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Original article

Application of radiotracer technique in remediation of Zn(II) from aqueous solutions by dry cowdung powder

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ABSTRACT

Heavy metal pollution is caused due to anthropogenic activities and is considered as a serious environmental problem which endangers human health and environment. The present study deals with biosorption, an eco-friendly technique for the removal of heavy metal Zn(II) from aqueous medium. Various natural materials have been explored for the uptake of metal ions, where most of them are physically or chemically enhanced. Dry cowdung powder (DCP) has been utilized as a low-cost, environmentally friendly humiresin without any pre-treatment, thus demonstrating the concept of Green Chemistry. Batch biosorption studies using ^{65}Zn(II) tracer were performed and the impact of different experimental parameters was studied. Results revealed that at pH 6, 94 ± 2% of Zn(II) was effectively biosorbed in 5 min, at 303 K. The process was spontaneous and exothermic, following pseudo-second-order reaction. The mechanism of heavy metal biosorption employing green adsorbent was therefore elucidated in order to determine the optimal method for removing Zn(II) ions. DCP has a lot of potential in the wastewater treatment industry, as seen by its ability to meet 3A's affordability, adaptability, and acceptability criteria. As a result, DCP emerges as one of the most promising challengers for green chemistry and the zero-waste idea.

1. Introduction

Heavy metals are non-biodegradable chemical species that accumulate in the environment and in living beings, causing serious damage to the entire ecosystem of the planet [1]. Water contaminated with heavy metals can easily reach surface water as well as ground water, and thereby possess significant threat to aquatic and human life. Thus to tackle water pollution, we have adopted Green Chemistry [2], which is a sustainable solution and one of the treatment method and waste disposal strategy.

The present study deals with the metal ion Zn(II), which in low concentration, is considered as an important micronutrient for living beings, while in elevated amounts it is highly toxic, leading to respiratory and abdominal disorders [3]. Although zinc is abundant in the environment, its deficiency related issues in animals and humans have been noted in the literature [4–6].

Zinc pollution is caused due to several anthropogenic activities but mining, steel production, smelting and petrochemical manufacturing are the primary activities that generate polluted remains [7]. There are several reports of water and soil pollution by zinc and other heavy metals in Nigeria, Brazil, etc. [8,9]. Zhang et al. [10], studied the effect of zinc smelting and mining on the health of humans and on the environment. As a result, the ever-expanding interest and applications of zinc have generated a great demand for accurate and reliable technique for removal of zinc from wastewaters and effluents.

Several methods have been employed over the years for eliminating heavy metals from waste waters, in particular, physical and chemical precipitation, ion-exchange, electrochemical treatment, flotation, coagulation and filtration [11–13]. Most of these techniques, however, have some shortcomings such as high expenditure, poor selectivity, complicated treatment technique as well as production of toxic chemical sludge [14]. Therefore, in comparison with these techniques, biosorption is one of the most economical and environment friendly method, particularly when the concentration of contaminants is not high.

According to literature review, Zn(II) has been removed from aqueous solutions by employing water hyacinth [15], corn cob [16], waste green sands [17], crab shell [18], wheat straw [19], lemon grass [20], papaya wood [21], spent mushroom substrate [22], microbial cultures like *Aspergillus niger* [23], *Saccharomyces cerevisiae*

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[24], *Ngella sativa* seeds [25], *Streptomyces rimosus* [26], *Bacillus subtilis* [27], *Pseudomonas putida* [27], etc. Most of these sorbents need complex pre-treatment procedures and higher reaction times; some even necessitate the use of living microbial fora for metal ion adsorption, which increases the amount of sludge generated and calls into question the process's economic and green credibility.

Dry cowdung powder (DCP), a biological sorbent has been used in the present investigation without any pre- or post-modifications, proving its benign composition for wastewater treatment. It possesses an innate property of sequestering heavy metal ions from aqueous systems due to the presence of in-active dead biomass like fungi, aerobic heterotrophic bacteria viz. *Acinetobacter* sp., and petroleum utilizing bacteria such as *Pseudomonas* sp. [28]. It also has a vital importance in Ayurveda research, owing to its unambiguous biological, chemical as well as microbiological properties. DCP is preferable to the others since it is a humified biological waste matter that does not require any pre-treatment. Moreover, it improves soil fertility while reducing erosion and acidity. It's also being looked at as a biofuel, as well as a green and clean source of energy. Thus, DCP, correctly characterizes itself as *"Nothing in Nature is a Waste" and "Waste is a Commodity."*

Over the past few years, DCP has been extensively studied as a green biosorbent for the remediation of several heavy metals and radionuclides from waste-waters [29,30]. Characterization of DCP was carried out by N. Barot and H. Bagla [31,32] using SEM and FTIR techniques, which confirmed the existence of phenol, quinol, amide, and carboxyl groups in the binding of metal ions. In addition, it also revealed that DCP has a heterogeneous, permeable and a rough surface with some holes and small openings, which increases the contact area during adsorption and promote pore diffusion. Hence, the potential of DCP, as a low-cost, zero-waste prototype green biosorbent has been proven to be a good alternative for warding off various environmental problems associated with heavy metal pollution.

