maintaining it at 600 °C for a 30-minute reaction under an N₂ atmosphere.

2.2 HTC and iron precipitation

Hydrochar was synthesized by mixing 5.0 g of OP with 20 mL of feedwater solution (FeCl₃·6H₂O, 0.48 M) in a 100 mL polytetrafluoroethylene (PTFE) vessel. HTC was performed using the Milestone Laboratory Microwave System Labstation at the following heating program: 5 min preheating up to 200 °C, 5–60 min reaction time (t) at 200 °C, and 60 min cooling in a water bath at room temperature. After cooling, the vessels were opened and left for 30 minutes under the fume hood. For each different reaction time, HTC was repeated twice inside independent vessels. The obtained hydrochar was recovered by vacuum filtration through 8–12 m filter paper, then washed with 70 mL distilled water through the filter, and finally dried at 105 °C (m_{HC}). Permeates were stored at 20 °C before pH analysis. Hydrochar mass yield (% w/w) was calculated by Eq. (1):

$$Y_{HC} (\%) = \frac{m_{HC}}{m_{OP}} 100 \quad (1)$$

where m_{OP} is the initial olive pomace mass. To obtain Fe-hydrochar, hydrochar was synthesized at 200 °C for 30 min, and after cooling, KOH 6.5 M was added dropwise to attain pH 9 to precipitate iron oxides. The precipitation stage was performed by maintaining the suspension under magnetic stirring at 25 °C for 30 min. After precipitation, the solid phase was recovered through 5 min of centrifugation at 4500 rpm and washed five times with 40 mL distilled water, filtered through 8–12 m filter paper, and dried at 105 °C. Fe precipitation yield (Y_{Fe/Fe}) was calculated by Eq. (2):

$$Y_{Fe/Fe} (\%) = \frac{m_{HC} f_{Fe/HC}}{m_{Fe}} 100 \quad (2)$$

where m_{HC} is the mass of hydrochar recovered after Fe precipitation, $f_{\text{Fe}/\text{HC}}$ is the Fe fraction inside the recovered hydrochar, and m_{Fe} is the whole Fe mass added in the reactor. Fe-biochar was obtained by suspending 5.0 g of biochar in 20 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 0.48 M solution and adding KOH till pH 9, in the same conditions as for Fe-hydrochar.

2.3 Batch adsorption tests

Batch adsorption tests were performed by mixing 20 mg of adsorbent (either Fe-hydrochar or Fe-biochar) inside a 50-mL glass bottle with 20 mL of arsenic solution (1–15 mg/L). The suspension was maintained under magnetic stirring for 20 h, and the pH was maintained throughout the test at 5.0 ± 0.2 by the addition of either 0.05 M NaOH or 0.05 M HCl. Finally, the suspension was centrifuged at 4500 rpm for 10 min, and the supernatant was stored at -20°C before AS analysis. The adsorption capacity (q) was calculated by Eq. (3):

$$q = \frac{(C_0 - C_f)m}{V} \quad (3)$$

where C_0 and C_f are the As concentrations before and after the adsorption test, respectively, V is the liquid volume, and m is the mass of the adsorbent.

2.4 Adsorption tests in packed bed column

Adsorption tests were performed by employing plexiglass cylindrical columns ($d = 3$ cm). To run the tests, 2.0 g of Fe-hydrochar were mixed at 4% (w/w) with silica sand ($90 < d < 1000$ μm) and stacked within the column, forming a packed bed height of 5 cm, sandwiched between two 10.5 cm-thick layers of pure silica sand. Before starting tests, the column was washed with distilled water until a constant conductivity of the outlet water was achieved. The entire collected washing water was collected and filtered to quantify mass losses. Then, NaNO_3 0.05 M was pumped through the column at a flow rate of 0.7 mL/min as a tracer, and the outlet conductivity was measured at different times to determine the breakthrough curve for the tracer. Finally, an arsenic adsorption test was performed by pumping 10 mg/L of arsenic solution and monitoring the outlet arsenic concentration over time.

