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Production of Biochar from Urban Sludge and its Effective Removal of Methylene Blue

M. Ben Ali[a]*, M. Flayou[b], M. Tangarfa[c], Y. Bakhtaoui[d,e], M. El Hazzat[a], A. Moussadik[a], S. Belekbir[a]

[a] *Laboratory of Materials, Nanotechnologies and Environment, Faculty of Sciences, Mohammed V University in Rabat, Morocco*
[b] *Laboratory of Quality Control of Waters, National Office of Electricity and Drinking Water (ONEE), Rabat, Morocco*
[c] *Department of Industrial Process, Mohammadia School of Engineering, Mohammed V University, B.P. 765, Agdal Rabat 10090, Morocco.*
[d] *Laboratory of Advanced Materials and Process Engineering, Department of Chemistry, Faculty of Sciences, Ibn Tofaïl University, B.P. 133, Kenitra 14000, Morocco*
[e] *National Higher School of Chemistry, Ibn Tofail University, PB 133-14050, Kenitra, Morocco*

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ABSTRACT

This study investigates the production of biochar from sludge derived from industrial and wastewater treatment processes for the removal of dyes from wastewater. Structural and mineralogical post-pyrolysis changes were analyzed using IR-ATR, showing significant alterations. The application of sewage sludge-derived biochar for methylene blue dye removal from aqueous solutions demonstrated a high adsorption capacity of 32.47 mg/g, according to the Langmuir isotherm model, which closely fits the experimental data, indicating monolayer adsorption with a high correlation coefficient (R^2=0.99). Kinetic analysis suggests that the adsorption process adheres to pseudo-second-order kinetics, implying chemisorption, with a higher correlation coefficient (R^2=0.9788) than pseudo-first-order kinetics (R^2=0.8445), highlighting the biochar's potential as an efficient and eco-friendly adsorbent for dye removal in wastewater treatment.

1. Introduction

In recent times, waste management has confronted unprecedented challenges, particularly in handling sewage sludge. This sludge, resulting from wastewater treatment processes, embodies a complex mixture of organic and inorganic substances, presenting potential environmental hazards [1]. The urgency for innovative and sustainable waste treatment and valorization methods has never been critical [2]. Among the myriad of valorization strategies, the chemical conversion of sewage sludge, especially through pyrolysis, stands out as a noteworthy solution [3-4]. This technique involves the thermal processing of sludge at elevated temperatures to transform its organic matter into valuable byproducts, such as biochar [5].

Pyrolysis, in addition to other thermochemical techniques such as hydrothermal treatment [6-7], gasification [8-9], and combustion [10], is a versatile and effective approach for sludge management. This research focuses on the pyrolysis process, aiming to convert the organic constituents of sewage sludge into biochar, a carbon-rich, porous material renowned for its exceptional adsorption properties. The focus is particularly riveted on biochar's ability to remove organic pollutants, notably dyes, from wastewater, leveraging its porous nature [11-12].

The utility of biochar as an adsorbent for removing organic contaminants, including dyes, through adsorption has emerged due to its high efficiency, cost-effectiveness, and straightforward application [13-14]. This study aimed to scrutinize the adsorptive properties of biochar, specifically in terms of reducing color contamination in water bodies, with a focus on methylene blue. Furthermore, efforts have been made to explore the feasibility and practicality of biochar for real-world applications in industrial and municipal wastewater treatment, thus presenting a sustainable solution to a pressing environmental challenge.

2. Experimental

2.1. Biochar production

This study utilized residual sludge from a wastewater treatment plant in Ifrane, Morocco. To produce biochar, the sludge was first dried in an oven at 150°C overnight to eliminate moisture. It was then ground and sieved to achieve a particle size of less than 120 µm. This fine powder underwent pyrolysis carbonization in a programmable furnace at 550°C for one hour at a heating rate of 10°C/min.

*Corresponding author.

E-mail address: majda-benali@um5r.ac.ma (M. BENALI).

2.2. Adsorbate (MB) preparation

Methylene blue (MB), a cationic dye with the chemical formula C16H18N3SCl·3H2O, was chosen as the adsorbate for this study. A stock solution was prepared by dissolving 1 g of methylene blue in 1 L of distilled water. This solution was then diluted to achieve concentrations ranging from 20 to 60 mg. L-1, intended for use in adsorption experiments.