Thus, by following the principles of Green Chemistry, batch biosorption study was carried out for the uptake of Zn(II) from aqueous solutions employing DCP as an eco-friendly biosorbent, and was investigated by using radioactive zinc tracer.

2. Experimental

2.1. Adsorbate & adsorbent

All the chemicals utilized in the experiment were of analytical grade. Stock solution of 1 mg/mL Zn(II) was prepared in distilled water using $ZnNO_3$, and was standardized using standard method of analysis [33].

Keshav Shrushti, Research Center on Cow Product (Thane, India) provided DCP of particle size of 100 mesh. Appropriate precautions were taken to avoid contamination of the adsorbent.

2.2. Tracer technique

Radiotracers can either be used qualitatively as a simple process marker or quantitatively to determine the measure of non-radioactive species. Besides, there is no substantial interference from any new species that can hinder the analysis. Compared to conventional technologies, tracer technique provides many unique advantages such as simplicity, high-sensitivity, non-destructive design, and low cost.

^{65}Zn (in HCl) was used as a radiotracer in the present study and was procured from Board of Radiation and Isotope Technology (BRIT), Trombay, Mumbai.

2.3. Batch biosorption mode

Batch adsorption studies were performed to efficiently remove Zn(II) metal ion using DCP, as a green biosorbent. Known amount of adsorbent was mixed at room temperature and pressure with 10 mL of solution comprising $^{65}Zn(II)$ radiotracer and 1 mg/mL $ZnNO_3$ carrier solution. pH of the solution was adjusted with dil. HNO_3 and NaOH as required, and total volume was made to 15 mL by using distilled water. The resulting solution was equilibrated with mechanical stirrer (Remi RQT 127 A/D) for 5 min and then centrifuged for the next 10 min.

Single channel NaI(Tl) well type gamma ray spectrometer (PSP649/N, PEA GRS-301) was used to determine the activity in the solution acquired, after the supernatant was separated.

The effect of various experimental parameters such as pH (from 1 to 10), metal ion concentration (0.1–20 mg/mL), contact time (0–30 min), adsorbent dose (3.33–53.33 g/L), temperature (278–363 K), were studied for an efficient adsorption process and to maximize the amount of zinc that can be recovered from the solution. Characterization of DCP (before and after biosorption) was also carried out using Energy Dispersive X-Ray Analysis (EDAX) technique (Model – XGT 7200, Source – Rhodium; HORIBA Micro X-Ray Analysis, Japan) for its quantitative as well as qualitative elemental composition [34]. Thermodynamic and kinetic studies were also conducted in order to optimize the system and make it feasible for real time application.

2.4. Statistical analysis of experimental data

To ensure the reproducibility of the experimental data, the measurements have been carried out in triplet and calculated using percentage biosorption formula [35] as given below:

$$\%\ \text{Biosorption} = \frac{A(i) - A(f)}{A(i)}\ X\ 100 \quad (1)$$

where, A(i) is the initial activity taken, and A(f) is the final activity in the supernatant.

Equilibrium adsorption capacity (q_e) was also calculated by the following formula.

$$q_e = \frac{(C_o - C_e)}{m}\ X\ V \quad (2)$$

where, C_o is the initial Zn(II) concentration, C_e is its concentration at equilibrium, m is the mass of the adsorbent used per batch experiment and V is the final solution volume.

3. Results and discussion

3.1. EDAX (Energy Dispersive X-ray analysis)

For confirmation of the biosorption process, we had carried out EDAX analysis of DCP, before and after biosorption of Zn(II), as shown in Fig. 1. The spectral studies clearly revealed that the mechanism involved in the adsorption process was not ion exchange, because the metal ion of interest, Zn(II) was present on DCP after biosorption, along with all other natural elements that were present before biosorption, this is obvious from the post-biosorption EDAX spectra. Fig. 1 (inset).

3.2. Effect of pH

Sorption studies were carried out at pH 1–10. By adding the necessary amount of dil. nitric acid and dil. sodium hydroxide in the

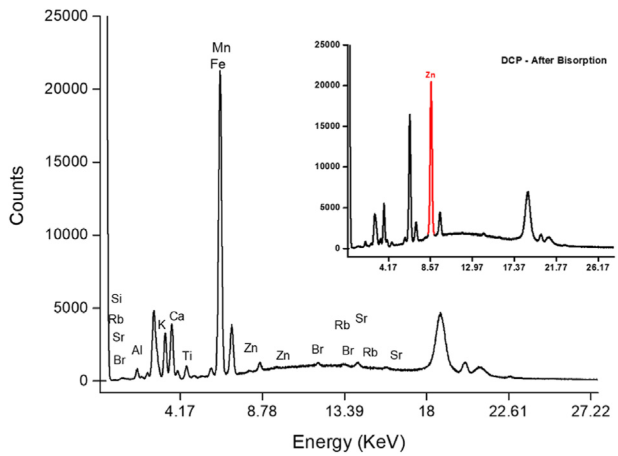

Fig. 1. EDAX spectrum of DCP before biosorption & (inset) DCP after bisorption of Zn(II).

solution, acidic and alkaline pH of the media was retained. Parameters such as adsorbent dose, initial metal ion concentration, contact time and temperature remained constant during the experiments.