2.5 Chemical analyses

To quantify the Fe content of the produced adsorbents, digestion was performed by mineralizing 100 mg of sample with 8 mL HNO_3 (65%) and 2 mL H_2O_2 (30%) in a 100 mL PTFE vessel, which was then heated by microwave as follows: 2 min from 25 to 85°C , 5 min from 85 to 145°C , 3 min from 145 to 200°C , 20 min at 200°C , and 30 min for cooling. At the end, samples were analyzed for Fe content. The pH was measured with a glass electrode (InLab® Expert Pro ISM®, Mettler Toledo) calibrated with standard solutions at pH 4.0, 7.0, and 9.0.

Fe and arsenic were analyzed by using an inductively coupled plasma optical emission spectrometer (ICP-OES; Vista MPX CCD Simultaneous; Varian, Victoria, Mulgrave, Australia), in axial view mode, and equipped with a cyclonic spray chamber (Capobianco et al., 2020). The content of phenols in the permeate of Fe-hydrochar filtration was measured by the Folin-Ciocalteu method as previously described (Di Caprio et al. 2018). A calibration line obtained with tyrosol was used to quantify phenol concentration, which was then expressed as tyrosol equivalents.

3. Results and Discussion

3.1 Synthesis of the Fe-hydrochar

Different HTC tests were performed at 200°C by varying the reaction time from 5 to 60 min. The hydrochar yield and the solution pH attained at the end of any test are reported in Fig. 1. It is apparent that the hydrochar yield initially decreases and then increases progressively, approaching a constant value. The pattern followed by the pH is qualitatively identical, with an initial acidification followed by a slight pH increase. These results can be explained by observing that hydrolysis takes place during the early stages of the HTC process, resulting in the degradation of sugars and the synthesis of organic acids. This determines a drop in the solution pH and a decrease in the mass of the solid. An increasing pH is then observed owing to the polymerization of the previously formed organic acids, which leads to the formation of secondary char and increases the mass of the suspended solid. Therefore, the prevailing mechanisms of the HTC process are an initial hydrolysis-mediated leaching of the biomass followed by the formation of secondary char through the polymerization of soluble compounds.

In accordance with the experimental results reported in Fig. 1, the synthesis of the hydrochars employed in the present study was performed by stopping the HTC stage at 30 min. Increasing the time above this value would not produce any significant variations in the hydrochar yield.

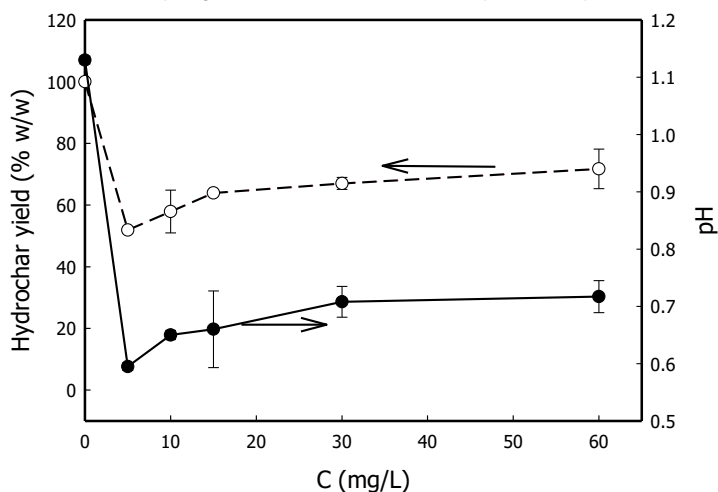


Figure 1: Analysis of HTC kinetics; evolution of the hydrochar yield (empty circles and dashed line) and pH (filled circles and solid line) during the HTC process.

Following the HTC test, iron precipitation was carried out at 25°C by adding KOH 6.5 M. To evaluate the effectiveness of the method to introduce iron oxide and hydrogen oxidation functional groups onto the hydrochar surface, the iron content of the solid filtered after precipitation was analyzed. A 5 ± 1 % (w/w) iron content was found, which is comparable to the values that were previously found to ensure satisfactory arsenic adsorption capacity. The same procedure was followed to introduce iron functional groups onto the surface of the biochar produced by biomass pyrolysis at 600 °C, leading to a comparable iron content of 53 % (w/w).

