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Equilibrium and kinetic study of Zn(II) ions biosorption on algae biomass and derived biochar

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Abstract. Removal of heavy metal ions from industrial effluents prior to discharge is still and important issue for environmental protection and biosorption can be a solution. That is why the use of low-cost materials in biosorption processes is a viable alternative which must be considered. In this study, two such materials, namely algae biomass (Ulva lactuca sp.) and the biochar obtained from this biomass, were examined as potential biosorbents for the removal of Zn(II) ions from aqueous solution. At an initial solution pH of 5.0 and 4.0 g biosorbent /L, the removal efficiency of Zn(II) ions is up to 63 % for marine algae biomass and up to 94 % for algae biochar, after 180 min of contact time and room temperature (22 ±1 °C). The equilibrium and kinetic modelling of the obtained experimental results have shown that biosorption process on both biosorbents follow Langmuir model (R^2> 0.99) and pseudo-second order kinetic model (R^2> 0.999). The maximum biosorption capacity, calculated from Langmuir model, was 2.1 time higher in the case of algae biochar than in the case of algae biomass, while the kinetics of the biosorption process on algae biomass is faster (k_2 = 0.1118 g/mg min) that the algae biochar (k_2 = 0.0353 g/mg min). The functional groups involved in the Zn(II) ions retention and the morphological changes during biosorption were analyzed using FTIR spectra and SEM microscopy, for both biosorbents. Based on this study, algae biomass and algae biochar have proved to have high efficiency for removing Zn(II) ions from aqueous media, and can be employed in decontamination processes at large scale.

Keywords. Algae biomass, algae biochar, Zn(II) ions biosorption, isotherm modelling, kinetic modelling.

1. Introduction

The contamination of the environment with heavy metal ions is a serious problem, which is mainly caused by the rapid development of industrial activities, intensive use of chemicals in agriculture, as well as incomplete treatment of waste [1, 2]. Such anthropogenic activities are responsible for the accumulation of heavy metal ions in the environment, which, due to their persistence and toxicity, are harmful to all life forms and significantly contribute to the decrease of ecosystems quality [3]. It is

therefore necessary to reduce the concentration of heavy metal ions in effluents resulting from such anthropogenic activities as much as possible, before they are discharged into the environment.

Currently, there are numerous physical, chemical and biological methods that can be used on an industrial scale to remove heavy metal ions from aqueous media. Chemical precipitation, reverse osmosis, biological/chemical oxidation, membrane processes, ion exchange, etc., [4-6] are just a few representative examples. However, most of these methods have some important disadvantages (such as high consumption of chemical reagents and energy, laborious operating conditions, generation of secondary sludge that also requires further treatment, etc.) [7], which lead to a significant increase the treatment cost. Unlike these methods, the biosorption of heavy metal ions is much more technologically and economically viable. This is because biosorption allows the effective removal of heavy metal ions in a wide range of concentration, in various experimental conditions, and the operations required to carry out such process are simple and easy to use in practice [8]. Thus, numerous natural materials, or industrial and agricultural waste and by-products have been tested in the literature [9-12] for the removal of heavy metal ions, in order to highlight their potential applications in the biosorption processes. Each time, the researchers focused on materials that could be obtained as easily as possible and at the lowest possible cost, so that biosorption could be included in the category off economical and environmental friendly methods [12].

Marine algae are an example of a solid material that has been shown to be useful and effective in removing of heavy metal ions from aqueous media [13, 14]. Their high availability in many regions of the world, ease of preparation, low number of practical applications, etc., have made the use of marine algae as biosorbents a way to increase the economic potential of these materials [15]. However, one problem remains that marine algae decomposed very easily in the air, and this reduces their efficiency in biosorption processes. There are two ways to prevent this, namely: (i) immediately after harvest the marine algae are dried in air at temperatures of 60-70 °C – this obtaining the algae biomass, or (ii) after harvest the marine algae are calcined at temperatures of 300 – 500 °C, when the algae biochar is obtained. Both methods make it possible to obtain materials with good biosorptive properties, which can be used to retain heavy metal ions in aqueous media.

