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Biosorption of zinc from aqueous solution by dried activated sludge biomass

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ABSTRACT

The biosorption potential of Zn(II) from aqueous solutions using activated sludge biomass was investigated. Optimum biosorption conditions were determined with respect to pH, adsorbent dose, contact time and temperature. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were applied to the equilibrium data. The maximum Zn(II) sorption capacity of activated sludge was found to be 76.92 mg g^{-1} at pH 6, biomass concentration 2 g L^{-1}, contact time 30 min and temperature 20°C. The calculated mean biosorption energy (9.82 kJmol^{-1}) using D–R model indicated that the biosorption of Zn(II) on the biomass was induced by chemical ion exchange.

Keywords: Biosorption; Activated sludge; Zinc; Isotherm parameters

1. Introduction

Water resources pollution caused by indiscriminate disposal of heavy metals has been causing worldwide concern in the last few decades. The effluents of industrial operations such as metal plating, electroplating, galvanizing plants, manufacture of batteries, textile, tannery operations, pigment and chemical manufacturing are major sources of zinc contaminants for surface waters [1,2]. Although zinc is an essential element in human health, as it participates in metabolism, which stimulates the enzymes and plays an important role in the functioning of immunologic system. It becomes toxic for humans at intake levels of 100–500 mg d^{-1} [3].

The WHO recommends the maximum acceptable concentration of zinc in drinking water as of 5.0 mg L^{-1} [4]. Therefore, the elimination of this metal from water and wastewaters is important to protect public health. The main techniques which have been used on zinc content reduction from industrial waste are chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis and solvent extraction [5,6]. These conventional techniques can reduce metal ions, but they are not sufficiently effective due to the limitations in the pH range as well as the high material and operational costs [7]. Hence, there is a crucial need for the development of a

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method which is highly selective, more efficient, easy to operate and hence cost-effective. Biosorption could be a good alternative technology.

Biosorption in natural or uncontrolled situations typically involves a combination of active and passive transport mechanisms starting with the diffusion of the metal ion to the surface of the microbial cell. Once the metal ion has diffused to the cell surface, it will bind to sites on the cell surface which exhibit some chemical affinity for the metal. These steps contain a number of passive accumulation processes and may include adsorption, ion exchange, coordination, complexation, chelation and micro-precipitation. Generally, such metal ion adsorption is fast, reversible and not a limiting factor in bioremoval kinetics when dealing with dispersed cells. Biosorption is often followed by a slower metal binding process in which additional metal ion is bound, often irreversibly. This slow phase of metal uptake can be due to a number of mechanisms, including covalent bonding, surface precipitation, redox reactions, crystallization on the cell surface or, most often, diffusion into the cell interior and binding to proteins and other intracellular sites [8–10].

The use of activated sludge biomass as adsorbent also offers a potential alternative to existing methods for heavy metal removal [11]. The cell walls of activated sludge biomass, essentially consisting of various organic compounds such as chitin, lipids, amino acids and other cellular components offer many functional groups which can bind metal ions such as carboxylate, hydroxyl, sulphate, phosphate and amino groups.

The goal of our study is to assess the Zn(II) biosorption potential of activated sludge. For this purpose, biosorption process was characterized with different operating conditions such as initial pH, contact time and temperature. The Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models were applied to the equilibrium data.

2. Materials and methods

2.1. Materials

The sludge was obtained from the municipal wastewater treatment plant of Kasserinein city in the central west of Tunisia. The biomass was centrifuged at 5,000 rpm for 15 min, dried at 70°C to constant weight and then grounded into powder. The modification was done by chemical treatment of 9 g of the sieved sludge with 400 mL of 0.15 mol L^{-1} HCl solution, the mixture was agitated for 10 h at 30°C. The activated sludge was washed with deionized water, until it reaches pH 5.5. It was later dried in the oven at about 80°C.The powder was sieved to obtain particle sizes under 250 μm, and was further used as the biosorbent.