Before performing the adsorption tests, the stability of the produced Fe-hydrochar was evaluated. To this purpose, the Fe-hydrochar was washed, and the pH, which was initially around 9, was corrected to 6.7 by the dropwise addition of HCl. The solid was maintained under these conditions for 2 h. A 30% decrease in the mass of the solid was observed, which can be imputed to the solubilization of low-molecular-weight organic compounds (e.g., organic acids) and/or previously precipitated potassium salts and hydroxides that were not tightly bonded to the hydrochar surface. This result clearly evidences the need to adequately wash the adsorbent before its application to prevent contamination of the treated water by the above organic and inorganic compounds.

To maximize the circularity of the proposed process, the possibility of directly using the permeate of Fe-hydrochar filtration as fertilizer was considered. In this framework, the concentration of phenols in the permeate was quantified. Indeed, phenols are phytotoxic compounds, and an exceedingly high concentration could hinder their application as fertilizer. A concentration of phenols equal to 1600–500 mg/L of tyrosol equivalents was obtained. This value is significantly lower than that typically found in olive mill wastewaters (5 g/L), which are already used as fertilizers, confirming the possibility to directly use them as fertilizer.

3.2 Adsorption isotherms

To evaluate the ability of the produced Fe-hydrochar to bind arsenic from water solutions, an adsorption isotherm was constructed by performing batch adsorption tests with varying initial arsenic concentrations. Under the same conditions, an arsenic adsorption isotherm was constructed by employing Fe-biochar. Experimental data were then fitted by the Langmuir model to estimate the maximum adsorption capacities (q_{\max}) and the affinity constants (b) of the two adsorbents for arsenic.

The equilibrium adsorption capacities found as the arsenic concentration in the liquid are reported in Fig. 2, along with the values predicted by the Langmuir model with the optimal q_{\max} and b values (see Fig. 2 caption for estimated model parameter values). The Fe-hydrochar exhibits an adsorption capacity that is always greater than that of the Fe-biochar. This can be mainly imputed to the significantly larger q_{\max} found for the Fe-hydrochar, whereas comparable affinity constants, b , were estimated for the two adsorbents.

It is worth noting that, in accordance with the reported experimental data and with model predictions, the Fe-hydrochar can ensure an adsorption capacity of about 1 mg/g with an arsenic concentration in the liquid of about 60 ppb, which is comparable to or even larger than that reported under the same conditions for different arsenic adsorbents (Nicomel et al., 2016).

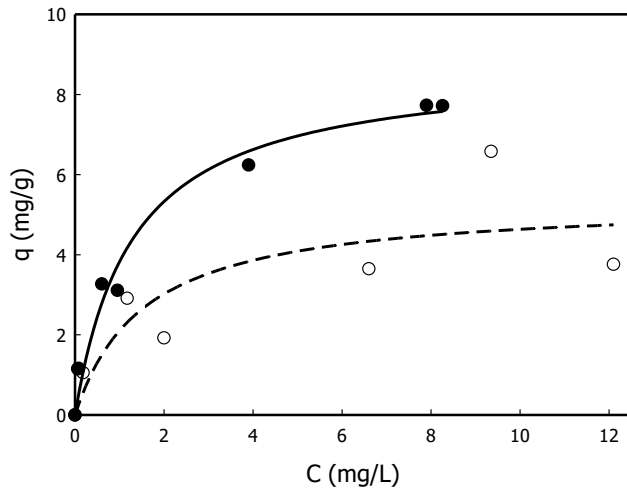


Figure 2: Arsenic adsorption isotherms of Fe-hydrochar (filled circles, solid line) and Fe-biochar (empty circle, dashed line); circles and lines denote the experimental data and the predictions of the Langmuir model with optimal parameters ($q_{max}=8.7$ mg/g, $b=0.8$ L/mg for Fe-hydrochar; $q_{max}=5.3$ mg/g, $b=0.6$ L/mg for Fe-biochar)

3.3 Arsenic adsorption in packed bed column

Before starting the adsorption test, the column was washed by pumping distilled water. Washing was stopped after the electric conductance was no longer varying. The whole loss of mass during washing was only 0.76% of the hydrochar in the column.