In this study, algae biomass and algae biochar were obtained by thermal treatment of marine green algae (Ulva lactuca sp.) in air at 70 °C and 320 °C, respectively. The obtained materials were tested as biosorbents for the removal of Zn(II) ions from aqueous media, in batch systems. The choice of Zn(II) ions for experimental studies was based on their industrial and economic importance. Based on the experimental results, the isotherm and kinetic characteristics of the biosorption processes were quantitatively evaluated and detailed discussed. These characteristics will be useful for evaluating the applicative potential of these two materials obtained from marine algae in biosorption processes.

2. Experimental

2.1. Materials

Marine green algae (Ulva lactuca sp.) were collected from the Black Sea coast, in July 2018. After washing several times with tap water (to remove solid impurities) and distilled water (to remove the salts form the algae leaves), the algae sample was dried in air (70 ◦C, for 8 h), crushing and sieving, until the granulation was less than 1.0 mm. Half of the obtained algae biomass was stored in a desiccators and used as biosorbent, while the other half was calcined to obtain the algae biochar. The calcinations of the algae biomass was done in a calcinations oven (Nabertherm LE4 type), in an oxygen-poor atmosphere (to prevent the oxidation of biochar), at a temperature of 320 °C, for 8 h. After calcinations, the obtained algae biochar was cooled (at room temperature), mortared for homogenization, and stored in desiccators until use. FTIR spectrometry (FTIR Bio-Rad Spectrometer, 400 – 4000 cm^{-1} spectral domain; resolution of 4 cm^{-1} , KBr pellet technique) and scanning electron microscopy (SEM Hitach S3000N, 20 kV) were used for the characterization of these two materials.

The chemical reagents used in experiments were of analytical grade, and were purchased from Chemical Company (Iaşi, Romania). The stock solution of Zn(II) ions (10^{-2} mol/L) were obtained by dissolving zinc nitrate in distilled water. This stock solution was then used to prepare all working solutions used in the biosorption experiments. 0.1-0.3 mL of 10^{-3} mol/L HNO3 solution was used to adjust the initial pH (measured with a pH/ion-meter MM-743 type, combined glass electrode) of the working solutions at 5.0.

2.2. Biosorption experiments

All experiments were performed in batch systems, contacting 25 mL of Zn(II) ions solution (of known concentration) with 0.1 g of biosorbent (algae biomass or algae biochar), at pH of 5.0 and room temperature (22 ± 1°C). The effect of the initial Zn(II) concentration on the biosorption efficiency was examined in the concentration range of 12-160 mg/L, while the effect of contact time was studied in the range of 5 – 180 min. At the end of each biosorption experiment, the two phases was filtrated, and the concentration of Zn(II) ions in filtrate was analyzed spectrophotometrically (color reagent: xylenol organge, λ = 570 nm, 1 cm glass cell). The efficiency of the biosorption process was quantitatively evaluated using: biosorption capacity (q, mg/g) and removal percent (R, %), calculated from experimental data based on the following equations:

$$q = \frac{(c_0 - c) \cdot V}{m} \quad (1)$$

$$R = \frac{c_0 - c}{c_0} \cdot 100 \quad (2)$$

where: c_o and c are the initial and equilibrium concentration of Zn(II) ions in solution (mg/L), V is volume of solution (L), and m is the mass of biosorbent used in each experiment (g).

Each measurement was done in triplicate, and the mean values of experimental results were used in graphs and calculation. The standard deviation less than ± 10 % was considered acceptable.

3. Results and discussion

3.1. Structural characteristics of biosorbents

For a biosorbent, the most important structural characteristics are the number and nature of the superficial functional groups, as well as the morphological heterogeneity of its surface [16]. These features can be easily highlighted by FTIR spectra and SEM images. In the case of algae biomass and algae biochar, the FTIR spectra and SEM images recorded for each biosorbent are illustrated in Fig. 1.

