

Continuous biosorption of nickel from aqueous solution using *Chrysanthemum indicum* derived biochar in a fixed-bed column

Sowmya Vilvanathan and S. Shanthakumar

ABSTRACT

The biosorption capability of *Chrysanthemum indicum* to remove nickel ions from aqueous solution in a fixed-bed column was examined in this study. Native *C. indicum* flower waste was improved for its biosorptive potential by pyrolysis to obtain its biochar form and thereby, both raw (CIF-R) and biochar (CIF-BC) forms of the flower were used for Ni(II) removal. Fixed bed column studies were conducted to examine the influence of bed height (1.0–3.0 cm), flow rate (1.0–5.0 mL min⁻¹) and initial metal ion concentration (25–75 mg L⁻¹). The breakthrough curves (C_{out}/C_{in} vs time) were modelled using different dynamic adsorption models, viz. Adam-Bohart, Thomas and Yoon-Nelson model. Interpretation of the data revealed a favorable correlation with the Thomas model with higher R² values and closer model-predicted and experimental biosorption capacity values. The equilibrium uptake capacity of CIF-R and CIF-BC for Ni(II) were found to be 14.02 and 29.44 mg g⁻¹, respectively. Further, the column was regenerated using HCl as eluent, to desorb the adsorbed Ni(II) ions. The experimental results implied and affirmed the suitability of the biosorbents for nickel ion biosorption with its nature being favorable, efficient, and environment friendly.

Key words | biochar, biosorption, breakthrough curve, *C. indicum*, fixed-bed column, nickel

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INTRODUCTION

Heavy metals discharged from untreated industrial and municipal effluents are among the main sources of water pollution in the recent past. In the environmental context, heavy metals are defined as those which form positive ions in solution and have densities five times greater than that of water (Anandkumar & Mandal 2009). The acute toxicity and carcinogenicity associated with metal ions discharged into the aquatic system pose a serious threat to the environment. These heavy metals find their way into the microenvironment, the aquatic flora and fauna and in turn into the food chain exhibiting direct health effects on humans (Hashim *et al.* 2011). Nickel is a hard, silvery white, ferromagnetic, naturally occurring transition metal. Anthropogenic sources of nickel release into the environment includes, nickel mining operations, and industries like nickel-cadmium battery, nickel mining and smelting, and nickel alloy production units that exploit nickel, nickel compounds and nickel alloys for their production process. Exposure to higher concentrations of nickel can

lead to lung embolism, respiratory failure, allergic dermatitis, higher chances of developing lung, nose, larynx and prostate cancer (Das *et al.* 2008). Considering the health hazards associated with nickel and its compounds and to meet the desired discharge standards, nickel concentration in industrial effluent should be reduced and treated effectively.

Various treatment techniques have been developed and adopted to mitigate heavy metal pollution, including, chemical precipitation, ion-exchange, adsorption, electrocoagulation, flocculation, membrane filtration (Fu & Wang 2011). The extent of applicability of a technique depends on the initial metal ion concentration, the capital investment and operating costs, presence of other components in wastewater, reliability of the technique and its environmental impacts. Considering all these factors, biosorption techniques prove to be advantageous in terms of economics, ease, and in being environment-friendly and sustainable in removing heavy metal ions from aqueous solution.

Biosorption is a metal ion sequestration process that utilizes biomaterials for sorbing, sequestering and immobilizing inorganic heavy metal ions from aqueous solution (Volesky 2001). Biosorption is recognized as an effective and economic method for heavy metal removal with the advantages of being flexible in design and operation, producing high-quality treated effluent, in addition to being reversible as the biosorbents can be regenerated by suitable desorption methods (Fang *et al.* 2013). Column studies are essential for the application of the technology at pilot-plant and industrial scale treatment. Laboratory fixed-bed column studies are conducted to determine the effect of bed height, initial metal ion concentration and flow rate that could possibly affect the capacity of the biosorbent in removing metal ions from aqueous solution. Based on the metal binding capacities of various plant-based biomass, heavy metals can be separated from industrial effluents by a passive binding process (Choi & Yun 2006). The efficiency of biosorbents is based on their capacity, affinity and specificity for metal ions along with their physicochemical nature. Plant-based wastes, agricultural and forestry residues in their natural or modified form have been effective in nickel ion sequestration, as reported by many researchers (Oliveira *et al.* 2005; Parab *et al.* 2006; Bhatnagar & Minocha 2010; Reddy *et al.* 2011; Flores-Garnica *et al.* 2013; Chithra *et al.* 2014; Sudha *et al.* 2015).

The biosorbents can be enhanced to have the desired physical and chemical attributes to enrich its biosorptive capability and increase its affinity towards metal ion uptake from aqueous solution. Physical activation of biosorbents includes a range of thermochemical conversion technologies including pyrolysis, combustion and gasification. Pyrolysis, considered as the representative technology has been widely employed for biomass conversion to biochar and its subsequent use as biosorbent for metal ion removal. The properties of biochar including the porous structure, aromatic surface and the presence of oxygen functional groups makes it appropriate for entrapping the metal ions from aqueous solution (Inyang *et al.* 2012). Conversion of waste biomass to biochar and further applying it for pollutant remediation is an eco-friendly way of waste management and pollutant alleviation. Application of biochar for various pollution remediation strategies has been gaining widespread attention, due to its characteristic affinity for contaminants and its potential carbon sequestration ability (Inyang & Dickenson 2015).