Influence of pH on biosorption of Zn(II) was determined and the results have been presented graphically in Fig. 2. The uptake of zinc by DCP was maximum in the acidic range and minimum in the basic, i.e., beyond pH 7. Literature study reveals [36,37] that at low pH values there is abundance of H^+ ions and at this stage adsorption becomes unfavorable. However, zinc is divalent and DCP has a greater affinity for divalent metal ions. Thus, biosorption is not affected at low pH. In alkaline pH range, $Zn(OH)_2$ is formed in the solution, which is mildly soluble in water. Since Zn(II) is trapped by the hydroxide ions, its uptake by the biosorbent decreases, as shown in Fig. 2.

3.3. Effect of amount of biosorbent and isotherm modelling

Adsorbent dosage has a great impact on the process of biosorption because it provides various binding sites for the uptake of metals. To attain maximum percentage biosorption, amount of DCP was varied from 3.33 to 53.33 g/L and their influence on biosorption of Zn(II) is displayed in Fig. 3.

Sorption of Zn(II) by DCP increased with an increase in the amount of biosorbent from 3.33 to 26.67 g/L, but stabilized at higher doses. This may be owing to the absence of metal binding sites as well as the blockage of sites because of surplus biosorbent, thereby reducing the effective biosorption surface area. Therefore, biosorbent dosage of 20 g/L was employed in the succeeding experiments. The findings of Munagapati et al., Subbaiah et al. back up these assertions [38,39].

Isotherm studies are important for every sorption system because they can provide insights into the binding reaction mechanisms. The experimental data was subjected to two important isotherm models: Langmuir [40] and Freundlich [41]. A monolayer sorption process on a homogenous adsorbent surface is implied by the Langmuir model, while, the Freundlich model predicts multilayer sorption on a heterogeneous surface [42]. For Zn(II) sorption on DCP, the Freundlich model was found to be the best fit, implying that the sorbent surface is heterogeneous and involves multilayer biosorption.

Equation (3) can be used to express the Freundlich model, as shown below [41].

$$\log q_e = (1/n) \log C_e + \log K_F \quad (3)$$

where, K_F is the Freundlich constant ($L\ g^{-1}$) and n is the Freundlich exponent ($g\ L^{-1}$). C_e is the concentration of metal ions in the supernatant at equilibrium ($mg\ L^{-1}$) and q_e is the adsorption capacity ($mg\ g^{-1}$). Fig. 4 depicts the plot of the Freundlich isotherm model.

The values of isotherm constants were computed using the aforementioned graph, as shown in Table 1. The graph displayed a good Freundlich isotherm plot for zinc removal by DCP, as evidenced by the value of the regression coefficient (R^2), which is 0.96.

As shown in Table 1, the value of 1/n (binding affinity) is less than 1, indicating that the process involves chemisorption with favorable adsorption at low metal ion concentrations

3.4. Effect of contact time and kinetic modelling

Influence of this parameter was determined by varying the contact time of the equilibrium process from 0 to 30 min and maintaining all other parameters constant, as obtained above.

Fig. 5 illustrates that as the contact time rises from 0 to 5 min, percentage biosorption increases and the sorption curve exhibits a short linear portion, followed by a plateau region, showing that there is no appreciable change in the percentage biosorption after 5 min. This may be attributed to the instantaneous utilization of the most readily available adsorbing sites on DCP. The trend in Fig. 5 showed rapid kinetics followed by equilibrium achievement. Therefore, 5 min of contact time proved sufficient for the system

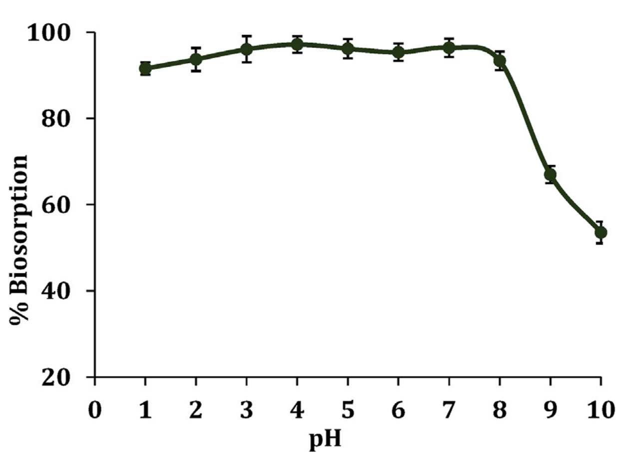

Fig. 2. Effect of pH on biosorption of Zn(II).