2.3. Characterizations of biochar

The biochar surface functional groups were identified using Fourier transform infrared spectroscopy (FTIR) on a Nicolet iS50 instrument set at a resolution of 4 cm-1 across a spectral range of 400 to 4000 cm-1. X-ray diffraction (XRD) analysis was performed to study the biochar's crystalline structure using a Shimadzu 6100 powder diffractometer with a monochromatic beam (λCuKα = 1.541838 Å). These measurements were carried out at room temperature, covering a 2θ range of 10 to 70° with a scanning speed of 2° per minute.

2.4. Adsorption Experiments

For the adsorption experiments, 0.6 g of the prepared biochar was dispersed in 50 mL of methylene blue solution (60 mg/L) in a beaker, and the solution was maintained at room temperature and a pH of 8.5. The mixtures were agitated for 3 hours to reach adsorption equilibrium and then filtered through a membrane with pore sizes between 16 and 40 µm. The filtrates were analyzed using a UV–visible spectrophotometer at 664 nm to determine the concentration of methylene blue remaining in solution. The adsorption capacity of the biochar was calculated using Equation 1[16]:

$$q = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of methylene blue (mg. L^{-1}), V is the volume of the solution (L), and m is the mass of the biochar used as adsorbent (g).

2.5. Theoretical background

2.5.1. Adsorption isotherms

The Langmuir and Freundlich models are critical for elucidating the adsorption mechanisms on surfaces [17]. The Langmuir model is calculated with the following equation [18]:

$$\frac{1}{Q_e} = \frac{1}{Q_m K_L} \times \frac{1}{C_e} + \frac{1}{Q_m} \quad (2)$$

elates to monolayer adsorption, where Q_m and K_L are the maximum adsorption capacity and adsorption constant, respectively. The Freundlich model is expressed as [19-20]:

$$lnQ_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

describes multilayer adsorption on heterogeneous surfaces, with K_f and $1/n_1$ indicating the adsorption capacity and intensity, respectively.

2.5.2. Adsorption kinetics

Kinetic analyses using pseudo-first order and pseudo-second order models help researchers understand the time-dependent adsorption process [20]. The pseudo-first-order model is depicted as [21]:

$$ln(Q_e - Q_t) = lnQ_t - K_1 t \quad (4)$$

focusing on the adsorption rate K_1. The pseudo-second-order model better accounts for the entire adsorption mechanism [22]:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \quad (5)$$

where K_2 represents the rate constant for the second-order reaction.

3. Results and discussion

3.1. *Characterization of biochar*

3.1.1. Infrared spectroscopy

Figure 1 shows the Fourier transform infrared spectroscopy (FTIR) spectra of the raw urban sludges and biochar, denoted as (a) and (b), respectively. The analysis of the spectrum for raw urban sludges reveals several distinct features. The broad peak at 3276.46 cm^{-1} indicates the presence of -OH groups involved in hydrogen bonding, which are typically found in alcohols or phenols. Absorption bands suggestive of aliphatic -CH groups, possibly originating from the glycidic components of lipids, are observed at 3050.08 cm^{-1}, 2973.30 cm^{-1}, and within the range of 2919.69 to 2844.49 cm^{-1}. Additionally, a peak at 1639.20 cm^{-1} signifies -C=O groups in lipids. The protein structures are indicated by the peak at 1537.95 cm^{-1}, which is related to amide II, while the peak attributed to the stretching of aromatic C=C bonds is noted at 1417.42 cm^{-1}. The spectrum also displays a band at 1240.97 cm^{-1}, indicative of C-O groups in carboxylic acids, and a peak at 1030.77 cm^{-1}, likely corresponding to C-O stretching in alcohols, ethers, or esters. The peak at 880.34 cm^{-1} is associated with Si-O valence vibrations. Following pyrolysis, significant changes are observed in the spectrum, including the disappearance of peaks at 3276.46 cm^{-1}, 3050.08 cm^{-1}, and 2973.30 cm^{-1}, within the range of 2919.69 to 2844.49 cm^{-1}, and at 1417.42 cm^{-1}. The intensities of the peaks at 1639.20 cm^{-1}, 1537.95 cm^{-1}, and 1030.77 cm^{-1} are notably reduced, whereas the peak at 880.34 cm^{-1} remains unchanged, highlighting the alterations in chemical composition and structure induced by the pyrolysis process [23].