In this research work, *Chrysanthemum indicum*, a flowering herb commonly called as 'chrysanthus' and known mostly for its ornamental and decorative purpose, is studied

here for its biosorptive potential. *C. indicum* are grown in abundance and the flowers of the plant after its decorative use have no significant value and are considered waste. Considering its relative adequacy and abundant availability, these flowers can be a potential resource of natural biosorbent (Teixeira da Silva *et al.* 2013). Hence, in this study, *C. indicum* in its native and biochar form were used as biosorbents to remove Ni(II) ions from aqueous solution in continuous mode in a fixed-bed column. The biosorption capacity of *C. indicum* was investigated in terms of its effect on varying bed height, flow rate and initial nickel ion concentration. The column experimental data were evaluated and fitted using different dynamic adsorption models, viz. Adam-Bohart, Thomas and Yoon-Nelson models.

MATERIALS AND METHODS

Preparation of Ni(II) stock solution

Nickel ion stock solution of 1.0 g L^{-1} was prepared by dissolving accurately weighed amounts of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (SDFCL, Mumbai) in one litre of double distilled water. The metal ion stock solution was diluted to obtain Ni(II) ion concentrations of 25, 50 and 75 mg L^{-1} . 0.1 M HCl was used as desorbing agent. Double distilled water was used for all dilutions and column experiments. All chemicals and reagents used in this study were of analytical reagent grade and were used without any further purification.

Preparation and characterization of biosorbents

The dried flowers of the *C. indicum* plant were collected and their petals were removed and washed with tap water to remove any dust particles adhered to them. The washed material was dried in an air oven at 80°C for twelve hours and subsequently powdered using a domestic mixer. The powder was further passed through a 150μ sieve to obtain *C. indicum* flower biomass in its raw state (CIF-R). CIF-R was carbonized in a muffle furnace at 650°C for a holding time of 60 minutes under oxygen limiting conditions to yield the biochar form of *C. indicum* (CIF-BC). The pyrolyzing temperature and holding time were chosen based on a series of trial experiments. CIF-R and CIF-BC were further used in column experiments to adsorb nickel ions from aqueous solution. The BET surface area of CIF-R and CIF-BC are 0.783 and $1.726 \text{ m}^2 \text{ g}^{-1}$, respectively (Vilvanathan & Shanthakumar 2016). The X-diffraction (XRD) pattern of the biosorbents, viz. CIF-R and CIF-BC were studied

before and after the biosorption of Ni(II) ions employing a BRUKER D8 Advance Powder XRD using Cu-K α radiation over the 2 θ angle range of 5°–80°.

Column biosorption experiments

Laboratory fixed-bed column studies were carried out using cylindrical glass columns at 303 K. A schematic representation of the glass column is presented in Figure 1. The columns were connected to a digital peristaltic pump (Ravel- RHP-S100, India) to deliver nickel ion solution of pH 5.0 at the desired flow rate in a downward flow. The influence of varying parameters, viz. bed height (1.0, 2.0, 3.0 cm), flow rate (1.0, 2.5, 5.0 mL min⁻¹) and initial Ni(II) concentration (25, 50, 75 mg L⁻¹) were studied to determine the column behavior in the continuous biosorption of nickel ions from aqueous solution. The adsorbent bed in the column was supported with a layer of glass wool at the bottom in order to avoid any loss of biosorbent. The effect of each parameter was studied by varying the parameter under study and holding the other parameters constant. The samples were collected at predetermined intervals and were analyzed using atomic absorption spectroscopy (Varian, AA240).

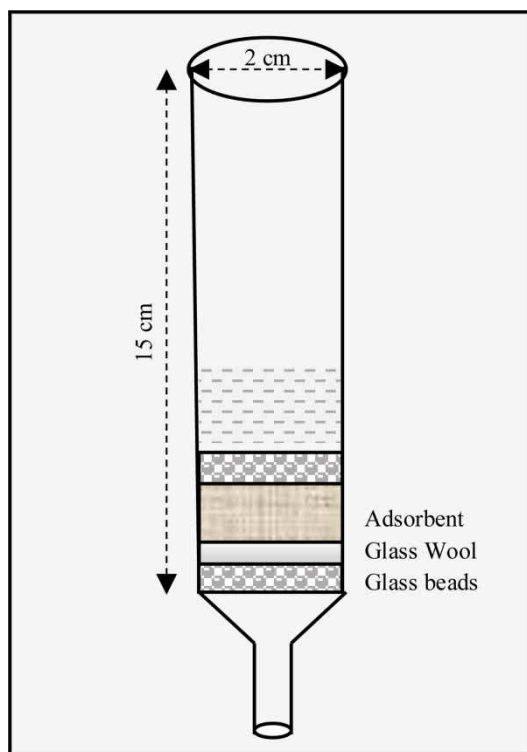


Figure 1 | Schematic representation of the fixed-bed column.