2.2. Reagents and equipment

A stock solution of zinc was prepared by dissolving appropriate amount of zinc chloride ($ZnCl_2$) in 1 L of Milli-Q water. The initial concentration of zinc used is in the range of 10 mg L^{-1} to optimize the process parameters, and for the equilibrium isotherm studies the metal concentrations were varied between 10 and 450 mg L^{-1}. The equilibrium metal concentrations were determined by inductively coupled plasma mass spectrometry ICP (ACTIVA; Horiba-JobinYvon, Ales, France).

2.3. Batch biosorption experiments

The biosorption equilibrium experiments of Zn(II) were performed using a batch process to determine the amount of metal ion adsorbed by biomass samples under the effect of contact time, biosorbant dosage, pH and temperature of adsorption medium. Necessary amount of the dried biomass was equilibrated in a series of aqueous solutions (25 mL) placed in conical flasks containing different amounts of metal at a constant pH, which was adjusted with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solution at the beginning of each experiment. The flasks were shaken for the desired contact time in an electrically thermostatic reciprocating shaker (HS 501 digital; KIKA Labortechnik,) at 150 rpm. The experiments were repeated at 20, 30 and 40°C. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time, till equilibrium was reached. The contents of the flask were centrifuged and the centrifuge was analysed for metal concentration by using ICP. The per cent biosorption of metal ion was calculated as follows Eq. (1).

$$\text{Biosorption } (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final (or equilibrium) metal concentrations, respectively.

To ensure the accuracy, reliability and reproducibility of the collected data, the measurements were carried out in duplicated and the average values are presented. Throughout the study, the contact time was varied from 5 to 90 min, the pH from 2 to 8 and the initial metal concentration C_i from 10 to 450 mg L^{-1}.

3. Results and discussion

3.1. Effect of pH solution

The metal biosorption depends on the protonation or unprotonation of functional groups (such as, amino, carboxyl and phosphate groups) on the surface of the cell wall. The ionic forms of the metal ions in solution and electrical charge of the cell wall components depend on the solution pH [12]. The biosorption of Zn(II) onto activated sludge was studied over a pH range of 2–8 at room temperature; this temperature was fixed according to the published works [13,14], the results are given in Fig. 1.

As seen from Fig. 1, the uptake of free ionic Zn(II) depends on pH, increasing with the increase in pH from 2 to 6 and then decreasing with increasing pH. At pH values lower than 3 Zn(II), removal was inhibited possibly as a result of the competition between hydrogen and Zn(II) ions on the sorption sites with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carboxylate groups in the cell walls of activated sludge would increase the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the sorption onto the cell surface [15]. Above pH 6, insoluble Zn(II) hydroxide starts precipitating from the solution, so that adsorption rate was decreased. As a result, the optimum pH for Zn(II) biosorption was found as 6 and the other biosorption experiments were performed at this pH value [16].

3.2. Effect of biomass dosage

The effect of biomass dosage on the biosorption of Zn(II) ions was studied using different biomass dosage in the range of 0.5–6 g L^{-1} (Fig. 2).

From this figure, it is observed that the biosorption yield firstly increased from 60 to 94.4% with an increase in the biomass concentration from 0.5 to 2 g L^{-1}. This is due to an increase in the surface area of the biosorbent, which consequently increases the number of binding sites [17]. Further increase in biosorbent dose did not entail an increase in the biosorption yield for Zn^{2+}. This can be explained by the decreased active binding sites on the biosorbent as a result of partial aggregation at higher amount of biosorbent [18]. Therefore, 2 g L^{-1} was selected as optimum biosorbent concentration that would be required for cost-effective treatment of Zn^{2+} ions.

3.3. Effects of contact time and temperature

The rate of sorption is of most important when designing batch adsorption experiments. Consequently, it is important to establish the time dependence of such systems under various process conditions. The experimental runs measuring the effect of contact time on the batch sorption of metal solution containing 10 mg L^{-1} of zinc and initial pH value 6 is shown Fig. 3.