3.1.2. Structural analysis

Figure 2 illustrates the mineralogical composition of the initial raw sludge and the resulting biochar after pyrolysis.

The diffractograms of the raw sludge reveal the presence of specific mineral compounds, including calcium carbonate

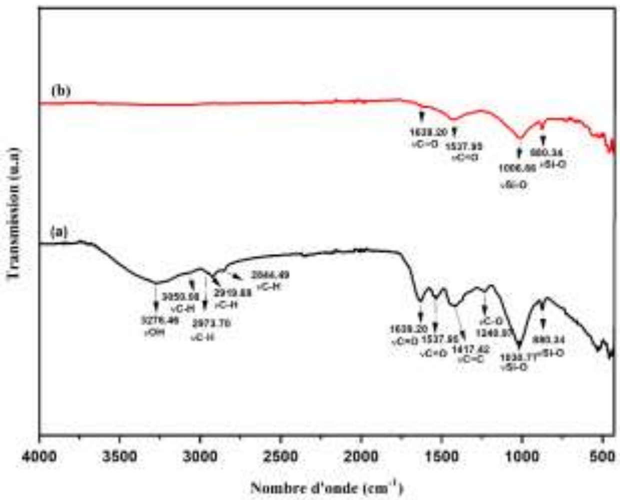

Fig. 1. Infrared Spectra of Raw Urban Sludge (a) and Biochar (b)

($CaCO_3$), quartz (SiO_2), dolomite ($Ca(Mg,Fe)(CO_3)_2$), and alumina (Al_2O_3). A significant peak indicative of organic matter is observed in the urban sludges. The presence of quartz is attributed to retained clay and sand particles from post-wastewater treatment processes. Additionally, $CaCO_3$ is detected, likely resulting from the intentional addition of lime to enhance sewage sludge dehydration and mitigate odors. After pyrolysis, as shown in Figure 2(b), the dolomite found in the sewage sludge partially decomposes into $CaCO_3$, and organic carbon is transformed into amorphous organic carbon, as evidenced by a shift in the peak toward lower 2θ angles. This indicates that the resulting biochar retains some mineralogical characteristics from the raw sludge, which is attributed to the relatively low temperature employed during the pyrolysis process [24].

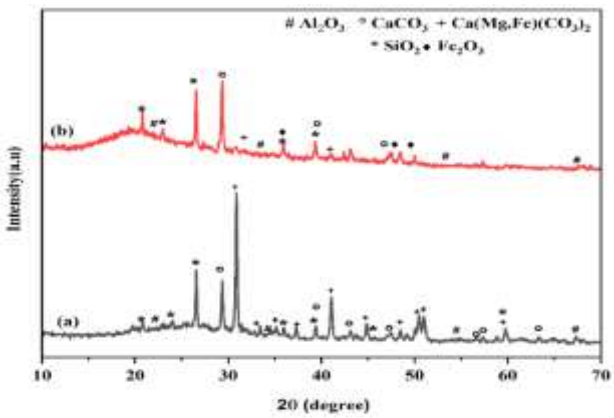

Fig. 2. XRD diffractograms of (a) urban sludge and (b) biochar

3.2. Kinetic analysis

The collected experimental data are graphically represented in Figure 3, illustrating the fit of the pseudo-first order (a) and pseudo-second order (b) models to the adsorption kinetics of methylene blue on biochar. The kinetic parameters derived from each model are summarized in Table 2.