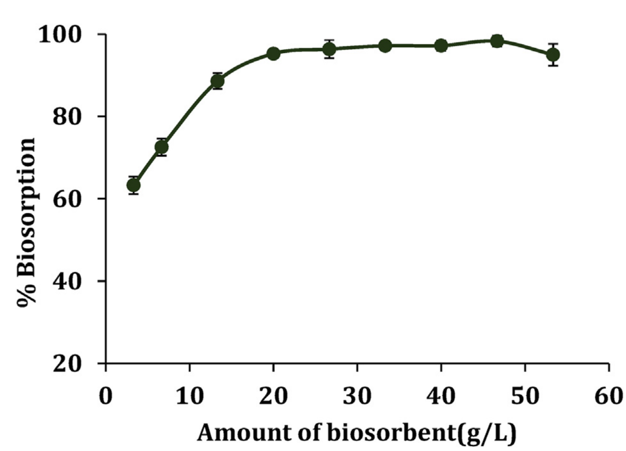

Fig. 3. Effect of amount of biosorbent on biosorption of Zn(II).

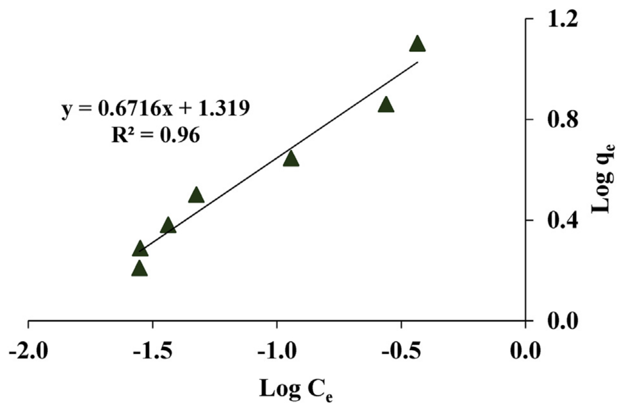

Fig. 4. Freundlich isotherm plot for the biosorption of Zn(II) on DCP.

Table 1
Freundlich isotherm variables for biosorption of Zn(II) on DCP.

Biosorbent	Adsorbent dose	% Biosorption	1/n	R^2
DCP	300 mg (20 g/L)	94 ± 2	0.67	0.96

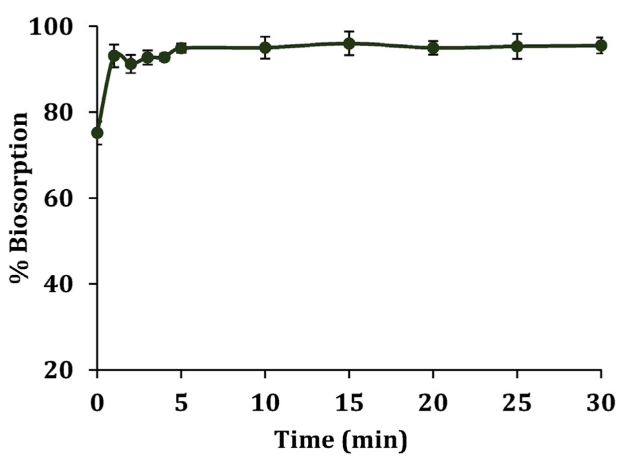

Fig. 5. Effect of contact time on biosorption of Zn(II).

and was taken as the optimum time for further experiments. Several previous studies on the biosorption of metal ions on varied biomasses revealed nearly identical trend [43–46].

In addition to establishing minimal time for the removal of Zn(II), effect of contact time also offers essential information regarding adsorption mechanism by studying its kinetics. Thus Lagergren pseudo-first order and Ho & McKay pseudo-second order kinetic models were fitted to the adsorption kinetic data, and among the two, pseudo-second order model was found to be the one with the best fit. The linear form of this model was applied to the experimental data, using the following rate expression [47].

$$\frac{t}{q_t} = \frac{1}{(k_2\, q_e^2)} + \left(\frac{1}{q_e}\right) t \tag{4}$$

where, q_e and q_t are the metal uptake capacities (mg/g), at equilibrium and at time t, respectively, and k_2 is the equilibrium rate constant (g/mg min) for pseudo-second order kinetic model.

Fig. 6 illustrates the plot of t/q_t versus t. As seen from the figure, a straight line plot representing a linear relationship was attained for the biosorption of Zn(II) on DCP, thereby proving the applicability of this model. Moreover, the value of regression coefficient, R^2 was equal to 1 (Table 2), which also proves the same. Accordingly, this model suggests that the sorption mechanism was based on chemical reaction between the metal ion and active biosorbent sites.

The kinetic variables, k_2 (rate constant) and q_e (adsorption capacity) were deduced with the help of slope and intercept of the plot t/q_t versus t. As seen from Table 2, calculated q_e value was found to be in good agreement with the experimental q_e value, which also suggests pseudo-second order to be a good fitting model.