Column data analysis

The concept of a fixed-bed column is expressed graphically as a breakthrough curve, a plot of C_{out}/C_{in} versus time (Chen *et al.* 2012). The time of breakthrough and the shape of breakthrough curve are essential features in determining the biosorption behavior and dynamic response of the fixed-bed column in metal ion removal from aqueous solution. There are a few important parameters associated with column studies, which need to be evaluated for the interpretation of column data: volume of effluent treated, V_{eff} (mL) (Equation (1)); total mass of metal ions sent to the column, m_{total} (mg) (Equation (2)); total mass of metal ions adsorbed, q_{total} (mg) (Equation (3)); and equilibrium adsorption capacity, q_{eq} (mg g⁻¹) of the column (Equation (4)):

$$V_{eff} = Q \times t_{total} \quad (1)$$

$$m_{total} = \frac{C_{in} Q t_{total}}{1000} \quad (2)$$

$$q_{total} = \frac{Q}{1000} \times \int (C_{in} - C_{out}) dt \quad (3)$$

$$q_{eq(exp)} = \frac{q_{total}}{m} \quad (4)$$

In the above equations, Q and t_{total} represent the volumetric flow rate (mL min⁻¹) and total flow time (min), respectively, C_{in} and C_{out} are the inlet and outlet metal ion concentrations (mg L⁻¹), respectively, and m is the unit mass of biosorbent packed in the column (g).

Column modelling

To examine the column parameters and its interdependence on the column performance, adsorption column models are applied to the experimental data. Various mathematical models have been proposed to evaluate the effect of process variables on the efficiency of biosorption process for heavy metal removal in a fixed-bed column. Adam-Bohart, Thomas and Yoon-Nelson models are among the widely applied models for column data interpretation.

Adam-Bohart model

Adam-Bohart model assumes that equilibrium is not attained instantaneously and is based on the surface

reaction theory. It also describes the relationship between C_{out}/C_{in} and time in the continuous biosorption of metal ions in a fixed-bed column (Bohart & Adams 1920). The model equation is expressed as Equation (5):

$$\ln \left[\frac{C_{out}}{C_{in}} \right] = K_{AB} C_{in} t - \frac{K_{AB} N_o Z}{v_o} \quad (5)$$

where, K_{AB} , N_o , v_o and Z are the Adam-Bohart rate constant ($L \text{ mg}^{-1} \text{ min}^{-1}$), maximum saturation metal ion concentration (mg L^{-1}), linear velocity (cm min^{-1}) and bed height (cm), respectively. The model constants are determined from the plot of $\ln(C_{out}/C_{in})$ vs time.

Thomas model

The Thomas model follows Langmuir kinetics of adsorption-desorption. It assumes no axial dispersion in column adsorption such that the rate driving force obeys second-order reversible kinetics. The model also predicts the relationship between concentration and time (Thomas 1944; Tofan *et al.* 2013). The linearized form of the model is expressed as Equation (6):

$$\ln \left[\frac{C_{in}}{C_{out}} - 1 \right] = \frac{K_{TH} q_o m}{Q} - K_{TH} C_{in} t \quad (6)$$

where, K_{TH} and q_o are the Thomas kinetic constant ($\text{mL min}^{-1} \text{ mg}^{-1}$) and equilibrium uptake capacities (mg g^{-1}), respectively. The values of K_{TH} and q_o can be computed from the plot of $\ln(C_{in}/C_{out} - 1)$ vs time.

Yoon-Nelson model

Yoon-Nelson model is mathematically equivalent to the Thomas model and it is generally applied to single component systems for a range of concentrations in the effluent between breakthrough and saturation time to investigate the breakthrough curve in fixed-bed column studies. The Yoon-Nelson model is expressed linearly as Equation (7) (Yoon & Nelson 1984):

$$\ln \left[\frac{C_{out}}{C_{in} - C_{out}} \right] = K_{YN} t - \tau K_{YN} \quad (7)$$

where, K_{YN} and τ represents the Yoon-Nelson rate constant (min^{-1}) and the time required for 50% adsorbate breakthrough, respectively. The model constants are determined

from the slope and intercept of plot $\ln(C_{out}/(C_{in}-C_{out}))$ vs time.

Desorption studies

Column desorption studies were carried to remove the adsorbed nickel ions from CIF-R and CIF-BC. After the biosorption of Ni(II) ions at 2.5 mL min^{-1} flow rate for an ion concentration of 50 mg L^{-1} at a bed height of 1.0 cm, the Ni(II) ions were eluted using 0.1 M hydrochloric acid solution. Every adsorption cycle followed washing with distilled water to remove any unabsorbed Ni(II) ion. The desorption cycle involved passing 0.1 M HCl at a flow rate of 5 mL min^{-1} for 60 minutes. The columns were then washed with distilled water at 5 mL min^{-1} for 30 minutes and similar adsorption-desorption cycles were carried out for up to four cycles. The concentration of metal ion at the end of each adsorption and desorption cycle were compared and the desorbing efficiency of the eluent was determined using Equation (8) (Lodeiro *et al.* 2006; Igerase & Osifo 2015):

$$\% \text{ Desorption} = \frac{C_{ads}}{C_{des}} \times 100 \quad (8)$$

where, C_{ads} and C_{des} are the concentration of metal ions adsorbed and desorbed (mg L^{-1}), respectively.