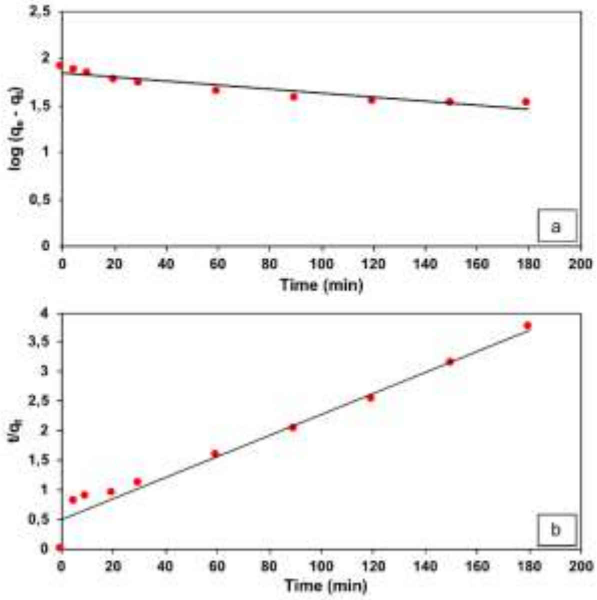

Fig. 3. Comparison of Pseudo-First Order (a) and Pseudo-Second Order (b) Models for the Adsorption Kinetics of Methylene Blue on Biochar

Table 2 reveals significant differences between the pseudo-first order and pseudo-second-order kinetic models. Notably, the correlation coefficient (R^2) for the pseudo-second-order model (0.9788) is substantially greater than that for the pseudo-first-order model (0.8445), indicating a better fit of the second-order model to the experimental data. This discrepancy highlights the limitations of the first-order model in accurately predicting the equilibrium adsorption capacity, as evidenced by the differences between the experimentally observed ($q_{e,exp}$) and calculated ($q_{e,cal}$)) values. In contrast, the pseudo-second-order model demonstrates a closer alignment between the experimental and calculated values, suggesting that the adsorption of methylene blue on biochar is better described by this model. The superior fit of the pseudo-second-order model underscores the likelihood of chemisorption as the predominant mechanism, characterized by electron exchange processes at the solid–liquid interface [26-27].

Table 1
Kinetic parameters for the adsorption of MB on biochar

Pseudo-First order model				Pseudo-Second order model			
$q_{e,exp}$	$q_{e,Cal}$	k_1 (min^{-1})	R^2	$q_{e,exp}$	$q_{e,cal}$	k_2 ($g.mg^{-1}.min^{-1}$)	R^2
33.25	22.86	0.016	0.845	33.25	37.59	0.00075	0.979

3.3. Isotherm analysis

Using the Langmuir and Freundlich mathematical models, we were able to derive essential adsorption parameters and ascertain the maximum adsorption capacity.

Figure 4 shows the adsorption isotherms of methylene blue, modeled by the Langmuir (a) and Freundlich (b) equations.

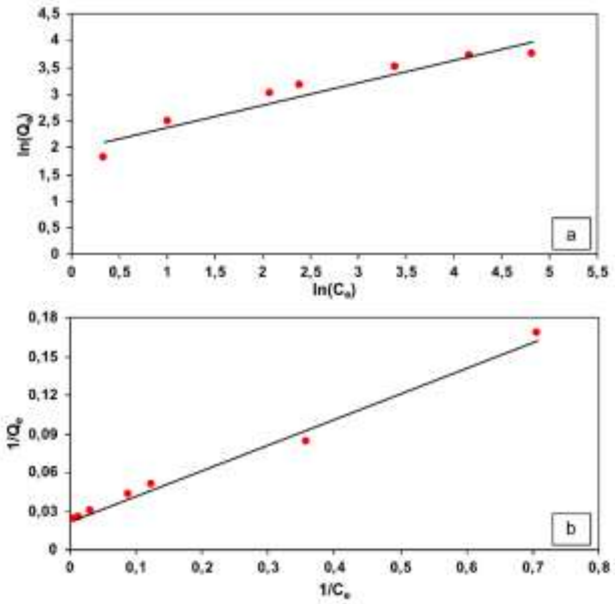

Fig. 4. Adsorption isotherms of methylene blue modeled by the (a) Freundlich and (b) Langmuir equations

Table 2
Adsorption parameters for MB on biochar

Langmuir Adsorption Isotherm				Freundlich Adsorption Isotherm		
q_m (mg g^{-1})	K_L ($L.g^{-1}$)	R^2	R_L	K_F	1/n	R^2
32.47	4.40	0.99	0.009-0.043	22.19	0.3322	0.9176