3.5. Effect of temperature

To study the influence of temperature, experiments were conducted by varying the temperature range from 278 to 363 K. It is clear from Fig. 7 that there is a minimal impact of temperature on biosorption of Zn(II) by DCP, i.e., it gradually increases from 88% to 95%. These results indicate the occurrence of chemisorption between DCP and Zn(II) ions, rather than a mere physical interaction. 93.2% of Zn(II) biosorption is obtained at room temperature (303 K).

Therefore, 303 K favors the rate of adsorption and thermodynamic studies have verified the same. All the further experiments were carried out at this temperature.

3.6. Thermodynamic parameters

In order to understand the effect of temperature, feasibility and nature of the biosorption method, different thermodynamic parameters such as enthalpy (ΔH°), change in free energy (ΔG°) and entropy (ΔS°) were assessed using the Vant Hoff's equations [48] given below.

$$\ln K_a = \frac{\Delta S^\circ}{R} - \frac{\Delta H}{RT} \tag{5}$$

$$\Delta G^\circ = -RT\ln K_a \tag{6}$$

where, R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K) and K_a is the distribution coefficient (L/g).

As seen in Fig. 8, a graph of $\ln K_a$ versus 1/T was plotted. The slope and intercept were obtained graphically and used to determine the values of enthalpy change ΔH° (kJ/mol) and entropy change ΔS° (J/mol K), as presented in Table 3.

If the value of ΔG° is negative, it implies that a reaction, at a given temperature occurs spontaneously. Thus, from Table 3, it is

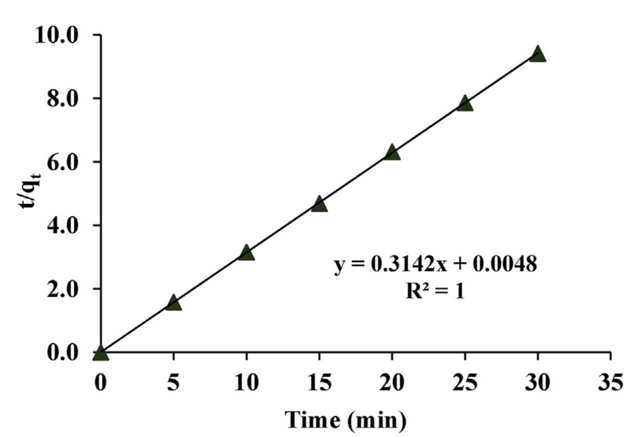

Fig. 6. Ho & McKay pseudo-second order kinetic plot for the biosorption of Zn(II) on DCP.

Table 2
Kinetic variables for Ho and McKay pseudo-second order model.

Biosorbent	k_2	$q_{e(Graph)}$(mg/g)	$q_{e(Calc.)}$(mg/g)	R^2
DCP	20.57	3.18	3.13	1

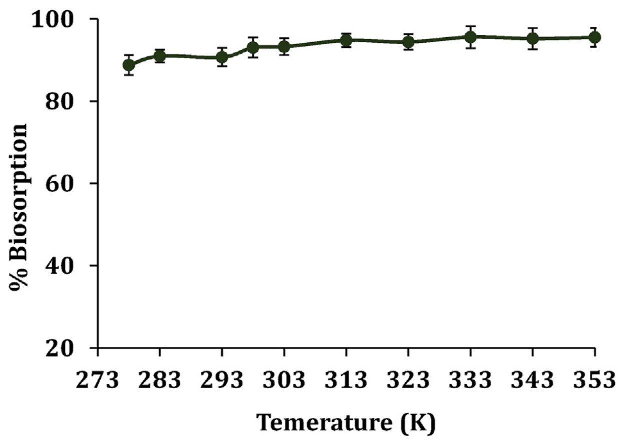

Fig. 7. Effect of temperature on biosorption of Zn(II).

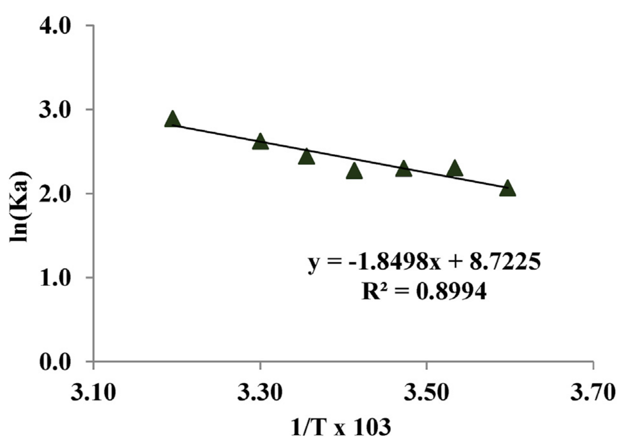

Fig. 8. Thermodynamic plot of lnk_a versus 1/T for the biosorption of Zn(II) on DCP.

clear that the biosorption process by DCP was favorable and spontaneous throughout the temperature range. The negative value of ΔH° revealed that the process was exothermic in nature. Whereas, positive entropy indicated an increase in randomness of the system, suggesting a favorable reaction with greater affinity of DCP for Zn(II) ions.

