chemistry proceedings

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Proceeding Paper

Synthesis and Application of ZIF-08 Supported on *Theobroma cacao* L. Biochar for the Adsorption of Loratadine in Aqueous Media †

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† Presented at The 28th International Electronic Conference on Synthetic Organic Chemistry (ECSOC 2024), 15-30 November 2024; Available online: https://sciforum.net/event/ecsoc-28.

Abstract: To address the problem of emerging water pollution by pharmaceuticals, a composite material based on cocoa pod husk biochar obtained by microwave pyrolysis and imidazole zeolitic structures (ZIF-08@BC) was developed. The resulting material was characterized using various analytical techniques (TGA, XRD, BET, pHpzc and FTIR). The adsorption capacity of ZIF-08@BC was evaluated, using the drug loratadine as a model compound, obtaining the following results: adsorbent dose 0.07 mg/L, pH 6, an initial concentration of 40 mg/L and a contact time of 40 min. Under these conditions, the compound reached a maximum adsorption capacity of 23.103 mg/g. The adsorption process was found to fit best to a pseudo-first order kinetic model ($R^2 = 0.966$, $Q_{e\,(calc)} = 22.46$ mg/g and $E = 0.009$) and to an isothermal unbinding model ($R^2 = 0.997$ and $ks = 0.182$). In conclusion, ZIF-08@BC is an effective adsorbent for the treatment of aqueous media contaminated with loratadine.

Keywords: emerging contaminants; zeolitic imidazole framework; loratadine; biochar; microwave-assisted pyrolysis

Citation: Vega, M.A.; Cabrera, E.V.; Stahl, U.; López, J.L.; Rodríguez-Díaz, J.M. Synthesis and Application of ZIF-08 Supported on *Theobroma cacao* L. Biochar for the Adsorption of Loratadine in Aqueous Media. *Chem. Proc.* **2024**, *6*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: 15 November 2024

1. Introduction

Global consumption of pharmaceuticals has grown exponentially in recent decades, resulting in an increased presence of potentially toxic chemical compounds in the environment [1,2]. These drugs are absorbed, metabolized and finally eliminated through urine and faeces. Population growth and improper use of these products have led to the pollution of aquatic ecosystems [3].

Freshwater ecosystems, such as rivers and lakes, have become the main recipients of these pharmaceuticals [4]. This is due to the limited management of industries and the discharge from wastewater treatment plants into water bodies, which carry a wide variety of compounds, such as analgesics, antibiotics, anticonvulsants, anticarcinogens, lipid regulators, antihistamines and even drugs. In Ecuador, substances such as carbamazepine, acesulfame *K*, paracetamol, diclofenac, sulfametaxol and loratadine have been found in water samples, sediments and biota [5], representing a considerable threat to public health and ecosystems. In this work, the use of zeolitic imidazolate materials (ZIFs) supported on biochar (BC) is presented as a promising alternative to determine whether the ZIF-

8@BC supported material can effectively act as an adsorbent for the antihistamine loratadine in synthetic waters.

2. Materials and Methods

2.1. Chemical Reagents

Zinc nitrate at 98% ($Zn(NO_3)_2.6H_2O$), 2-Methylimidazole at 99% ($CH_3C_3H_2N_2H$) and methanol at 99.8% ACS reagent (CH_3OH) were purchased from Sigma-Alrich. For the stock solution, a blister of commercial loratadine 5 mg was used and, in all experiments, water type I.

2.2. Synthesis of Zeolitic Imidazolate Framework Impregnated (ZIF-8) on Biochar (BC)

For the synthesis of ZIF-8 nanocrystals on the BC surface, 0.774 g of Zn $(NO_3)_2.6H_2O$ and 0.21 g of BC are mixed in 60 mL methanol and stirred for 6 h. Then 0.789 g of 2-methylimidazole is weighed and dissolved in 60 mL methanol. The two solutions are mixed and stirred for 12 h. The resulting product is filtered and washed with methanol. Finally, it is dried for 12 h at 70 °C [6], thus obtaining purified ZIF-8@BC.

2.3. Characterization

For the characterization of the ZIF-8@BC material, a proximal analysis of the material was carried out using a Mettler Toledo thermogravimetric analyzer (TGA1). X-ray diffraction (XRD) was performed with a Bruker D8 Advance, with a CuKα1 radiation and a step size of 0.02035. Brunauer Emmett-Teller (BET) surface area (SSA) and pore volume were measured using Micromeritics, Autochem II 2920. Infrared fourier transform spectra were measured using the Perkin Elmer Spectrum FTIR instrument from 4000 to 450 cm^{-1}.