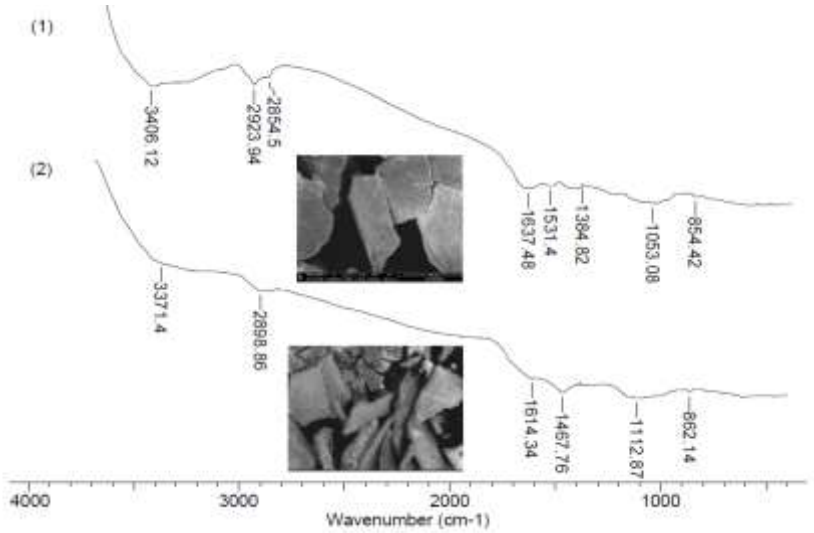
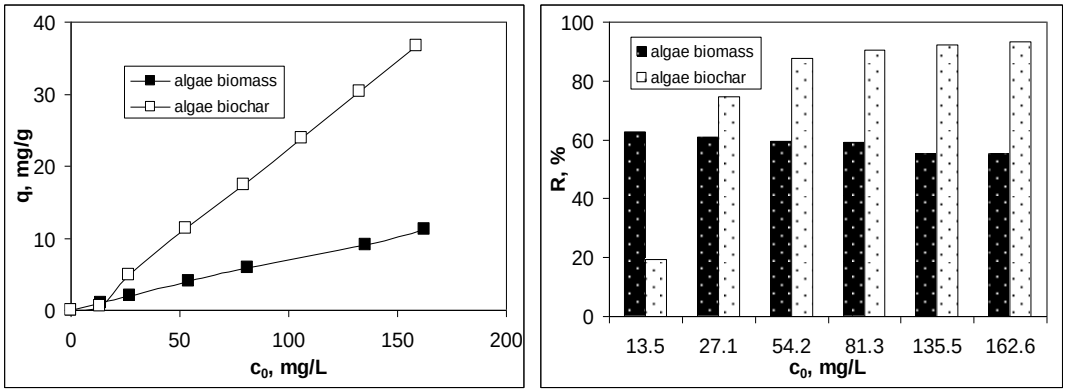


Fig. 1. FTIR spectra and SEM images of algae biomass (1) and algae biochar (2).

It can be seen from Fig. 1 that both biosorbents contains in their structure hydroxyl and amine groups (3406-3371 cm^{-1}), carbonyl and carboxyl groups (1637-1614 cm^{-1}), and other oxygenated functional groups (1112-1053 cm^{-1}). It should be noted, however, that in the case of algae biomass, the absorption bands are more intense and more numerous that in the case of algae biochar. This shows that the calcination of algae biomass at 320 °C only leads to a decrease in the number of superficial functional groups, and not to their complete disappearance. Moreover, from the SEM images (inside-Fig. 1) it can be seen that both biosorbents have an irregular morphology, which shows numerous cracks and wrinkles. All these structural particularities are important in biosorption processes, and highlight the potential applications of these materials.

3.2. Effect of initial Zn(II) ions concentration and isotherm modelling

The effect of initial Zn(II) concentration on the biosorption efficiency of algae biomass and algae biochar was studied in a concentration range of 12 to 160 mg/L, at pH of 5.0, 4.0 g biosorbent /L and room temperature (22 ± 1 °C). These experimental conditions were established to be optimal in a previous study [17]. The obtained values of the biosorption capacity and of the removal percent are presented in Fig. 2.