3.7. Effect of metal ion concentration

The influence of initial concentration of zinc ions on the biosorption process was studied in the range of 0.1–20.0 mg/mL.

As demonstrated in Fig. 9, biosorption of Zn(II) was dependent on the initial metal ion concentration. At low concentration, number of Zn(II) ions was less than the available sites of adsorbent.

Table 3
Thermodynamic variables for the biosorption of Zn(II) on DCP.

Biosorbent	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)	R^2
DCP	−15.38	72.52	−6.61	0.89

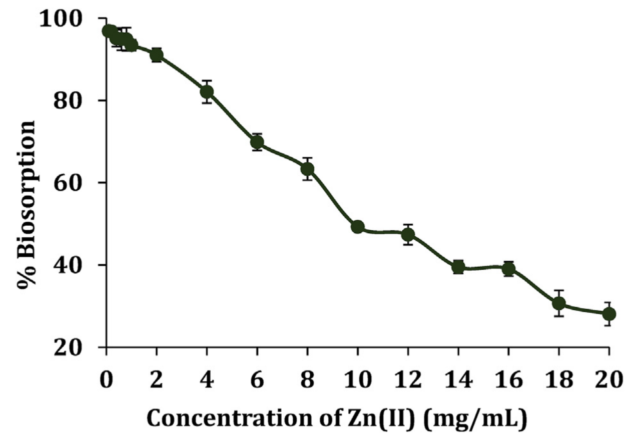

Fig. 9. Effect of metal ion concentration on biosorption of Zn(II).

Thus, adsorption became independent of metal ion concentration. However at higher concentration of Zn(II), the available sites on DCP became fewer in comparison with the available metal ions, and hence the percentage adsorption decreased. A similar pattern was discovered by a number of other researchers [49–51]. This was owing to an increase in the number of ions competing for the available binding sites of the biomass.

4. Conclusion

In this work, removal of Zn(II) from aqueous solutions by DCP was investigated. From the above batch biosorption study we conclude that at pH 6 with 20 g/L DCP, at room temperature (303 K), having 5 min of contact time and 500 rpm of agitation speed, 94 ± 2% of Zn(II) removal was obtained.

Kinetic studies revealed that the process followed Ho & McKay pseudo-second order model, which indicated that the chemical reaction between Zn(II) and active sites of DCP was fundamental in the biosorption process. Thermodynamic studies confirmed the biosorption to be spontaneous and exothermic chemical process. It's worth noting that all of the sorption experiments in this study were set up for a 5-min contact period. As a result, the method's green nature is underlined by the quicker reaction time, chemical-free process, and simple adsorbent supply.

From the results and discussions, it can therefore be confirmed that DCP has a significantly high biosorption efficiency to extract Zn(II) ions, thereby proving to be an eco-friendly, sustainable and feasible adsorbent that can play a great role in the treatment of industrial wastewaters and effluents. This can be achieved by initial pilot-scale plants and further scale-up depending on experimental parameters.