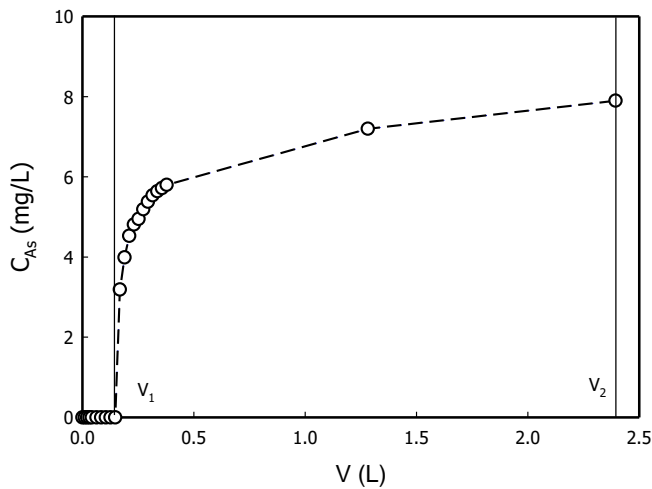


Figure 3: Evolution of the arsenic concentration at the outlet of the adsorption column as the volume of treated liquid varies. $F = 0.7$ mL/min, Inlet $C (C_F) = 10$ mg/L.

Once the washing phase was completed, the test with the NaNO_3 was performed, finding a breakthrough curve after 0.07 L. The adsorption test was then started by switching the feed to a 10 mg/L As solution. The breakthrough curve describing the evolution of the outlet as concentration increases with the volume of liquid pumped through the column is reported in Fig. 3. A sudden increase in the arsenic concentration was found after a volume equal to 0.15 L of solution was pumped through the column. The outlet arsenic concentration then progressively increased, approaching a plateau. The amount of As adsorbed by the bed after a volume V of solution is pumped through the column is then determined as follows:

$$M_{As}(V) = C_F V - C_F V_T - \int_0^V C(V) dV \quad (4)$$

where $C_F = 10$ mg/L is the arsenic feed concentration, V_T is the volume fed till the point of tracer breakthrough, and $C(V)$ is the outlet concentration attained after the volume V has flowed through the bed. By substituting the

volume $V=V_1$ at which the outlet As concentration starts to increase (Fig. 3), Eq. (4) yields $M_{As}(V_1) = C_F(V_1-V_T)$ since the $C(V)=0$ at any $V<V_1$ and thus the integral of $C(V)$ from 0 to V_1 is equal to zero. If the volume V_2 attained at the end of the test is selected (Fig. 3), then Eq. (4) gives the amount of arsenic that was adsorbed by the bed during the whole test. By dividing $M_{As}(V)$ by the mass of Fe-hydrochar in the column ($m_{HC} = 2.0$ g), an average adsorption capacity $\langle q(V) \rangle$ can be calculated. This way, we found that $\langle q(V_2) \rangle = 3.4$ mg/g while $\langle q(V_1) \rangle = 0.37$ mg/g. Since an equilibrium adsorption capacity of 7.7 mg/g is expected based on the adsorption isotherms (Fig. 3), it can be deduced that, under the selected operating conditions, only 5% of the bed adsorption capacity was exploited at the breakthrough. This percentage can be increased by increasing the length of the bed. Increasing this length can allow the concentration front through the bed to become sharper before reaching the outlet, which can increase the fraction of the adsorption capacity exploited at the time arsenic is detected in the outlet. It should be noticed that the adsorption capacity at the end of the test, $\langle q(V_2) \rangle$, was about 45% of that expected based on the adsorption isotherms of Fe-hydrochar. This can be partially explained by observing that a volume larger than V_2 can be treated before the outlet as the concentration becomes equal to the feed concentration.