According to this figure, the biosorption yield of Zn(II) increases with rise in contact time up to 25 min at 20–40°C. After this time there was no considerable increase. Therefore, the optimum contact time was

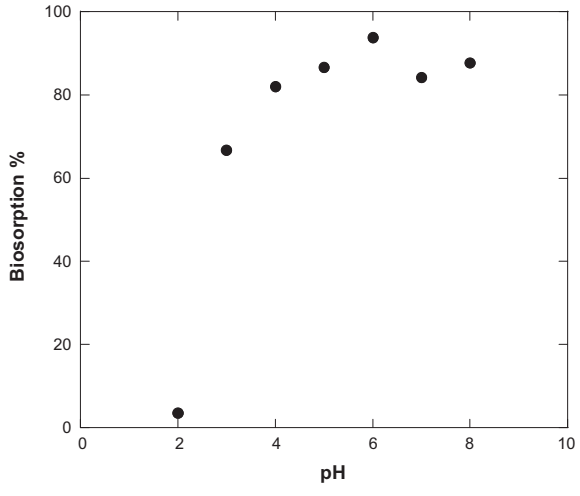

Fig. 1. Effect of pH on biosorption of Zn(II) onto activated sludge (metal concentration C_i = 10 mg L^{-1} and temperature = 20°C).

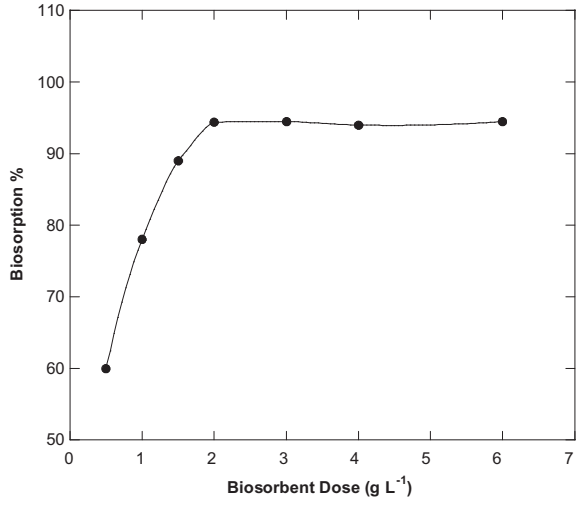

Fig. 2. Effect of biomass dosage on biosorption of Zn(II) by activated sludge (metal concentration: 10 mg L^{-1}; pH 5 and temperature: 20°C).

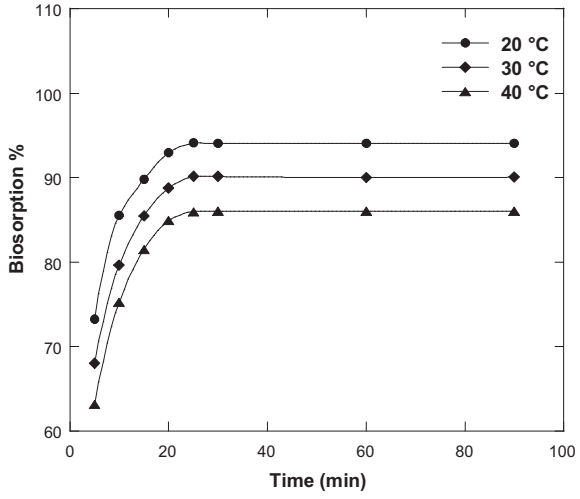

Fig. 3. Effect of contact time and temperature on biosorption of Zn(II) by activated sludge (metal concentration $C_i = 10$ mg L^{-1}, pH 6 and biomass dosage = 2 g L^{-1}).

selected as 25 min for further experiments. On the other hand, the biosorption percentage decreased from 94 to 86% as temperature was increased from 20 to 40°C for the equilibrium time 25 min. This result indicated the exothermic nature of Zn(II) biosorption onto activated sludge biomass. A decrease in the biosorption of Zn(II) ions with the rise in temperature may be due to either the damage of active binding sites in the biomass or increasing tendency to desorb metal ions from the interface to the solution [19,20]. The optimum temperature was selected as 20°C for further biosorption experiments.