RESULTS AND DISCUSSION

XRD analysis of CIF-R and CIF-BC

The powder XRD patterns of CIF-R and CIF-BC prior and subsequent to adsorption of Ni(II) ions are presented in Figure 2(a) and 2(b), respectively. XRD Pattern was studied in the 2θ range $0-80^\circ$. A significant difference can be observed in the diffraction patterns of CIF in its raw and bio-char state. The XRD pattern of CIF-R before and after the adsorption of Ni(II) shows a broad diffraction peak at a 2θ range of 20 to 24° (Figure 2(a)). The absence of any sharp peak in the pattern describes its amorphous nature, which is a favorable feature of a biosorbent. Figure 2(a) exhibits the characteristic peak of nickel at 2θ angles 23.9° and 43.5° , affirming the biosorption of Ni(II) ions onto CIF-R. Figure 2(b) depicting the diffraction pattern of CIF-BC shows the characteristic silicon dioxide peak besides presenting the characteristic nickel peak, further suggesting its biosorption onto CIF-BC.

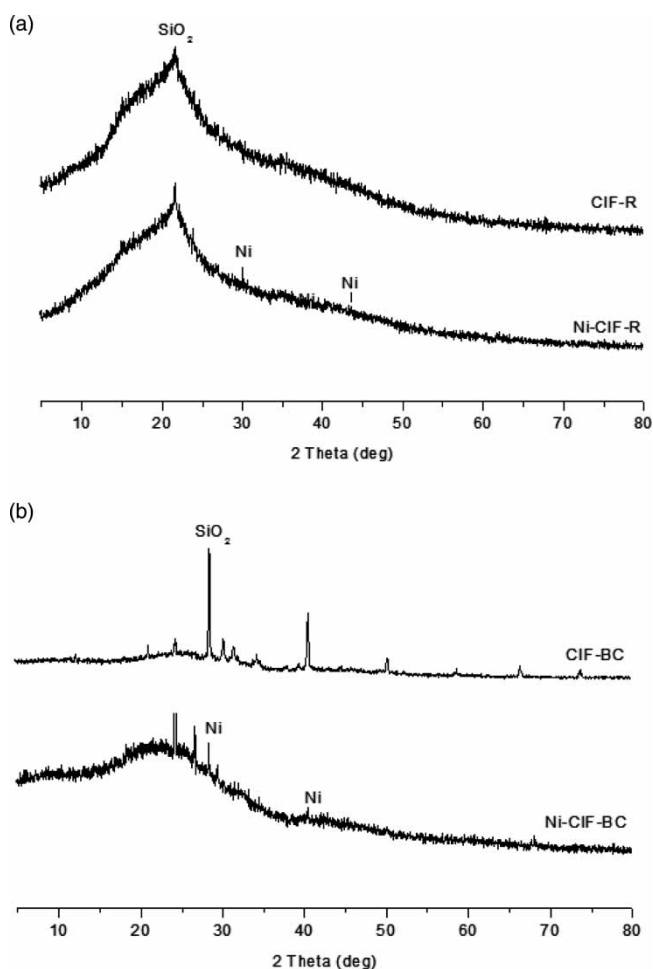


Figure 2 | XRD patterns of (a) CIF-R (b) CIF-BC before and after the biosorption of Ni(II) ions.

Influence of process parameters

Fixed-bed column biosorption studies were carried out to evaluate the effect of various process variables, viz. bed height, flow rate and initial concentration of Ni(II) on the breakthrough curve and biosorption capacity. The shape of the breakthrough curve (C_{out}/C_{in} vs time) and time of breakthrough point are predominant factors that determine the dynamic behavior of the column. In this study, breakthrough time (t_b) is taken as the time at which the metal ion concentration in the outlet (C_{out}) reaches 5% of the inlet metal ion concentration (C_{in}) and the saturation time (t_{sat}) is the point when C_{out} is 95% of C_{in} .

Effect of bed height

In column studies, bed height has a strong influence on the column breakthrough time and adsorbent bed performance.

Hence, the effect of varying bed height was evaluated in this study. The influence of bed heights 1.0, 2.0 and 3.0 cm corresponding to a biosorbent mass of 1.0, 2.0 and 3.0 g, respectively, for CIF-R and 0.5, 1.0 and 1.5 g, respectively, for CIF-BC were studied in terms of breakthrough curve for the biosorption of Ni(II) onto CIF-R (Figure 3(a)) and CIF-BC (Figure 3(b)). A Ni(II) solution of concentration 50 mg L^{-1} was passed through the respective columns at a fixed flow rate of 1.0 mL min^{-1} . It can be observed from the figure that the breakthrough and saturation times increase with increasing bed height. The interpretation of the breakthrough curve for various column parameters, V_{eff} , m_{total} , q_{total} and q_{eq} , are presented in Tables 1 and 2 for CIF-R and CIF-BC, respectively. For Ni(II) removal using CIF-R (Figure 3(a)), it can be seen that, the t_b increases from 25 min to 90 min and t_{sat} increases from 600 min to 720 min with an increase in bed height from 1.0 to 3.0 cm, implying that higher bed height saturates more slowly than a lower bed height. The slope of the breakthrough curves also decreased with increasing bed height, which results in a broadened mass transfer zone. From Table 1, it can be observed that, the V_{eff} increased with increasing bed height due to the increased time of contact until saturation and q_{total} was also found to increase from 14.02, 19.24 to 20.76 mg with an increasing bed height of 1.0, 2.0 and 3.0 cm, respectively. The increase in ion adsorption with increasing bed height might be due to the increased biosorbent dose at higher bed heights, which essentially provides greater service area and adsorption sites (Sun *et al.* 2014). A similar trend was observed in the removal of Ni(II) ion onto CIF-BC. Bed height is thus shown to have a stronger influence on the column performance for Ni(II) ion biosorption.