(a) (b)

Fig. 2. Effect of initial Zn(II) concentration on biosorption efficiency ((a) – variation of biosorption capacity; (b) – variation of the removal percent).

The increase of the initial Zn(II) ions concentration in the studied range determines an increase of the biosorption capacity from 1.05 to 13.63 mg/g in the case of algae biomass, and from 0.62 to 36.63 mg/g in the case of algae biochar (Fig. 2a). These results clearly show that algae biochar is more effective in the biosorption process of Zn(II) ions compared to algae biomass, even if the number of superficial functional groups is smaller (Fig. 1).

The higher efficiency of biochar obtained from biomass compared to the initial biomass has been reported in many studies in the literature [18-20]. This behavior is most often attributed to the fact that the functional groups of the biochar, although smaller, have a much great availability to interact with metal ions in biosorption processes. This assumption can be easily verified by analyzing the variation of the removal percent shown in Fig. 2b. Thus, if in the case of algae biomass, the increase of the initial Zn(II) ions concentration leads to the decrease of the removal percent (from 62.70 to 50.34 %), in the case of algae biochar it can be observed the increase of this parameter (from 19.37 to 94.39 %) in the same interval of initial Zn(II) ions concentration (Fig. 2b). In addition, at initial Zn(II) ions concentration higher than 80 mg/L, the removal percent is higher than 90 %, and therefore the algae biochar can be considered an effective biosorbent.

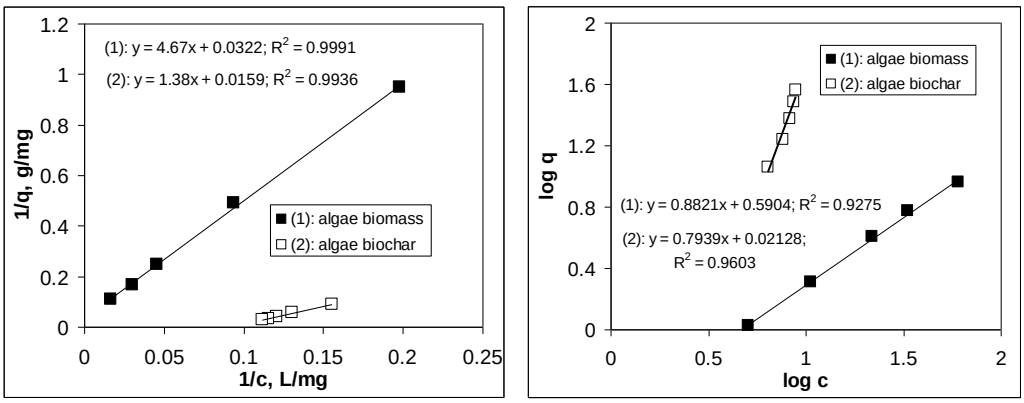
For the quantitative evaluation of the studied biosorption processes, the experimental data were modeled using the Langmuir and Freundlich isotherm models. The linear equations of these two models are the following [21, 22]:

(a) Langmuir model: $\frac{1}{q} = \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c}$ (3)

(b) Freundlich model: $\log q = \log K_F + \frac{1}{n} \cdot \log c$ (4)

where: q is the biosorption capacity at equilibrium, (mg/g); q_{max} is the maximum biosorption capacity, (mg/g); K_L is Langmuir constant, (L/g); c is equilibrium concentration of Zn(II) ions in solution, (mg/L); K_F is Freundlich constant, (L/g); n is the heterogeneity factor.

The linear representations of the Langmuir and Freundlich isotherm models for the biosorption of Zn(II) ions on algae biomass and algae biochar are illustrated in Fig. 3, while the obtained values of the characteristic parameters for each model are summarized in Table 1.



(a) (b)

Fig. 3. Linear representations of Langmuir (a) and Frendlich (b) isotherm models for Zn(II) ions biosorption on algae biomass and algae biochar.