2.4. Preparation of the Stock Solution

A commercial blister of loratadine was used to prepare a stock solution (60 mg/L) in water and a 50%v/v ethanol solution. All adsorption experiments were performed by diluting the stock solution to the desired concentration.

2.5. Adsorption Experiments

All adsorption experiments were carried out in 250 mL beakers with 100 mL of loratadine diluted from the stock solution. Each experiment was performed in triplicate at a temperature of 293.15 K, stirring at 300 rpm and filtration at the end of the adsorption process (Hawach Scientific 2.5 μm filter paper). To study the influence of pH on the adsorption of loratadine, different pH values (2, 4, 6, 8, 10), with a mass of ZIF-8@BC of 50 mg were mixed with a 50 mg/L solution of loratadine solution during 60 min. The effect of adsorbent dose was tested by mixing different masses of ZIF-8@BC (5, 25, 50, 75, 100, 125, 150, 175, 200 mg) with a 50 mg/L solution in a 100 mL volume and periodically regulating the pH 6 with the addition of HCl (0.1 M). For the determination of the influence of time vs. concentration the following parameters were taken into account (1, 5, 10, 15, 20, 20, 40, 60, 80, 100, 120 min) and the loratadine solutions had a concentration of (3, 5, 10, 20, 40, 50, 60 mg/L), maintaining a ZIF-8@BC dose of 75 mg. The experimental data were subjected to various kinetic models and isotherms to analyze the data.

3. Results and Discussion

3.1. ZIF-8@BC Characterization

The thermogravimetric analysis allows the quantification of the proximate analysis, showing that the ZIF-8@BC material contains 1.22% moisture, 41.92% volatile compounds from the decomposition of the imidazole, 25.09% representing the fixed carbon of the BC and 31.40% ash which refers to the final decomposition of the ZIF-8 to zinc oxide (ZnO) [7].

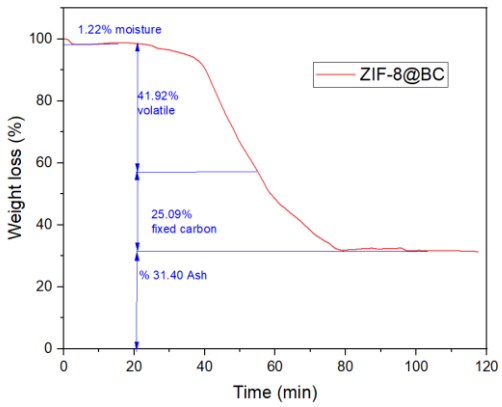

Figure 1. Proximal analysis of ZIF-8*@BC.*

The crystallographic characteristics of ZIF-8@BC were determined by XRD. The prominent peaks of the synthesized ZIF-8 on the BC surface were compared with theoretical patterns of the Crystallography Open Database (COD). The peaks between 7° to 20° correspond to the organic ligand imidazolate, responsible for the coordination of the metal sites. Signals beyond 30° represent the Zn^{2+} forming chemical bonds with the nitrogen atoms of the metal-imidazole groups. From the diffraction pattern the crystallite size was calculated via the Scherrer equation, obtaining an average crystal size of 52.68 nm [8].

FTIR spectroscopic analysis was performed to identify the functional groups on the ZIF-8@BC surface. Peaks can be visualized between 1461 to 1313 cm^{-1} (stretching of the imidazole ring), 1147 cm^{-1} (vibration of C-N group), 693 cm^{-1} (vibration of the imidazole out-of-plane ring bending) and 419 cm^{-1}, (Zn-N stretching) [9].

Finally, the experimental result of the zero-charge point (pH_{pcz}) of ZIF-8@BC is close to 9.67. This is similar to the literature which evaluates the ZIF-8 molecule and BC and reports a pH_{pcz} of 9.5 and 9.48 respectively [10,11]. At this pH, the surface is negatively charged and attracts positively charged molecules, through electrostatic interactions.