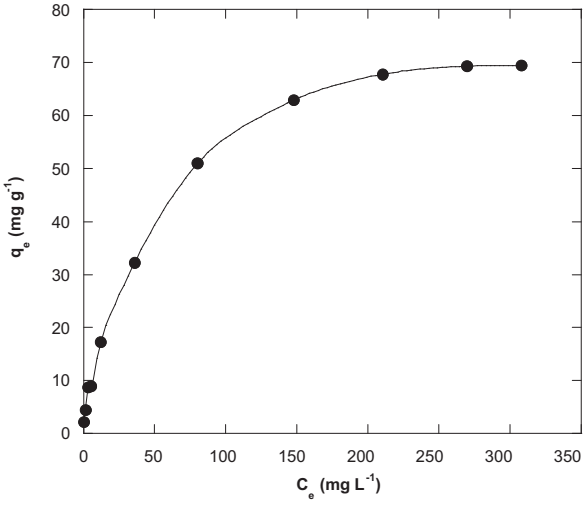

Fig. 4. Zn(II) sorption isotherms using activated sludge (metal concentration $C_i = 10$ mg L^{-1}, temperature = 20°C, pH 6, biomass dosage = 2 g L^{-1} and contact time = 25 min).

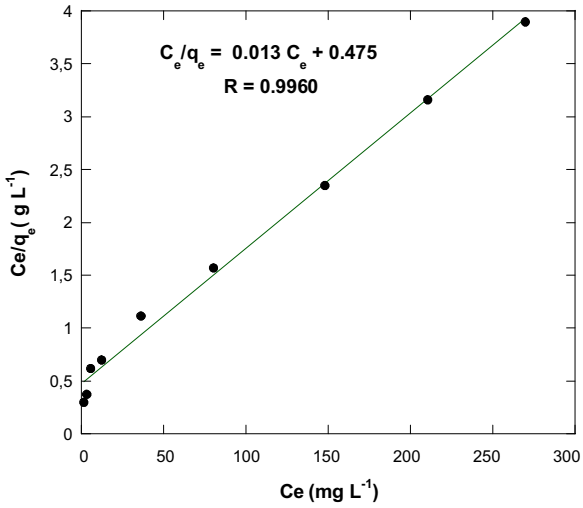

Fig. 5. Langmuir isotherm plots for biosorption of Zn(II) onto activated sludge (metal concentration $C_i = 10$ mg L^{-1}, temperature = 20°C, pH 6, biomass dosage = 2 g L^{-1} and contact time = 25 min).

3.4. Biosorption isotherms

The isotherm represents the equilibrium relationship between the adsorption capacity of the adsorbent (q_e) and the final metal concentration in the aqueous phase (C_e). For optimization of the biosorption process design, it is necessary to obtain the appropriate correlation for the equilibrium curve. The isotherm studies were carried out at optimum temperature 20°C [21]. Fig. 4 illustrates the dynamic biosorption of zinc onto