Effect of flow rate

Flow rate of metal ion solution in a fixed-bed column is an important parameter that affects the uptake capacity of the biosorbent bed. In this study, the effect of flow rate was studied in the range of 1.0, 2.5 and 5.0 mL min^{-1} at a constant bed height of 1.0 cm and initial nickel ion concentration of 50 mg L^{-1} . Breakthrough curves for the biosorption of Ni(II) onto CIF-R and CIF-BC are presented in Figure 4(a) and 4(b), respectively. Tables 1 and 2 give the values of the different column parameters as obtained from breakthrough curve interpretation for varying flow rates on the uptake of nickel ions onto the biosorbents. It can be inferred from the figures that the column breakthrough and saturation time are shorter for increased flow rates. This is because, at higher flow rates, the metal ions stay in

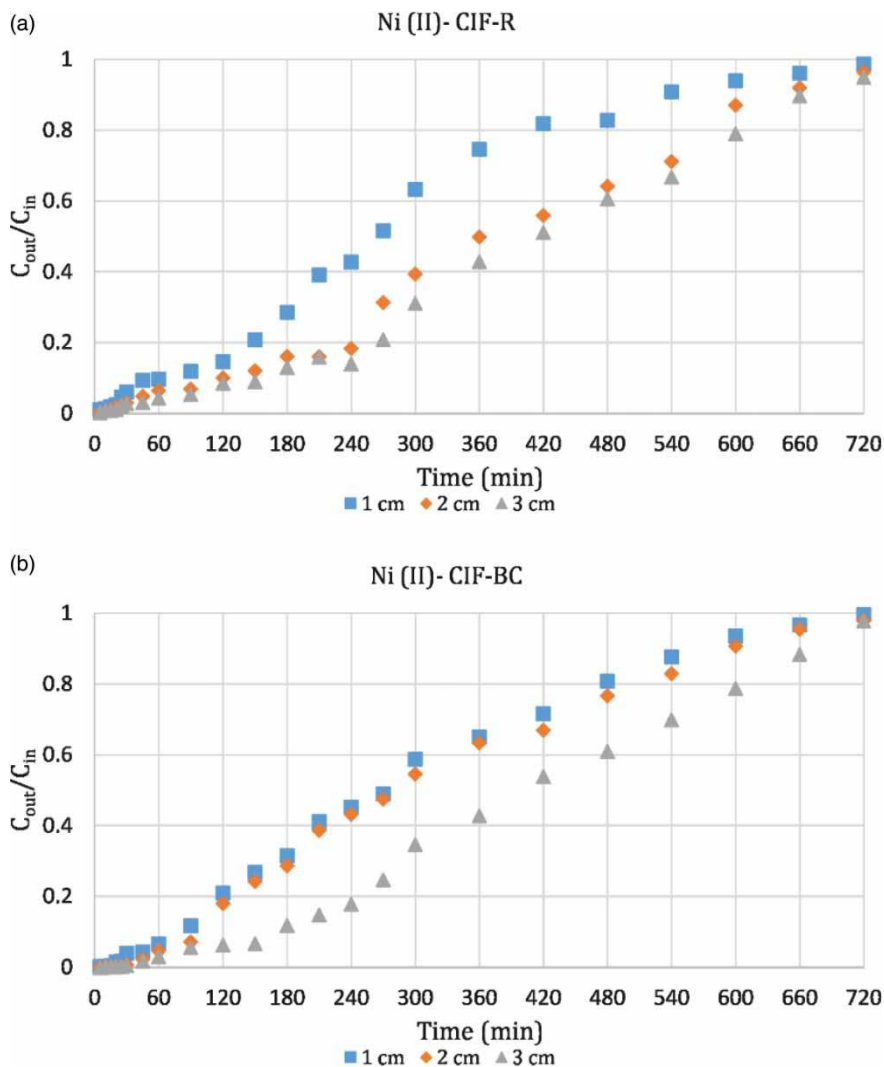


Figure 3 | Effect of bed height on Ni(II) removal using (a) CIF-R and (b) CIF-BC.

the column for a relatively shorter time making it less efficient in contacting and reacting with the biosorbent bed, further resulting in early breakthrough and saturation of the column (Chen *et al.* 2011). It can be observed from the table values that, the biosorption capacity decreases with increasing flow rate due to the insufficient residence time of metal ions in the column, which also predicts that better column performance can be attained at lower flow rate. Thus, flow rate is a vital parameter that affects the biosorption of Ni(II) ions in the fixed-bed column.