Table 1. Isotherm parameters obtained for Zn(II) ions biosorption on algae biomass and algae biochar.

Model	Parameter	Algae biomass	Algae biochar
Langmuir	R^2	0.9991	0.9275
	q_{max}, mg/g	31.06	62.89
	K_L, L/g	0.007	0.012
Freundlich	R^2	0.9975	0.9603
	n	1.13	1.26
	K_F, L/g	3.89	1.05

Although each of the two isotherm models acceptably describes the experimental data, the Langmuir model is more relevant because it corresponds to a higher regression coefficient ($R^2 > 0.99$). This means that the biosorption of Zn(II) ions takes place mainly on the external surface of the biosorbents until a monolayer coverage is obtained. The maximum biosorption capacities (q_{max}, mg/g) calculated from the Langmuir isotherm model (Table 1), are much higher than the experimentally obtained values, suggesting that both biosorbents can be successfully used to remove high concentrations of Zn(II) ions from aqueous solution. Moreover, the almost double value of the maximum biosorption capacity obtained in the case of algae biochar compared to algae biomass shows that this biosorbent is much more efficient in the biosorption processes of metal ions. The superior biosorptive performance of algae biochar compared to algae biomass is also supported by the values of the Langmuir constants (K_L, L/g). The much higher value of this parameter (by an order of magnitude) (Table 1) suggests that the retention of metal ions on the surface of algae biochar involves more interactions, which are stronger (probably ion-exchange type), than in the case of algae biomass.

The values of heterogeneity factor (n), calculated from the Freundlich isotherm model, is higher than 1, indicating that both biosorbents have heterogeneous surfaces, on which the active sites are located on different geometric planes. However, the retention of Zn(II) ions takes place on the surface of the biosorbents, which means that some of the active sites will remain unoccupied, but inaccessible to interactions with metal ions. This is most likely the reason why the values of the biosorption capacities obtained experimentally and those calculated from the Langmuir model are so different.

3.3. Effect of contact time and kinetic modelling

The influence of contact time on the Zn(II) ions biosorption on algae biomass and algae biochar was examined at an initial Zn(II) ions concentration of 55 mg/L, pH of 5.0, biosorbent dosage of 4.0 g/L and room temperature (22 ± 1 °C). The obtained experimental results are illustrated in Fig. 4.

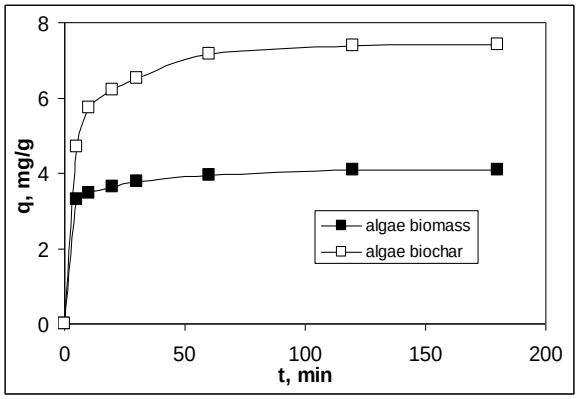


Fig. 4. Effect of contact time on Zn(II) ions biosorption efficiency on algae biomass and algae biochar.

As can be seen from Fig. 4, under the mentioned experimental conditions, the biosorption capacities of both biosorbents increase with the increase of the contact time over the entire studied interval. On the other hand, the variations illustrated in Fig. 4 shows that: (i) the biosorption capacities obtained in the case of algae biochar are higher than those obtained in the case of algae biomass, over the entire contact time interval, and (ii) for both biosorbents, the biosorption efficiency increases significantly up to 60 min, after which this increase is much slower, indicating that the biosorption processes have reach the equilibrium. The first observation shows once again that algae biochar is a much more efficient biosorbent for retaining Zn(II) ions from aqueous solution, and this is consistent with the experimental results presented in the previous section. The second observation indicates that in the initial stage of contact between the two phases, due to the large number of free active sites on biosorbents surface, the biosorption process is very fast. As contact time increases, the number of unoccupied sites decreases, making metal ions binding more difficult and, as a result, the rate of biosorption processes becomes much slower. This is a typical behavior for biosorption processes in which the binding of metal ions from aqueous solution occurs predominantly through electrostatic interactions [23]. Under these conditions, a contact time of 60 min can be considered sufficient for the quantitative removal of Zn(II) ions by biosorption on algae biomass and algae biochar, since the values of removal percent are higher than 90 %. In addition, reaching equilibrium in such a short time highlights the applicative potential of these biosorbent for large-scale systems.