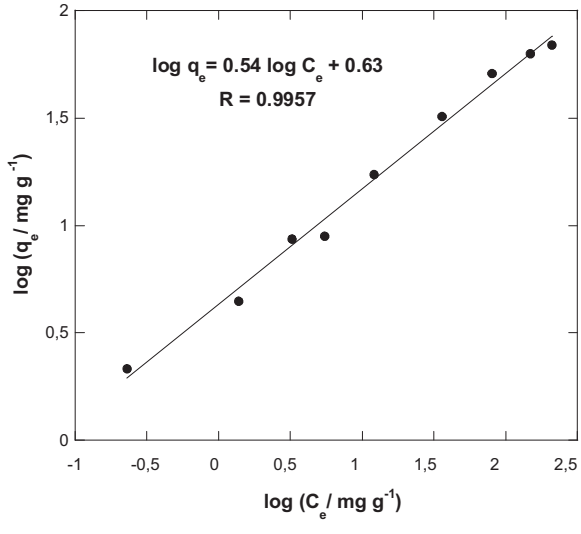

Fig. 6. Freundlich isotherm plots for biosorption of Zn(II) onto activated sludge (metal concentration $C_i = 10$ mg L^{-1}, temperature = 20°C, pH 6, biomass dosage = 2 g L^{-1} and contact time = 25 min).

Table 1
The isotherm parameters for the biosorption of Zn(II) onto activated sludge biomass

Langmuir parameters				Freundlich parameters			D–R parameters		
q_m (mg g^{-1})	b (L mg^{-1})	R_L	R	k_F		R	β (mol J^{-2})	E (kJ mol^{-1})	R
76.92	2.73×10^{-2}	0.78	0.9960	4.26	0.54	0.9957	5.18×10^{-9}	9.82	0.9958

activated sludge. The amount of Zn(II) uptake by activated sludge (q) was determined using the mass balance equation

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

In this study, the equilibrium data were evaluated by three isotherms models, which are namely the Langmuir, Freundlich and D–R isotherm models were analysed.

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent [22]. This model can be written in linear form

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (3)$$

where q_e is the equilibrium metal ion concentration on the biosorbent (mg g^{-1}), C_e is the equilibrium metal ion concentration in the solution (mg L^{-1}), q_{max} is the monolayer biosorption capacity of the biosorbent (mg g^{-1}) and b is the Langmuir biosorption constant (L mg^{-1}) relating the free energy of adsorption. The values of q_{max} and Langmuir constant b were calculated from the slope and intercept of the linear plot of C_e/q_e vs. C_e (Fig. 5).

As seen from the figure, the value of correlation coefficient ($R^2 = 0.9920$) shows that the biosorption of zinc ions onto activated sludge biomass fitted well with the Langmuir model indicates the formation of monolayer coverage of heavy metal ions on the outer surface of biosorbant [23,24]. The maximum biosorption capacity (q_m) and Langmuir constant (b) were found to be 76.92 mg g^{-1} and -2.73×10^{-2}L mg^{-1}, respectively. To determine if sorption process is favourable or unfavourable for the Langmuir-type sorption process, the isotherm can be classified by the dimensionless constant separation factor, R_L, can be defined by the Eq. (3)

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

The value of $R_L < 1$ indicates unfavourable, $R_L = 1$ linear, $0 < R_L < 1$ favourable or $R_L = 0$ irreversible sorption [25]. The R_L value for the study was found to be 0.78 for Zn(II) biosorption onto activated sludge.

The Freundlich isotherm model is employed to describe the adsorption on heterogeneous surface and is not restricted to the formation of monolayer. The linear form of the Freundlich adsorption isotherm can be defined by the following equation [26]:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (5)$$

where k_f is the constant related to the biosorption capacity and $1/n$ is the empirical parameter related to the biosorption intensity of the adsorbent. The dimensionless constant $1/n$ (or heterogeneity factor) gives an indication of the adsorption intensity [27]. It is generally admitted that low values of $1/n$ ($0.1 < 1/n < 0.5$) are characterized by good adsorption, whereas higher values indicate a moderate adsorption ($0.5 < 1/n < 1$) or a low one ($1/n > 1$) [28,29]. The Freundlich isotherm constants k_f and $1/n$ were calculated from the slopes and intercepts of the linear plot of $\log q_e$ vs. $\log C_e$(Fig. 6). The values of k_f and $1/n$ are listed in Table 1. The $1/n$ values were between 0 and 1, indicating that the biosorption of Zn(II) onto activated sludge biomass was favourable at studied conditions.