There are several areas of research that are yet to be covered. A major part of our future work will be interference of different organic as well as inorganic salts, and cationic effect on the metal ion. To ensure the green nature of the technique, desorptive nature of the biosorbent will also be taken into account for the complete remediation of Zn(II).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] M.V. Blanco, D.I. Cattoni, P. Carriquiriborde, J.R. Grigera, O. Chara, Kinetics of bioaccumulation of heavy metals in Odontesthes bonariensis is explained by a single and common mechanism, Ecol. Model. 274 (2014) 50–56.
[2] P. Anastas, J. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.
[3] L. Zhu, A.H. Younes, Z. Yuan, R.J. Clark, 5-Arylvinylene-2,2'-bipyridyls: bright "push-pull" dyes as componentes in fluorescente indicators for zinc ions, J. Photochem. Photobiol. Chem. 311 (2015) 1–15.
[4] J. Nriagu, Zinc toxicity in humans: Encycl. Environ. Heal. (2011) 801–807.
[5] L.M. Gaetke, C.K. Chow, Copper toxicity, oxidative stress, and antioxidant nutrients, Toxicology 189 (2003) 147–163.
[6] A. Prasad, Zinc deficiency: its characterization and treatment, Met. Ions Biol. Syst. 41 (2004) 103–137.
[7] R.C. Sahu, R. Patel, B.C. Ray, Adsorption of Zn(II) on activated red mud: neutralized by CO2, Desalination 266 (2011) 93–97.
[8] A.O. Oje, N.P. Uzoegwu, N.I. Onwurah, U.U. Nwodo, Environmental pollution levels of lead and zinc in ishiagu and uburu communities of Ebonyi state, Nigeria, Bull. Environ. Contam. Toxicol. 85 (2010) 313–317, https://doi.org/10.1007/s00128-010-0082-1.
[9] A. Goncalves, H. Nacke, D. Schwantes, G. Coelho, Heavy metal contamination in Brazilian agricultural soils due to application of fertilizers, in: Environ. Risk Assess. Soil Contam., In Tech Open, 2014, https://doi.org/10.5772/57268.
[10] X. Zhang, L. Yang, Y. Li, H. Li, W. Wang, B. Ye, Impacts of lead/zinc mining and smelting on the environment and human health in China, Environ. Monit. Assess. 184 (2012) 2261–2273, https://doi.org/10.1007/s10661-011-2115-6.
[11] A.I. Zouboulis, K.A. Matis, B.G. Lanara, Removal of cadmium from dilute solutions by hydroxylapatite II. Flotation studies, Separ. Sci. Technol. 32 (1997) 1755–1767.
[12] L. Charerntanyarak, Heavy metals removal by chemical coagulation and precipitation, Water Sci. Technol. 39 (1999) 135–138.
[13] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere 56 (2004) 91–106.
[14] A. Witek-Krowiak, R.G. Szafran, S. Modelski, Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, Desalination 265 (2011) 126–134.
[15] R. Gandhimathi, S.T. Ramesh, V.M. Arun, P.V. Nidheesh, Biosorption of Cu(II) and Zn(II) ions from aqueous solution by water hyacinth (Eichhornia crassipes), Int. J. Environ. Waste Manag. 11 (2013) 365–386.
[16] A. Buasri, N. Chaiyut, K. Tapang, S. Jaroensin, S. Panphrom, Equilibrium and kinetic studies of biosorption of Zn(II) ions from wastewater using modified corn cob, APCBEE Procedia 3 (2012) 60–64.
[17] T. Lee, J.-W. Park, J.-H. Lee, Waste green sands as reactive media for the removal of zinc from water, Chemosphere 56 (2004) 571–581.
[18] C. Zhou, X. Gong, J. Han, R. Guo, Removal of Pb(II) and Zn(II) from aqueous solutions by raw crab shell: a comparative study, Water Environ. Res. 88 (2016) 374–383.
[19] M. Gorgievski, D. Boziu, V. Stankoviu, N. Strbac, S. Serbula, Kinetics, equilibrium and mechanism of Cu^{2+}, Ni^{2+} and Zn^{2+} ions biosorption using wheat straw., Ecol. Eng. 58 (n.d.) 113–122.
[20] X. Zuo, R. Balasubramanian, D. Fu, H. Li, Biosorption of copper, zinc and cadmium using sodium hydroxide immersed Cymbopogon schoenanthus L. Spreng (lemon grass), Ecol. Eng. 49 (2012) 186–189.
[21] A. Saeed, M.W. Akhter, M. Iqbal, Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, Separ. Purif. Technol. 45 (2005) 25–31, https://doi.org/10.1016/j.seppur.2005.02.004.
[22] M. Corral-Bobadilla, A. González-Marcos, E.P. Vergara-González, F. Alba-Elías, Bioremediation of waste water to remove heavy metals using the spent mushroom substrate of Agaricus bisporus, Water (Switzerland) (2019) 11, https://doi.org/10.3390/w11030454.
[23] M. do S. Vale, R.F. do Nascimento, R.C. Leitão, S.T. Santaella, Cr and Zn biosorption by Aspergillus Niger, Environ. Times. Earth Sci 75 (2016) 462–473, https://doi.org/10.1007/s12665-016-5343-9.
[24] C. Chen, J. Wang, Cation (K+, Mg2+, Na+, Ca2+) release in Zn (II) biosorption by Saccharomyces cerevisiae, Huanjing Kexue 27 (2006) 2261–2267.
[25] F. Al-Tohami, M.A. Ackacha, R.A. Belaid, M. Hamaadi, Adsorption of Zn(II) ions from aqueous solutions by novel adsorbent: Ngella sativa seeds, APCBEE Procedia 5 (2013) 400–404.