Effect of initial Ni(II) concentration

The effect of initial ion concentration on the biosorption of nickel ions onto the biosorbents were studied at

varying concentrations of 25, 50 and 75 mg L⁻¹ for a fixed bed height of 1.0 cm and a constant flow rate of 1.0 mL min⁻¹. The column breakthrough curves for removal of Ni(II) ions using CIF-R and CIF-BC are presented in Figure 5(a) and 5(b), respectively. The interpreted column parameters for Ni(II) biosorption onto different bioorbents are presented in Tables 1 and 2. It can be inferred from the figure that the adsorbent bed tends to get saturated earlier with increasing amounts of metal ions introduced to the fixed-bed column, which could be reasonably attributed to the higher concentration gradient causing a faster transfer of metal ions due to increased diffusion and or mass transfer co-efficient (Meng *et al.* 2013). In addition, an increase in m_{total} , q_{total} and q_{eq} can be observed for an increasing initial ion

Table 1 | Fixed-bed column model parameters of Ni(II) biosorption onto CIF-R

Column parameters			Experimental conditions				Adam-Bohart Model			Thomas Model			Yoon- Nelson Model		
C_o (mg L ⁻¹)	Q (mL min ⁻¹)	Z (cm)	V_{eff} (mL)	m_{total} (mg)	q_{total} (mg)	q_{eq} (mg g ⁻¹)	K_{AB} (L mg ⁻¹ min ⁻¹)	N_o (mg L ⁻¹)	R^2	K_{TH} (mL min ⁻¹ mg ⁻¹)	q_o (mg g ⁻¹)	R^2	K_{YN} (min ⁻¹)	τ (min)	R^2
50	1	1	600	30	14.02	14.02	0.00032	117.45	0.805	0.00022	14.75	0.950	0.01149	294.97	0.926
50	1	2	660	33	19.24	9.62	0.00030	195.42	0.754	0.00020	9.82	0.935	0.01009	292.95	0.912
50	1	3	720	36	20.76	6.92	0.00028	370.47	0.776	0.00018	7.05	0.989	0.00999	287.79	0.954
50	1	1	600	30	14.02	14.02	0.00032	117.45	0.805	0.00022	14.75	0.950	0.01149	294.97	0.926
50	2.5	1	1,050	52.5	6.48	6.48	0.00042	62.89	0.655	0.00024	8.00	0.824	0.01213	168.03	0.813
50	5	1	1,500	75	4.55	4.55	0.00047	45.02	0.720	0.00028	5.17	0.757	0.01234	156.68	0.724
25	1	1	720	18	8.09	8.09	0.00088	52.78	0.462	0.00039	9.36	0.986	0.01184	374.46	0.964
50	1	1	600	30	14.02	14.02	0.00032	117.45	0.805	0.00022	14.75	0.950	0.01149	294.97	0.926
75	1	1	540	40.5	19.27	19.27	0.00024	149.91	0.749	0.00012	21.31	0.824	0.00904	286.48	0.513

Table 2 | Fixed-bed column model parameters of Ni(II) biosorption onto CIF-BC

Column parameters			Experimental conditions				Adam-Bohart Model			Thomas Model			Yoon- Nelson Model		
C_o (mg L ⁻¹)	Q (mL min ⁻¹)	Z (cm)	V_{eff} (mL)	m_{total} (mg)	q_{total} (mg)	q_{eq} (mg g ⁻¹)	K_{AB} (L mg ⁻¹ min ⁻¹)	N_o (mg L ⁻¹)	R^2	K_{TH} (mL min ⁻¹ mg ⁻¹)	q_o (mg g ⁻¹)	R^2	K_{YN} (min ⁻¹)	τ (min)	R^2
50	1	1	600	30	14.72	29.44	0.00053	95.14	0.795	0.00025	32.14	0.946	0.01259	321.42	0.931
50	1	2	660	33	15.82	15.82	0.00051	184.08	0.862	0.00023	18.23	0.835	0.01140	284.59	0.814
50	1	3	720	36	20.54	13.69	0.00048	338.90	0.666	0.00020	14.14	0.972	0.01063	262.07	0.943
50	1	1	600	30	14.72	29.44	0.00053	95.14	0.795	0.00025	32.14	0.946	0.01259	321.42	0.931
50	2.5	1	1,050	52.5	6.76	13.52	0.00064	45.50	0.758	0.00029	14.74	0.942	0.01457	218.97	0.916
50	5	1	1,350	67.5	3.99	7.98	0.00069	34.08	0.475	0.00032	9.05	0.821	0.01542	132.10	0.807
25	1	1	660	16.5	9.15	18.30	0.00111	53.45	0.729	0.00052	18.85	0.957	0.01311	376.93	0.926
50	1	1	600	30	14.72	29.44	0.00053	95.14	0.795	0.00025	32.14	0.946	0.01259	321.42	0.931
75	1	1	420	31.5	15.16	30.33	0.00044	127.69	0.798	0.00021	32.15	0.960	0.01557	267.66	0.926