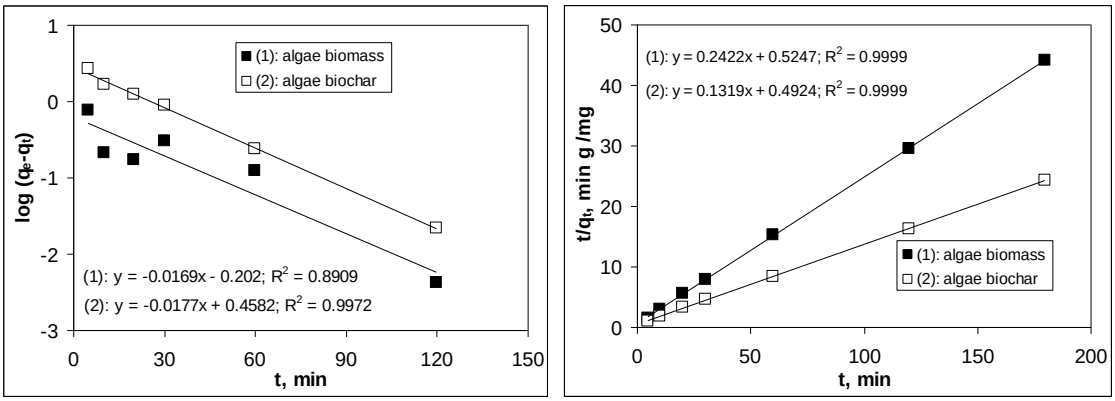
The modeling of the kinetic data obtained in the case of Zn(II) ions biosorption on algae biomass and algae biochar was performed using pseudo-first order and pseudo-second order kinetic models. The linear equations of these two models are [23, 24]:

(a) Pseudo-first order model: $\log(q_e - q_t) = \log q_e - k_1 \cdot t$ (5)

(b) Pseudo-second order model: $\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$ (6)

where: q_e, q_t are biosorption capacity at equilibrium and at time t, (mg/g); k_1 - rate constant of pseudo-first order kinetics model, (1/min); k_2 - pseudo-second order rate constant, (g/mg min).

In Fig. 5 are presented the linear representations of these two models for the biosorption of Zn(II) ions on algae biomass and algae biochar, while the kinetic parameters are summarized in Table 2. And in this case, the most appropriate kinetic model to describe the experimental data was selected based on the values of the regression coefficients (R^2), obtained from the statistic.



(a) (b)

Fig. 5. Linear representation of (a) pseudo-first order model and (b) pseudo-second order model for the biosorption of Zn(II) ions on algae biomass and algae biochar.

Table 2. Kinetic parameters obtained for Zn(II) ions biosorption on algae biomass and algae biochar.

Model	Parameter	Algae biomass	Algae biochar
	q_e^{exp}, mg/g	4.0781	7.4124
Pseudo-first order	R^2	0.8909	0.9972
	q_e^{calc}, mg/g	0.6281	2.8721
	k_1, 1/min	0.0169	0.0177
Pseudo-second order	R^2	0.9999	0.9999
	q_e^{calc}, mg/g	4.1288	7.5815
	k_2, g/mg min	0.1118	0.0353

The values of regression coefficients (R^2) indicate that the experimental data are best fit by the pseudo-second order kinetic model (Table 2), for both biosorbents. This observation is also supported by the close values of biosorption capacity calculated from model equation and obtained experimentally (Table 1). Therefore, the biosorption of Zn(II) ions on algae biomass and algae biochar involves chemical interactions, probably ion exchange type, and the binding of metal ions on the surface of biosorbents requires two binding sites in favourable geometric positions.