3.2. Results of Adsorption

The surface charge of the adsorbent and the state of the molecules are affected by the pH of the solution. For the removal of loratadine in synthetic wastewater, the highest removal (60.88%) was obtained at a pH of 6; however, as the solution begins to have a basic pH, the adsorption decreases, obtaining a minimum removal of 18.92% at pH 10, due to the electrostatic repulsion between the negative charges present in ZIF-8 and the adsorbate.

Optimizing the amount of adsorbent in an adsorption system is important to obtain an efficient system, where the material is not wasted and there is a cost-benefit optimization. Therefore, in this study, the adsorption capacity (Q_e) and the percentage of removal (%R) were evaluated for different doses of ZIF-8@BC material, and a Q_{emax} = 36.06 mg/g and $\%R_{max}$= 56. 52% was obtained at 0.07 mg/L. The efficiency of the process was affected at a higher amount of adsorbent, decreasing the adsorption capacity, due to the excess of adsorbent generated by a small amount of adsorbate, allowing a large part of the active sites on the surface of the ZIF-8@BC material to become unsaturated.

The adsorption process of loratadine occurs rapidly during the first 20 min. After this time, adsorption was slow until reaching equilibrium after 40 min. During the equilibrium stage, the removal efficiency stabilizes at approximately 22 mg/g. This phenomenon can be attributed to the availability of active sites of ZIF-8@BC which tend to become saturated with time. The data were subjected to the analysis of 3 kinetic models: pseudo-first order (PFO), pseudo-second order (PSO) and Elovich model. It was found that the adsorption process fits best to a pseudo-first order kinetic model (R^2 = 0.966, $Q_{e\,(calc)}$ = 22.46 mg/g and E = 0.009) (Figure 2).

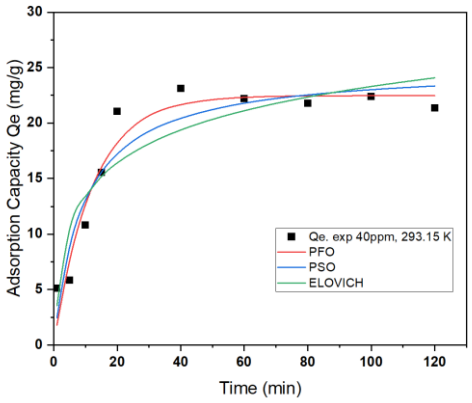

Figure 2. Graph of the effect of contact time and non-linear kinetic models.

The PFO model resulted well in a fast adsorption system.

Knowing the adsorption isotherms one can generate an interpretation of the possible adsorption mechanism. For this purpose, the experimental data were subjected to a non-linear regression for Langmuir, Freundlich and Sips models. In this study the Sips model exhibits a superior nonlinear fit performance with $R^2 = 0.997$.

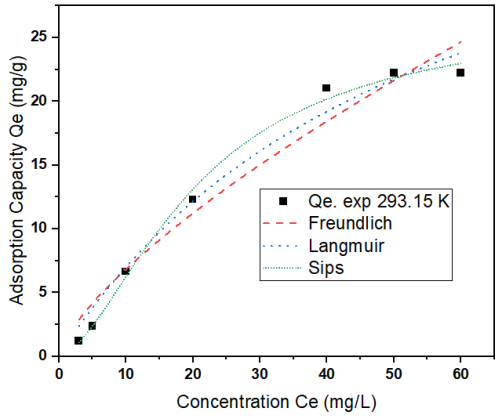

Figure 3. Graph of isothermal models.

4. Conclusions

In this work, the ZIF-08@BC composite has proven to be an effective adsorbent for the treatment of aqueous media contaminated with loratadine. This composite material represents a promising alternative to mitigate the presence of this emerging contaminant in the environment. Furthermore, it was determined that the best conditions for the adsorption of loratadine were at pH 6, 300 rpm, 75 mg of adsorbent material (ZIF-8@BC) and a time of 40 min, achieving an adsorption capacity of 23.103 mg/g at a concentration of 40 ppm.