4. Conclusion

This study successfully produced biochar from urban sludge and demonstrated its efficacy as an adsorbent for the removal of methylene blue from aqueous solutions, underscoring the potential of sustainable materials in wastewater treatment. Characterization revealed significant differences in the material properties and provided insights into the changes in mineral composition that are critical to the adsorption process. The Langmuir isotherm model, with an adsorption capacity of 32.47 mg/g, underscored the suitability of this model for describing the adsorption behavior, suggesting a monolayer adsorption mechanism. Kinetic analyses supported the predominance of pseudo-second-order kinetics, indicative of a chemisorption process involving electron exchange at the solid–liquid interface. These findings not only highlight the potential of biochar as an effective adsorbent for dye removal in wastewater treatment but also contribute to the broader search for environmentally friendly and efficient pollution mitigation strategies.

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Conflicts of interest statement

The authors declare no competing financial interests.

References

[1] A. S. Giwa, N. J. Maurice, A. Luoyan, X. Liu, Y. Yunlong, Z. Hong. Advances in sewage sludge application and treatment: Process integration of plasma pyrolysis and anaerobic digestion with the resource recovery. Heliyon. 9 (2023) 19765.

[2] A. Sarker, R. Ahmmed, S. M. Ahsan, J. Rana, M. K. Ghosh, R. Nandi. A comprehensive review of food waste valorization for the sustainable management of global food waste. Sustainable Food Technol. 2 (2024) 48- 69, DOI: 10.1039/D3FB00156C.

[3] N. Gao, K. Kamran, C. Quan, P. T. Williams. Thermochemical conversion of sewage sludge: A critical review. Progress in Energy and Combustion Science. 79 (2020) 100843, DOI: 10.1016.

[4] M. Hu, Z. Ye, H. Zhang, B. Chen, Z. Pan, J. Wang. Thermochemical conversion of sewage sludge for energy and resource recovery: technical challenges and prospects. Environmental Pollutants and Bioavailability. 33 (2021) 145- 163, DOI: 10.1080/26395940.2021.1947159.

[5] M. K. Hossain, V. Strezov, P. F. Nelson. Thermal characterization of the products of wastewater sludge pyrolysis. Journal of Analytical and Applied Pyrolysis. 85 (2009), 442- 446, DOI: 10.1016/j.jaap.2008.09.010.

[6] Y. Fan, U. Hornung, N. Dahmen. Hydrothermal liquefaction of sewage sludge for biofuel application: A review on fundamentals, current challenges and strategies. Biomass and Bioenergy. 165 (2022) 106570, DOI: 10.1016/j.biombioe.2022.106570.

[7] M. C. Ozoemena, S. R. Coles. Hydrothermal Treatment of Waste Plastics: An Environmental Impact Study. J Polym Environ. 31(7) (2023) 3120- 3130, DOI: 10.1007/s10924-023-02792-3.

[8] X. Yang, al. Sorption-enhanced thermochemical conversion of sewage sludge to syngas with intensified carbon utilization. Applied Energy. 254 (2019) 113663, DOI: 10.1016/j.apenergy.2019.113663.

[9] A. W. Bhutto, A. A. Bazmi, G. Zahedi. Underground coal gasification: From fundamentals to applications. Progress in Energy and Combustion Science. 39 (2013) 189- 214, DOI: 10.1016/j.pecs.2012.09.004.

[10] M. Bagheri, E. Wetterlund. Introducing hydrothermal carbonization to sewage sludge treatment systems—a way of improving energy recovery and economic performance?. Waste Management. 170 (2023) 131- 143, DOI: 10.1016/j.wasman.2023.08.006.

[11] E. Goldan, al. Evaluation of the Use of Sewage Sludge Biochar as a Soil Amendment—A Review. Sustainability. 14(9) (2022), DOI: 10.3390/su14095309.

[12] H. Zeghioud, L. Fryda, H. Djelal, A. Assadi, A. Kane. A comprehensive review of biochar in removal of organic pollutants from wastewater: Characterization, toxicity, activation/functionalization and influencing treatment factors. Journal of Water Process Engineering. 47 (2022) 102801, DOI: 10.1016/j.jwpe.2022.102801.