On the other hand, the values of the rate constants of the pseudo-second order kinetic model indicate that the biosorption of Zn(II) ions from aqueous solution take place easily on algae biomass compared to algae biochar. The significant difference between the values of the rate constants (of one order of magnitude) shown that if in the case of algae biomass, most of functional groups are located at the external surface of the biosorbent, in the case of algae biochar, the metal ions must also penetrate inside the pores to interact with the functional groups. This leads to higher biosorption capacities in the case of algae biochar compared to algae biomass, as seen in the previous section.

Based on these observations, two important practical consequences can be deduced, namely: (i) algae biochar obtained from algae biomass is a much more efficient biosorbent in the metal ions

retention processes, and (ii) in this case the biosorption processes occur predominantly trough an ion exchange mechanism, which will allow the quantitative recovery of the retained metal ions.

4. Conclusions

In this study, algae biomass (Ulva lactuca sp.) and the algae biochar (obtained from this biomass) were used as biosorbents for the removal of Zn(II) ions from aqueous media. Under optimal experimental conditions (initial pH of 5.0, 4.0 g biosorbent /L, 180 min of contact time and room temperature), the removal efficiency of Zn(II) ions is up to 63 % for marine algae biomass and up to 94 % for algae biochar. However, the isotherm and kinetic modelling of the experimental data have shown that algae biochar is more effective biosorbent compared with algae biomass. Thus, the maximum biosorption capacity, calculated from Langmuir model, was 2.1 time higher in the case of algae biochar than in the case of algae biomass. The analysis of the kinetic parameters shows that if in the case of algae biomass, most of functional groups are located at the external surface of the biosorbent, in the case of algae biochar, the metal ions must also penetrate inside the pores to interact with these. The experimental results included in this study show that algae biochar obtained from algae biomass is a much more efficient biosorbent in the metal ions removal processes, and that the biosorption processes occur predominantly trough an ion exchange mechanism, which will allow the quantitative recovery of the retained metal ions.

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References

[1] V.O. ARIEF, K. TRILESTARI, J. SUNARSO, N. INDRASWATI, S. ISMADJI: Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: Characterization, biosorption parameters and mechanism studies. *CLEAN–Soil Air Water*, ISSN 1863-0669, **36**, 937 (2008).

[2] A.T. JAN, M. AZAM, K. SIDDIQUI, A. ALI, I. CHOI, Q.M.R. HAQ: Heavy metals and human health: mechanistic insight into toxicity and counter defense system of antioxidants. *Int. J. Mol. Sci*., ISSN 1422-0067, **16**, 29592 (2015).

[3] S. MARTIN, W. GRISWOLD: Human health effects of heavy metals. *Environ. Sci. Technol. Br. Citizens*, **15**, 1 (2009).

[4] O.A. RAMIREZ CALDERON, O.M. ABDELDAYEM, A. PUGAZHENDHI, E.R. RENE: Current updates and perspectives of biosorption technology: an alternative for the removal of heavy metals from wastewater. *Curr. Pollut. Rep*., ISSN 21986592, **6**, 8 (2020).

[5] S. SARODE, P. UPADHYAY, M.A. KHOSA, T. MAK, A. SHAKIR, S. SONG, A. ULLAH: Overview of wastewater treatment methods with special focus on biopolymer chitin-chitosan. *Int. J. Biol. Macromol*., ISSN 0141-8130, **121**, 1086 (2019).

[6] T. HENNEBEL, N. BOON, S. MAES, M. LENZ: Biotechnologies for critical raw material recovery from primary and secondary sources: R&D priorities and future perspectives. *New Biotechnol*., ISSN 1871-6784, **32**, 121 (2015).