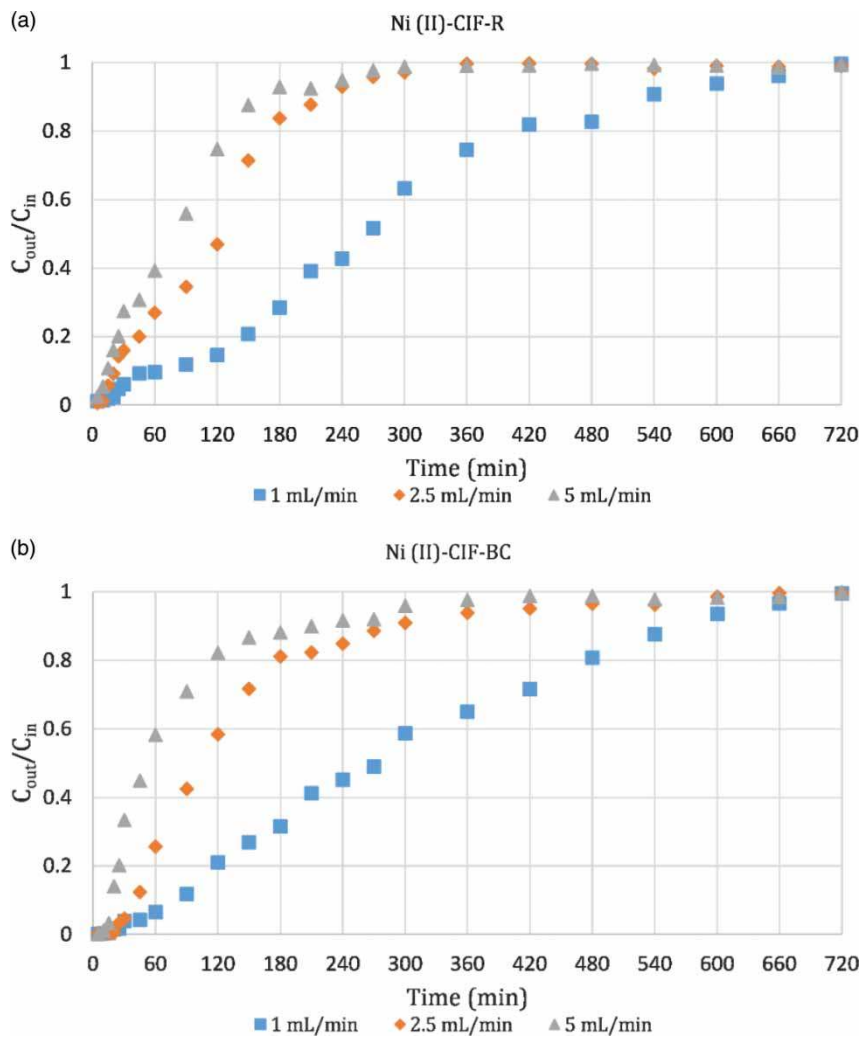


Figure 4 | Effect of flow rate on Ni(II) removal using (a) CIF-R and (b) CIF-BC.

concentration from 25 to 75 mg L⁻¹ for both the biosorbents used in this study.

Column biosorption modelling

Adam-Bohart model

Experimental column biosorption data of Ni(II) removal using CIF-R and CIF-BC were analyzed using Adam-Bohart model. The values of the model characteristic parameters, viz. maximum saturation metal ion concentration (N_0) and Adam-Bohart rate constant (K_{AB}) are determined from the slope and intercept of the model plot. Tables 1 and 2 present the calculated Adam-Bohart constant values for Ni(II) biosorption onto CIF-R and CIF-BC, respectively, for the different experimental parameters. It

can be observed that, the correlation co-efficient ($R^2 < 0.8$) values are relatively less and the values of K_{AB} increased with increasing flow rate, while it decreased with increasing bed height and initial Ni(II) concentration. In addition, N_0 values increased with increasing bed height and initial ion concentration and decreased with increasing flow rate for both the biosorbents (Woumfo *et al.* 2015). The phenomena can be reasonably attributed to the system kinetics that is explicitly dominated by external mass transfer in the initial part of the breakthrough curve.

Thomas model

Breakthrough curves for the biosorption of nickel ions onto CIF-R and CIF-BC were analyzed using the Thomas model. The values of the constants, K_{TH} and q_0 , and