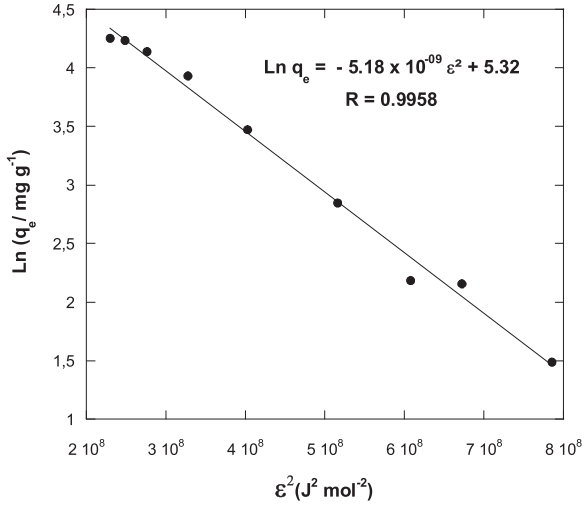

Fig. 7. D–R isotherm plots for adsorption of Zn(II) onto activated sludge (metal concentration $C_i = 10$ mg L^{-1}, temperature = 20°C, pH 6, biomass dosage = 2 g L^{-1} and contact time = 25 min).

Table 2
Comparison of biosorption capacity of activated sludge biomass for Zn(II) with that of other adsorbent

Adsorbents	pH	Temperature (°C)	Biosorption capacity (mg g^{-1})	References
Orange peel	5	30	25.00	[36]
Short hemp fibre	5.5	20–25	8.00	[37]
Lignin	5.5	20	28.30	[38]
Commercial activated carbon	5–6	27	20.52	[39]
Activated sludge	6	20	76.92	Present study

The D–R isotherm is more general than Langmuir isotherm since it does not assume a homogeneous surface or constant biosorption potential. It was applied to distinguish between the physical and chemical biosorption of Zn(II) [30].

The linear presentation of the D–R isotherm equation [31] is expressed by Eq. (6)

$$\text{Ln } q_e = \text{Ln } q_m - \beta\varepsilon^2 \quad (6)$$

where q_e is the amount of metal ions adsorbed on per unit weight of adsorbent (mol L^{-1}), q_m is the maximum adsorption capacity (mol g^{-1}), β is the activity coefficient related to adsorption mean free energy (mol^2 J^{-2}) and ε is the Polanyi potential $\left[\varepsilon = RT \text{ Ln } (1 + \frac{1}{C_e})\right]$.

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.9914 (Fig. 7). From the intercept of the plots, the adsorption mean free energy E (kJ mol^{-1}) is as follows [32,33]

$$E = \frac{1}{\sqrt{2\beta}} \quad (7)$$

Within DR equation the E (kJ mol^{-1}) value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ mol^{-1}, the adsorption process takes place chemically and while, $E < 8$ kJ mol^{-1} the adsorption process proceeds physically [34].

The mean adsorption energy was calculated as 9.82 kJ/mol for the biosorption of Zn(II) ions. This result indicated that the biosorption process of Zn(II) onto activated sludge may be carried out via chemical ion-exchange mechanism because the sorption energy lies within 8–16 kJ/mol [35]. All the isotherm parameters are listed in Table 1.

3.5. Comparison of adsorption capacities of the adsorbents for the removal of Zn(II) with different adsorbents reported in literature

The sorption capacity of activated sludge biomass for the removal of Zn(II) has been compared with capacities of different biosorbents reported in literature (Table 2). Generally, the maximum adsorption capacity depends on experimental conditions such as temperature, adsorbent dose and pH. According to the published works [36–39], the q_{max} of activated sludge was higher than that of others, but despite that several methods have been used to modify natural adsorbents either physically or chemically in order to improve the sorption capacity especially in acidic condition. However, it can be noteworthy that the activated sludge biomass has important potential for the removal of Zn(II) ions from aqueous solution.