[7] M. BILAL, T. RASHEED, J.E. SOSA-HERNANDEZ, A. RAZA, F. NABEEL, H.M.N. IQBAL: Biosorption: An Interplay between Marine Algae and Potentially Toxic Elements - A Review. *Mar Drugs*, ISSN 1660-3397, **16**, 65 (2018).

[8] G. CRINI, E. LICHTFOUSE: Advantages and disadvantages of techniques used for wastewater treatment. Environm. *Chem. Lett*., ISSN 0366-7022, **17**, 145 (2019).

[9] E. ROMERA, F. GONZALEZ, A. BALLESTER, M.L. BLAZQUEZ, J.A. MUNOZ: Comparative study of biosorption of heavy metals using different types of algae. *Biores. Technol*., ISSN 0960-8527, **98**, 3344 (2007).

[10] B.A. AJI, Y. YAVUZ, A.S. KOPARAL: Electrocoagulation of heavy metals containing model

wastewater using monopolar ion electronedes. *Sep. Purif. Technol*., ISSN 1383-5866, **86**, 248 (2012).

[11] F. FU, Q. WANG: Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manag*., ISSN 0301-4797, **92**, 407 (2011).

[12] P.X. SHENG, Y.P. TING, P. CHEN, L. HONG: Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J. Colloid. Interface Sci*., ISSN 0021-9797, **275**, 131 (2004).

[13] K. CHOJNACKA: Biosorption and bioaccumulation – the prospects for practical applications. *Environ. Int*., ISSN 0160-4120, **36**, 299 (2010).

[14] T.A.H. NGUYEN, H.H. NGO, W.S. GUO, J. ZHANG, S. LIANG, Q.Y. YUE, Q. LI, T.V. NGUYEN: Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Biores. Technol*., ISSN 0960-8524, **148**, 574 (2013).

[15] A.A. EL GAMAL: Biological importance of marine algae. *Saudi Pharmaceut. J*., ISSN 1319-0164, **18**(1), 1, (2010).

[16] J. HE, J.P. CHEN: A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry, and modelling simulation tools. *Bioresour. Technol*., ISSN 0960-8524, **160**, 67 (2014).

[17] D. KUMAR, L.K. PANDEY, J.P. GAUR: Metal sorption by algal biomass: From batch to continuous system. *Algal Res*., ISSN 2211-9264, **18**, 95 (2016).

[18] Z. LIN, J. LI, Y. LUAN, W. DAI: Application of algae for heavy metal adsorption: A 20-year meta-analysis. *Ecotox. Environ. Safety*., ISSN 0147-6513, **190**, 110089 (2020).

[19] A.K. ZERAATKAR, H. AHMADZADEH, A.F. TALEBI, N.R. MOHEIMANI, M.P. MCHENRY: Potential use of algae for heavy metal bioremediation, a critical review. *J. Environ. Manag*., ISSN 0301-4797, **181**(1), 817 (2016).

[20] H. DEMEY, T. VINCENT, E. GUIBAL: A novel algal-based sorbent for heavy metal removal. *Chem. Eng. J*., ISSN 1385-8947, **332**, 582 (2018).

[21] K.H. CHONG, B. VOLESKY: Description of two-metal biosorption equilibria by Langmuir-type models. *Biotechnol. Bioeng*., ISSN 1097-0290, **47**(4), 451 (1995).

[22] S. RANGABHASHIYAM, N. ANU, M.S. NANDAGOPAL GIRI, N. SELVARAJU: Relevance of isotherm models in biosorption of pollutants by agricultural by-products. *J. Environ. Chem. Eng*., ISSN 2213-3437, **2**(1), 398 (2014).

[23] Y.S. HO, G. MCKAY: Pseudo-second-order model for sorption processes. *Process Biochem*., ISSN 1359-5113, **34**, 451 (1999).

[24] K.L. TAN, B.H. HAMEED: Insight into the adsorption kinetics models for the removal of contaminants from aqueous solutions. *J. Taiwan Inst. Chem. Eng*., ISSN 1876-1070, **74**, 25 (2017).