Caffeine removal by Spent Coffee Grounds (SCG) biochar

M.A. Stylianou[1*], A. Tsiampartas[1], E. Elia[2], A. Zorpas[1], A. Agapiou[2]

[1]Laboratory of Chemical Engineering and Engineering Sustainability, Faculty of Pure and Applied Sciences, Open University of Cyprus, Nicosia 2231, Cyprus

[2]University of Cyprus, Department of Chemistry, P.O. Box 20537, CY-1678 Nicosia, Cyprus

**Corresponding author*: marinos.stylianou@ouc.ac.cy

Abstract

Caffeine is one of the most used compounds due to its inclusion in widely used products such as beverages, food products and pharmaceuticals (Anastopoulos and Pashalidis 2019). Due to its extensive use, it can enter the environment through human activities and furthermore, can impact ecosystems and aquatic life (Marasco et al. 2019). Its occurrence in ecosystems can be characterized as a human pollution marker. It was correlated to fecal coliforms and is proposed as an indicator of the level of contamination by sanitary sources (Sauvé et al. 2012; Gonçalves et al. 2017). Caffeine is considered an emerging pollutant and the need for reducing its content from effluents by conventional wastewater treatment but also its removal at the source will decrease the impact to the environment (Anastopoulos et al. 2020; Raj et al. 2021).

The present research aims to investigate the production of a sorbent material –biochar - derived from Spent Coffee Grounds (SCG) in order to be used for the removal of Caffeine from aqueous solutions. This targets the transformation of high volumes of waste produced from cafeterias, restaurants *etc.*, in the circular economy framework (Stylianou et al. 2018). To achieve this, SCG were collected from a campus cafeteria and were dried at ~ 35 °C. Samples were subjected to slow pyrolysis in a small scale kiln with a capacity of 20–24 kg. They were heated under a nitrogen atmosphere for approximately 6–7 °C min^{-1} up to the target temperature (550 °C) and held for 1.5 h (Stylianou et al. 2020).

Adsorption studies were conducted by equilibrating 0.2 - 2 g of SCG biochar with 10 mL of Caffeine solution of 50 ppm concentration (pH = 3.5) in 15 mL glass tubes. The content of the tubes was agitated on a rotator at 125 rpm at constant temperatures for 24 h. After rotation, the suspensions were filtered and the residual caffeine concentration was determined by LC-MS/MS.

The effect of contact time was explored using a caffeine concentration of 50 mg/L at 25 °C and pH 3.5, following adsorption in successive time intervals between 1 and 480 min (1 gr/10 mL). Furthermore, two concentrations of zeolite (clinoptilolite) were also used (0.5 and 1 gr) to compare its efficiency against the produced biochar. Also, a mixture of biochar:zeolite (0.8:0.2 gr) was examined.

Quantitative analysis of caffeine solutions was performed using an Alliance 2695 Separation Module hyphenated to a Quattro Premier XE triple quadrupole mass spectrometer (Waters Cor. UK). Chromatographic separation was achieved using a Waters Symmetry C18 (2.1 x 150 mm, 3.5 μm) column, kept at 30 °C with H_2O + 0.1 % FA as mobile phase A and ACN + 0.1% FA as mobile phase B. The mobile

phase flow rate was 0.3 mL/min and a gradient elution was used. The mass spectrometer was operated in positive ion mode with the following parameters: capillary voltage 3 kV, cone voltage 22 eV, source temperature 120 ^{o}C, desolvation temperature 500 ^{o}C, desolvation flow 950 L/hr. A single MRM transition was used to detect caffeine (195.1 > 138.0) with a collision voltage of 18 eV.

The results showed that as sorbent mass increases the % removal of Caffeine from solutions is increased and a 70% of caffeine the removal was achieved (24 h). Zeolite has almost twice removal efficiency than biochar under the parameters studied and furthermore, the mixture of biochar:zeolite (0.8:0.2 gr) achieved increased caffeine removal by 28 %. Short contact times needed (over 60 min) to achieve > 35 % removal efficiencies. It was also concluded that the activation of biochar should be examined for increasing the removal efficiency of caffeine.

REFERENCES

Anastopoulos I, Pashalidis I (2019) The application of oxidized carbon derived from Luffa cylindrica for caffeine removal. Equilibrium, thermodynamic, kinetic and mechanistic analysis. J Mol Liq 296:112078. https://doi.org/10.1016/j.molliq.2019.112078

Anastopoulos I, Pashalidis I, Orfanos AG, et al (2020) Removal of caffeine, nicotine and amoxicillin from (waste)waters by various adsorbents. A review. J Environ Manage 261:. https://doi.org/10.1016/j.jenvman.2020.110236

Gonçalves ES, Rodrigues ilvana V, Silva-Filho EV da (2017) The use of caffeine as a chemical marker of domestic wastewater contamination in surface waters: seasonal and spatial variations in Teresópolis, Brazil. Ambient Água - An Interdiscip J Appl Sci 12:192–203. https://doi.org/10.4136/1980-993X

Marasco J, Augusto C, Luchiari, et al (2019) Occurrence of caffeine in wastewater and sewage and applied techniques for analysis: a review. Eclética Química J 44:11. https://doi.org/10.26850/1678-4618eqj.v44.4.2019.p11-26

Raj R, Tripathi A, Das S, Ghangrekar MM (2021) Removal of caffeine from wastewater using electrochemical advanced oxidation process: A mini review. Case Stud Chem Environ Eng 4:100129. https://doi.org/10.1016/j.cscee.2021.100129

Sauvé S, Aboulfadl K, Dorner S, et al (2012) Fecal coliforms, caffeine and carbamazepine in stormwater collection systems in a large urban area. Chemosphere 86:118–123. https://doi.org/10.1016/j.chemosphere.2011.09.033

Stylianou M, Agapiou A, Omirou M, et al (2018) Converting environmental risks to benefits by using spent coffee grounds (SCG) as a valuable resource. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-018-2359-6

Stylianou M, Christou A, Dalias, Panagiotis, Polycarpou P, et al (2020) Physicochemical and structural characterization of biochar derived from the pyrolysis of biosolids, cattle manure and spent coffee grounds. Under Rev