4. Conclusion

The potential of activated sludge biomass for the removal of Zn(II) ions from aqueous solutions was dependent on biosorption process such as pH, biosorbant dose, contact time and temperature. The Langmuir biosorption isotherm was demonstrated to provide the best correlation for the biosorption of Zn(II) ions onto activated sludge. The maximum biosorption capacity was found to be 76.92 mg of Zn(II) per gram of activated sludge. The calculated mean free energy (9.82 kJ mol^{-1}) from the D–R model indicated that the biosorption of Zn(II) using activated sludge was taken place by chemical ion-exchange. The comparative study revealed that the retention capacity of the activated sludge is substantially greater than that of the commercial activated carbon thus, indicating that this support can be an effective alternative to the removal of the ions Zn(II) from aqueous solutions.

References

[1] H. Weng, C.P. Huang, Adsorption characteristics of Zn(II) from dilute aqueous solution by fly ash, Colloid Surf., A. 247 (2004) 137–143.
[2] F. Arias, T.K. Sen, Removal of zinc metal ion (Zn^{2+}) from its aqueous solution by kaolin clay mineral: A kinetic and equilibrium, Colloid Surf., A. 348 (2009) 100–108.

[3] USDHHS, Toxicological profile for zinc, Agency for Toxic Substances and Disease Registry, US Department of Health & Human Services, Atlanta, GA, 1993.
[4] A.K. Bhattacharya, S.N. Mandal, S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents, Chem. Eng. J. 123 (2006) 43–51.
[5] A.C. Abuk, T. Akar, S. Tunalı, O. Tabak, Biosorption characteristics of *Bacillus* sp. ATS-2 immobilized in silica gel for removal of Pb(II), J. Hazard. Mater. B136 (2006) 317–323.
[6] A.I. Zouboulish, M. Loukidou, K.A. Matis, Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal polluted soils, Biochem. Eng. J. 39 (2004) 909–916.
[7] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by Mucor hiemalis, Biochem. Eng. J. 23 (2005) 185–192.
[8] S. Al-Asheh, F. Banat, D. Al-Rousan, Beneficial reuse of chicken feathers in removal of heavy metals from wastewater, J. Clean. Prod. 11 (2003) 321–326.
[9] A. Gundogdu, D. Ozdes, C. Duran, V.N. Bulut, M. Soylak, H.B. Senturk, Biosorption of Pb(II) ions from aqueous solution by pine bark (*Pinus brutia Ten*.), Chem. Eng. J. 153 (2009) 62–69.
[10] A. Witek-Krowiak, Analysis of influence of process conditions on kinetics of malachite green biosorption onto beech sawdust, Chem. Eng. J. 171 (2011) 976–985.
[11] Z. Aksu, D. Akpınar, Modelling of simultaneous biosorption of phenol and nickel(II) onto dried aerobic activated sludge, J. Sep. Purif. Technol. 21 (2000) 87–99.
[12] L. Deng, Y. Su, H. Su, X. Wang, X. Zhu, Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*, J. Hazard. Mater. 143 (2007) 220–225.
[13] R. Katal, H. Zare, H.T. Rahmati, G.N. Darzi, Biosorption of zinc from aqueous solutions using dried activated sludge, Eng. Manag. J. 11(4) (2012) 857–865.
[14] T. Phuengprasop, J. Sittiwong, F. Unob, Removal of heavy metal ions by iron oxide coated sewage sludge, J. Hazard. Mater. 186 (2011) 502–507.
[15] S.T. Akar, S. Arslan, T. Alp, D. Arslan, T. Akar, Biosorption potential of the waste biomaterial obtained from Cucumis melo for the removal of Pb^{2+} ions from aqueous media: Equilibrium, kinetic, thermodynamic and mechanism analysis, Chem. Eng. J. 185–186 (2012) 82–90.