Author Contributions: Conceptualization, M.A.V.; methodology, M.A.V.; investigation, M.A.V., E.V.C. and U.S.; writing—original draft preparation, M.A.V.; writing—review and editing, E.V.C., U.S. and J.L.L.; supervision, E.V.C. and J.M.R.-D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received funding from the Universidad Central del Ecuador via the Senior Research Projects DI-CONV-2023-029 and DI-CONV-2022-025.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors express their gratitude to the Universidad Central del Ecuador for financing the Senior Research Projects DI-CONV-2023-029 and DI-CONV-2022-025, and Laboratorios de Investigación y servicios especializados from the faculty of chemical engineering of the Universidad Central del Ecuador.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kosonen, J.; Kronberg, L. The occurrence of antihistamines in sewage waters and in recipient rivers. *Environ. Sci. Pollut. Res.* **2009**, *16*, 555–564. https://doi.org/10.1007/s11356-009-0144-2.
2. Teixeira, M.; Almeida, Â.; Calisto, V.; Esteves, V.I.; Schneider, R.J.; Wrona, F.J.; Soares, A.M.; Figueira, E.; Freitas, R. Toxic effects of the antihistamine cetirizine in mussel Mytilus galloprovincialis. *Water Res.* **2017**, *114*, 316–326. https://doi.org/10.1016/j.watres.2017.02.032.
3. Jones, O.A.H.; Voulvoulis, N.; Lester, J.N. Potential Ecological and Human Health Risks Associated With the Presence of Pharmaceutically Active Compounds in the Aquatic Environment. *Crit. Rev. Toxicol.* **2004**, *34*, 335–350. https://doi.org/10.1080/10408440490464697.
4. Buser, H.-R.; Poiger, T.; Müller, M.D. Occurrence and Environmental Behavior of the Chiral Pharmaceutical Drug Ibuprofen in Surface Waters and in Wastewater. *Environ. Sci. Technol.* **1999**, *33*, 2529–2535. https://doi.org/10.1021/es981014w.
5. Jara-Negrete, E.; Cipriani-Avila, I.; Molinero, J.; Pinos-Vélez, V.; Acosta-López, S.; Cabrera, M.; Medina-Villamizar, E.J.; Leiva-Andrade, D.; Pozo, A.; Martínez, O.; et al. Pharmaceutical compounds in urban drinking waters of Ecuador. *Front. Environ. Sci.* **2023**, *11*, 1232405. https://doi.org/10.3389/fenvs.2023.1232405.
6. Luo, M.; Zhu, C.; Chen, Q.; Song, F.; Hao, W.; Shen, Z.; Konhauser, K.O.; Alessi, D.S.; Zhong, C. In-situ growth of ZIF-8 nanocrystals on biochar for boron adsorption. *Colloids Surfaces A: Physicochem. Eng. Asp.* **2023**, *657*, 130504. https://doi.org/10.1016/j.colsurfa.2022.130504.
7. Filho, O.A.E.; Rivadeneira-Mendoza, B.F.; Fernández-Andrade, K.J.; Zambrano-Intriago, L.A.; da Silva, F.F.; Luque, R.; Curbelo, F.D.; Rodríguez-Díaz, J.M. Imidazolate framework material for crude oil removal in aqueus media: Mechanism insight. *Environ. Res.* **2023**, *241*, 117680. https://doi.org/10.1016/j.envres.2023.117680.
8. Li, K.; Miwornunyuie, N.; Chen, L.; Jingyu, H.; Amaniampong, P.S.; Koomson, D.A.; Ewusi-Mensah, D.; Xue, W.; Li, G.; Lu, H. Sustainable Application of ZIF-8 for Heavy-Metal Removal in Aqueous Solutions. *Sustainability* **2021**, *13*, 984. https://doi.org/10.3390/su13020984.
9. Zhang, Y.; Jia, Y.; Hou, L. Synthesis of zeolitic imidazolate framework-8 on polyester fiber for $PM_{2.5}$ removal. *RSC Adv.* **2018**, *8*, 31471–31477. https://doi.org/10.1039/c8ra06414h.
10. Jian, M.; Liu, B.; Zhang, G.; Liu, R.; Zhang, X. Adsorptive removal of arsenic from aqueous solution by zeolitic imidazolate framework-8 (ZIF-8) nanoparticles. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *465*, 67–76. https://doi.org/10.1016/j.colsurfa.2014.10.023.
11. Correa-Abril, J.; Stahl, U.; Cabrera, E.V.; Parra, Y.J.; Vega, M.A.; Taamalli, S.; Louis, F.; Rodríguez-Díaz, J.M. Adsorption dynamics of Cd2+(aq) on microwave-synthetized pristine biochar from cocoa pod husk: Green, experimental, and DFT approaches. *iScience* **2024**, *27*, 109958. https://doi.org/10.1016/j.isci.2024.109958.