[13] T. G. Ambaye, M. Vaccari, E. D. Van Hullebusch, A. Amrane, S. Rtimi. Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from industrial wastewater. Int. J. Environ. Sci. Technol. 18(10) (2021) 3273- 3294, DOI: 10.1007/s13762-020-03060-w.

[14] Z. Liu, al. Modified biochar: synthesis and mechanism for removal of environmental heavy metals. carbon res. 1(1) (2022), DOI: 10.1007/s44246-022-00007-3.

[15] P. Srivatsav, B. S. Bhargav, V. Shanmugasundaram, J. Arun, K. P. Gopinath, A. Bhatnagar. Biochar as an Eco-Friendly and Economical Adsorbent for the Removal of Colorants (Dyes) from Aqueous Environment: A Review. Water. 12(12) (2020) 3561, DOI: 10.3390/w12123561.

[16] M. Gouamid, M. R. Ouahrani, M. B. Bensaci. Adsorption Equilibrium, Kinetics and Thermodynamics of Methylene Blue from Aqueous Solutions using Date Palm Leaves. Energy Procedia. 36 (2013) 898- 907, doi: 10.1016/j.egypro.2013.07.103.

[17] Amrutha, G. Jeppu, C. R. Girish, B. Prabhu, K. Mayer. Multicomponent Adsorption Isotherms: Review and Modeling Studies. Environ. Process. 10(2) (2023) 38, DOI: 10.1007/s40710-023-00631-0.

[18] M. A. Islam, M. A. Chowdhury, Md. S. I. Mozumder, Md. T. Uddin. Langmuir Adsorption Kinetics in Liquid Media: Interface Reaction Model. ACS Omega. 6(22) (2021), 14481- 14492, DOI: 10.1021/acsomega.1c01449.

[19] M. Vigdorowitsch, A. Pchelintsev, L. Tsygankova, E. Tanygina. Freundlich Isotherm: An Adsorption Model Complete Framework. Applied Sciences. 11(17) (2021) 8078, DOI: 10.3390/app11178078.

[20] S. Sinha, al. Removal of Congo Red dye from aqueous solution using Amberlite IRA-400 in batch and fixed bed reactors. Chemical Engineering Communications. 205(4) (2018) 432- 444, DOI: 10.1080/00986445.2017.1399366.

[21] E. D. Revellame, D. L. Fortela, W. Sharp, R. Hernandez, M. E. Zappi. Adsorption kinetic modeling using pseudofirst order and pseudosecond order rate laws: A review. Cleaner Engineering and Technology.1 (2020) 100032, DOI: 10.1016/j.clet.2020.100032.

[22] H. N. Tran. Applying Linear Forms of Pseudo-Second-Order Kinetic Model for Feasibly Identifying Errors in the Initial Periods of Time-Dependent Adsorption Datasets. Water. 15(6) (2023) 1231, DOI: 10.3390/w15061231.

[23] M. Ben Ali, al. Kinetic Study of Urban Sludge Using Iso-conversional Kinetic Analysis. NanoWorld J. 9 (2023), DOI: 10.17756/nwj.2023-s2-071.

[24] Y. Liu, X. Zhao, J. Li, D. Ma, et R. Han. Characterization of biochar from pyrolysis of wheat straw and its evaluation on methylene blue adsorption. Desalination and Water Treatment. 46(1- 3) (2012) 115- 123, DOI: 10.1080/19443994.2012.677408.

[25] L. Lonappan, al. Adsorption of methylene blue on biochar microparticles derived from different waste materials. Waste Management. 49 (2016) 537- 544, DOI: 10.1016/j.wasman.2016.01.015.

[26] H. N. Tran. Applying Linear Forms of Pseudo-Second-Order Kinetic Model for Feasibly Identifying Errors in the Initial Periods of Time-Dependent Adsorption Datasets. Water. 15(6) (2023) 1231, DOI: 10.3390/w15061231.

[27] A. H. Mansee, D. M. Abdelgawad, E. H. El-Gamal, A. M. Ebrahim, M. E. Saleh, Influences of Mg-activation on sugarcane bagasse biochar characteristics and its PNP removing potentials from contaminated water. Sci Rep. 13(1) (2023) 19153, DOI: 10.1038/s41598-023-46463-8.