[16] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, X. Wang, Biosorption of cadmium(II), zinc(II) and lead(II) by Penicillium simplicissimum: Isotherms, kinetics and thermodynamics, J. Hazard. Mater. 160 (2008) 655–661.
[17] A.Y. Dursun, A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*, Biochem. Eng. J. 28 (2006) 187–195.
[18] B. Cordero, P. Lodeiro, R. Herrero, M.E.S. de Vicente, Biosorption of cadmium by *Fucus spiralis*, Environ. Chem. 1 (2004)180–187.
[19] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, J. Hazard. Mater. 122 (2005) 161–170.
[20] A. Sarı, M. Tuzen, Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (*Ulva lactuca*) biomass, J. Hazard. Mater. 152 (2008) 302–308.
[21] S. Veli, B. Alyüz, Adsorption of copper and zinc from aqueous solutions by using natural clay, J. Hazard. Mater. 149 (2007) 226–233.
[22] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[23] E. Kusvuran, D. Yildirim, A. Samil, O. Gulnaz, A study: Removal of Cu(II), Cd(II), and Pb(II) ions from real industrial water and contaminated water using activated sludge biomass, Clean Soil, Air, Water 40 (11) (2012) 1372–1283.
[24] J.M. Lezcano, F. González, A. Ballester, M.L. Blázquez, J.A. Muñoz, C.G. Balboa, Biosorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) using different residual biomass, Chem. Ecol. 26 (2010) 1–17.
[25] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.
[26] H.M.F. Freundlich, Adsorption in solution, Phys. Chem. Phys. 40 (1906) 1361–1368.
[27] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—An agricultural waste, Water Res. 36 (2002) 2304–2318.
[28] D.A. Boast, Large scale chrome recovery from chrome wash liquors, J. Am. Leather Chemists Assoc. 83 (1988) 17–23.
[29] W.J. Weber Jr., Physico-Chemical Processes for Water Quality Control, Wiley, New York, NY, 1972.
[30] U.R. Malik, S.M. Hasany, M.S. Subhani, Sorptive potential of sunflower stem for Cr(III) ions from aqueous solutions and its kinetic and thermodynamic profile, Talanta 66 (2005) 166–173.
[31] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Sorption and structure of active carbons. I. Adsorption of organic vapors, Zh. Fiz. Khim. 21 (1947) 1351–1362.
[32] A. Dąbrowski, Adsorption from theory to practice, Adv. Colloid Interface Sci. 93 (2001) 135–224.
[33] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces, Chem. Rev. 60 (1960) 235–241.
[34] F. Helfferich, Ion Exchange, McGraw Hill, New York, NY, 1962, p. 166.
[35] A. Sari, M. Tuzen, Cd(II) adsorption from aqueous solution by raw and modified kaolinite, Appl. Clay Sci. 88–89 (2014) 63–72.
[36] S. Liang, X. Guo, Q. Tian, Adsorption of Pb^{2+} and Zn^{2+} from aqueous solutions by sulfured orange peel, Desalination 275 (2011) 212–216.
[37] M. Vukcevic, B. Pejic, M. Lausevic, I. Pajic-Lijakovic, M. Kostic, Influence of chemically modified short hemp fiber structure on biosorption process of Zn^{2+} ions from waste water, Fiber Polym. 15(4) (2014) 687–697.
[38] X. Guo, S. Zhang, X.Q. Shan, Adsorption of metal ions on lignin, J. Hazard. Mater. 151 (2008) 134–142.
[39] U. Kouakou, A.S. Ello, J.A. Yapo, A. Trokourey, Adsorption of iron and zinc on commercial activated carbon, J. Environ. Chem. Ecotoxicol. 5 (2013) 168–171.