4. Conclusions

A two-stage process was investigated to produce an arsenic adsorbent from olive pomace. The process includes HTC treatment of olive pomace followed by Fe precipitation. The analysis of solid mass variation during the HTC suggests that the mechanisms dictating the evolution of the hydrochar yield are biomass hydrolysis and polymerization of organic soluble compounds. Around 30 minutes were sufficient to obtain a hydrochar yield close to the maximum. However, maintaining the produced hydrochar at pH=5 for about 2 hours determined a 30% drop in the mass of the hydrochar, evidencing the need of washing before application in adsorption plants. By the analysis of the adsorption isotherms, it was evidenced that the Fe-hydrochar exhibits a larger adsorption capacity compared to a Fe-biochar produced from the pyrolyzed olive pomace, confirming the competitiveness of the proposed two-stage adsorbent production route. In the application of the Fe-hydrochar in a packed bed column, a 15% exploitation of the bed adsorption capacity was attained at the point of breakthrough. Further optimization of the column design and operation is therefore deemed necessary.

References

- Capobianco, L., Di Caprio, F., Altimari, P., Astolfi, M.L., Pagnanelli, F., 2020. Production of an iron-coated adsorbent for arsenic removal by hydrothermal carbonization of olive pomace: effect of the feedwater pH. *J. Environ. Manag.* 273, 111164.
- Carneiro M.A., Pintor A.M.A., R. A.R. Boaventura, C. M. S. Botelho, 2021, Current Trends of Arsenic Adsorption in Continuous Mode: Literature Review and Future Perspectives, *Sustainability* 13(3), 1186.
- Di Caprio F, Pellini A, Zanoni R, Astolfi ML, Altimari P, Pagnanelli F., 2022. Two-phase synthesis of Fe-loaded hydrochar for As removal: The distinct effects of initial pH, reaction time and Fe/hydrochar ratio. *J. Environ. Manage.* 302, 114058.
- Di Caprio F, Scarponi P, Altimari P, Iaquaniello G, Pagnanelli F., 2018. The influence of phenols extracted from olive mill wastewater on the heterotrophic and mixotrophic growth of *Scenedesmus* sp. *J. Chem. Technol. Biotechnol.* 93, 3619-3626.
- Driehaus, W., 2002. Arsenic removal - experience with the GEH® process in Germany, *Water Supply* 2, 275–280.
- IARC, 2012. Arsenic, Metals, Fibres, and Dusts, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans/World Health Organization. International Agency for Research on Cancer. (pubmed.ncbi.nlm.nih.gov/23189751/)
- Jain A, Balasubramanian R, Srinivasan MP. Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review. *Chem Eng J* 2016;283:789–805. doi:10.1016/j.cej.2015.08.014.
- Khan, N., Mohan, S., Dinesha, P., 2021. Regimes of hydrochar yield from hydrothermal degradation of various lignocellulosic biomass: a review. *J. Clean. Prod.* 288, 125629.
- Li, R., Wang, J.J., Gaston, L.A., Zhou, B., Li, M., Xiao, R., Wang, Q., Zhang, Z., Huang, Hui, Liang, W., Huang, Heteng, Zhang, X., 2018. An overview of carbothermal synthesis of metal–biochar composites for the removal of oxyanion contaminants from aqueous solution. *Carbon N. Y.* 129, 674–687.
- Mourao P., Di Caprio F., Cansado I.P.P., Castanheiro J.E., Falcone I., Astolfi M.L., Altimari P., Pagnanelli F., 2022, Granulation and Activation of an Arsenic Adsorbent Made of Iron Oxide Doped Hydrochar, *Chemical Engineering Transactions*, 93, 91-96.
- Nicomel N.R., Leus K., Folens K., Van Der Voort P., Laing G. D., 2016, Technologies for Arsenic Removal from Water: Current Status and Future Perspectives, *Int. J. Environ. Res. Public Health*, 13(1), 62.
- Pecchi M., Goldfarb J. L., Baratieri M., 2022, Hydrothermal carbonization enthalpy using differential scanning calorimetry: Assessing the accuracy of the exhaust sample method. *Thermochimica Acta*, 718, 179388