[26] A. Chergui, M. Bakhti, A. Chahboub, S. Haddoum, A. Selatnia, G. Junter, Simultaneous biosorption of Cu^{2+}, Zn^{2+} and Cr^{6+} from aqueous solution by Streptomyces rimosus biomass, Desalination 206 (2007) 179–184.
[27] S.Z. Sabae, M. Hazaa, S.A. Hallim, N. Awny, D. S, Bioremediation of Zn^{+2}, Cu^{+2} and Fe^{+2} using Bacillus subtilis D215 and Pseudomonas putida biovar A D225, Biosci. Res. 3 (2006) 189–204.
[28] S.B. Akinde, O. Obire, Aerobic heterotrophic bacteria and petroleum-utilizing bacteria from cow dung and poultry manure, World J. Microbiol. Biotechnol. 24 (2008) 1999–2002, https://doi.org/10.1007/s11274-008-9700-z.
[29] N.S. Barot, H.K. Bagla, Biosorption of radiotoxic ^{90}Sr by green adsorbent: dry cow dung powder, J. Radioanal. Nucl. Chem. 294 (2012) 81–86, https://doi.org/10.1007/s10967-011-1539-3.
[30] S.A. Shaikh, H.K. Bagla, Comparative study of ^{110m}Ag(I) removal from aqueous media by humic substances, J. Radioanal. Nucl. Chem. 322 (2019) 225–230, https://doi.org/10.1007/s10967-019-06691-7.
[31] N.S. Barot, H.K. Bagla, Eco-friendly waste water treatment by cow-dung powder (Adsorption studies of Cr(III), Cr (VI) & Cd(II) using Tracer Technique), Desalin. Water Treat. 38 (2012) 104–113.
[32] N.S. Barot, H.K. Bagla, Studies on biosorption of Cr(VI) on a green resin : dry cow dung poeder and tracer technique, Radiochim. Acta 100 (2012) 833–842, https://doi.org/10.1524/ract.2012.1973.
[33] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, Fifth Edit, Longman Scientific & Technical Copublished with John Wiley and Sons Inc., New York, 1989.
[34] G. Balasubramanian, S.A. Muthukumaraswamy, Element analysis with fundamental parameters using an XRF spectrum analysis MATLAB algorithm, Int. J. Eng. Appl. Sci. 3 (2016) 2394–3661. www.ijeas.org.
[35] S. Faust, O. Aly, Adsorption Processes for Water Treatment, first ed., Elsevier, 1986.
[36] K. Uthra, K. Kadirvelu, Biosorption of nickel using mixed cultures of Pseudomonas aeruginosa and Bacillus subtilis, Def. Life Sci. J. 2 (2017) 442, https://doi.org/10.14429/dlsj.2.12278.
[37] W.T. Tan, K. Majid, Removal of lead, cadmium and zinc by waste tea leaves, Environ. Technol. Lett. 9 (1988) 1223–1232.
[38] V. Munagapati, V.S. Yarramuthi, S.K. Nadavala, S.R. Alla, K. Abburi, Biosorption of Cu(II), Cd(II) and Pb(II) by Acacia leucocephala bark powder: kinetics, equilibrium and thermodynamics, Chem. Eng. J. 157 (2010) 357–365, https://doi.org/10.1016/j. cej.2009.11.015.
[39] M.V. Subbaiah, Y.S. Yun, Biosorption of nickel(II) from aqueous solution by the fungal Mat of Trametes versicolor (rainbow) biomass: equilibrium, kinetics, and thermodynamic studies, Biotechnol. Bioproc. Eng. 18 (2013) 280–288, https://doi.org/10.1007/s12257-012-0401-y.
[40] L. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.
[41] H. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.
[42] O.E. Okeola FO, Freundlich and Langmuir isotherms parameters for adsorption of methylene blue by activated carbon derived from agrowastes, Adv Nat Appl Sci 4 (2010) 281–288.
[43] Z.Z. Abidin, A.N. Bakar, M.Y. Harun, M.M.A. Salleh, Biosorption of Zn (II) from aqueous solution by jatropha curcas press cake, J. Sci. Ind. Res. 73 (2014) 191–194.
[44] U. Israel, U.M. Eduok, Biosorption of zinc from aqueous solution using coconut (Cocos nucifera L) coir dust, Arch. Appl. Sci. Res. 4 (2012) 809–819. www.scholarsresearchlibrary.com.
[45] E. Valdman, L. Erijman, F.L.P. Pessoa, S.G.F. Leite, Continuous biosorption of Cu and Zn by immobilized waste biomass Sargassum sp, Process Biochem. 36 (2001) 869–873, https://doi.org/10.1016/S0032-9592(00)00288-0.
[46] M. Horsfall, F. Ogban, E.E. Akporhonor, Sorption of chromium(VI) from aqueous solution by cassava (Manihot sculenta cranz.), Waste Biomass, Chem. Biodivers. 3 (2006) 161–174, https://doi.org/10.1002/cbdv.200690019.
[47] E. Bulut, M. Ozacar, Adsorption of malachite green ontobentonite: equilibrium and kinetic study and process design, Microporous Mesoporous Mater. 115 (2008) 234–246.
[48] H.E. Bakouri, J. Usero, J. Morillo, A. Ouassini, Adsorptive features of acid-treated olive stones for drin pesticides: equilibrium, kinetic and thermodynamic modeling studies, Bioresour. Technol. 100 (2009) 4147–4155.
[49] R.R. Navarro, S. Wada, K. Tatsumi, Heavy metal precipitation by polycation–polyanion complex of PEI and its phosphonomethylated derivative, J. Hazard Mater. 123 (2005) 203–209.
[50] P. King, N. Rakesh, S. Beena, Y. Prsanna, V.S.R.K. Prasad, Biosorption of zinc onto Syzygium cumini L.: equilibrium and kinetic studies, Chem. Eng. J. 144 (2008) 181–187.
[51] T.W. Tee, M.A.R. Khan, Removal of lead, cadmium and zinc by waste tea leaves, Environ. Technol. Lett. 9 (1988) 1223–1232.