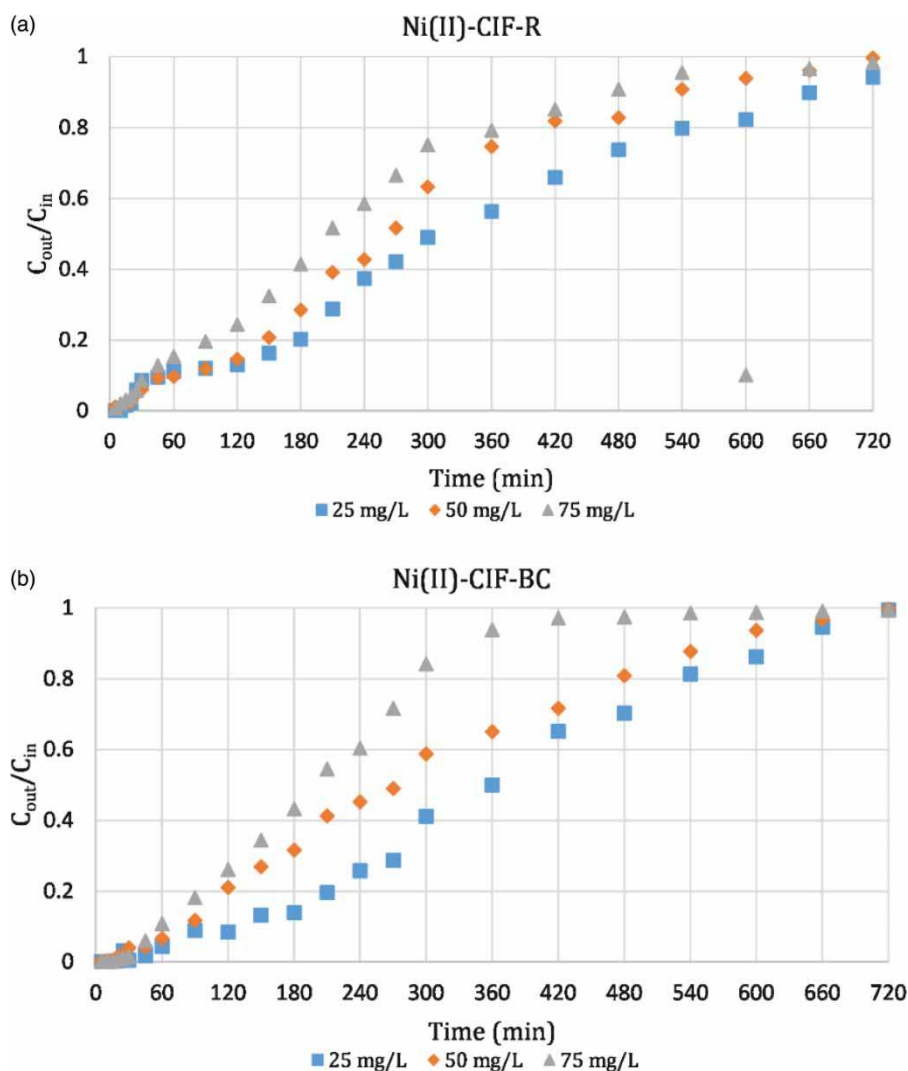


Figure 5 | Effect of initial ion concentration on Ni(II) removal using (a) CIF-R and (b) CIF-BC.

correlation coefficients were determined from the model plot of $\ln(C_{in}/C_{out} - 1)$ versus time and are presented in Tables 1 and 2 for CIF-R and CIF-BC, respectively. It can be observed from the tables that, as the bed height and inlet Ni(II) ion concentration increases, the K_{TH} value decreases while it increases for increasing flow rate. The R^2 values are found to be higher for the biosorption of nickel ions onto both the biosorbents. The q_0 values calculated from the Thomas model were also found to be closer to the experimentally obtained values. Thus, the linearized Thomas model adequately describes the experimental breakthrough data as evident from the values obtained from the model. The suitability of Thomas model to the experimental data indicates external and internal diffusions are not the only rate-limiting steps in the biosorption

process. Similar trends have also been reported in previous studies (Xu *et al.* 2013).

Yoon-Nelson model

The Yoon-Nelson model was applied to determine the extent of its suitability to the column biosorption of Ni(II) onto CIF-R and CIF-BC. The model constants (K_{YN} and τ) and correlation coefficient values are presented in Tables 1 and 2, respectively, for all the experimental conditions. The interpolation of the model plot showed that the values of K_{YN} decreased for increasing bed depth and inlet nickel ion concentration, while it increased for increasing flow rate (Foo *et al.* 2013). The 50% breakthrough time ' τ ' decreased for the increasing range of flow rate and initial

ion concentrations, as the column saturates quickly. The difference in experimental and predicted τ values indicated that the Yoon-Nelson model does not give an appropriate fit to the experimental column data on continuous biosorption of nickel ions.

Column desorption studies

The desorbing efficiency of hydrochloric acid to elute the adsorbed Ni(II) ions from CIF-R and CIF-BC in four consecutive adsorption–desorption cycles are presented in Figure 6(a) and 6(b), respectively. It can be observed from the figure that the desorbing efficiency decreases slightly with less significant values at the end of four cycles suggesting the efficient capacity of HCl to desorb nickel ions and the desirable nature of the studied biosorbents, viz. CIF-R and CIF-BC for a reasonable regeneration and reusability potential. The decrease in efficiency could be attributed to the loss of adsorbent mass in subsequent adsorption–desorption cycles.

CONCLUSION

Continuous biosorption studies for the removal of nickel ions using native and biochar forms of *C. indicum* flower waste were carried out in this study. The study revealed a promising potential of both the biosorbents, viz. CIF-R and CIF-BC, to remove the metal ion with biosorption capacity values of 14.02 and 29.44 mg g⁻¹, respectively, for an initial Ni(II) concentration of 50 mg L⁻¹, 1.0 cm bed height and 1.0 mL min⁻¹ flow rate in a fixed-bed column. The study of influencing factors including bed height, flow rate and initial ion concentration elucidated the interdependence of each factor on the dynamic adsorption of nickel ions from aqueous solution. Breakthrough curve modelling using different models provided the best fit of experimental column data with the Thomas model for both the biosorbents for nickel ion removal. Column desorption studies further elicited the significance of CIF-R and CIF-BC as being efficient and eco-friendly in adsorbing as well as desorbing the adsorbed nickel ions.

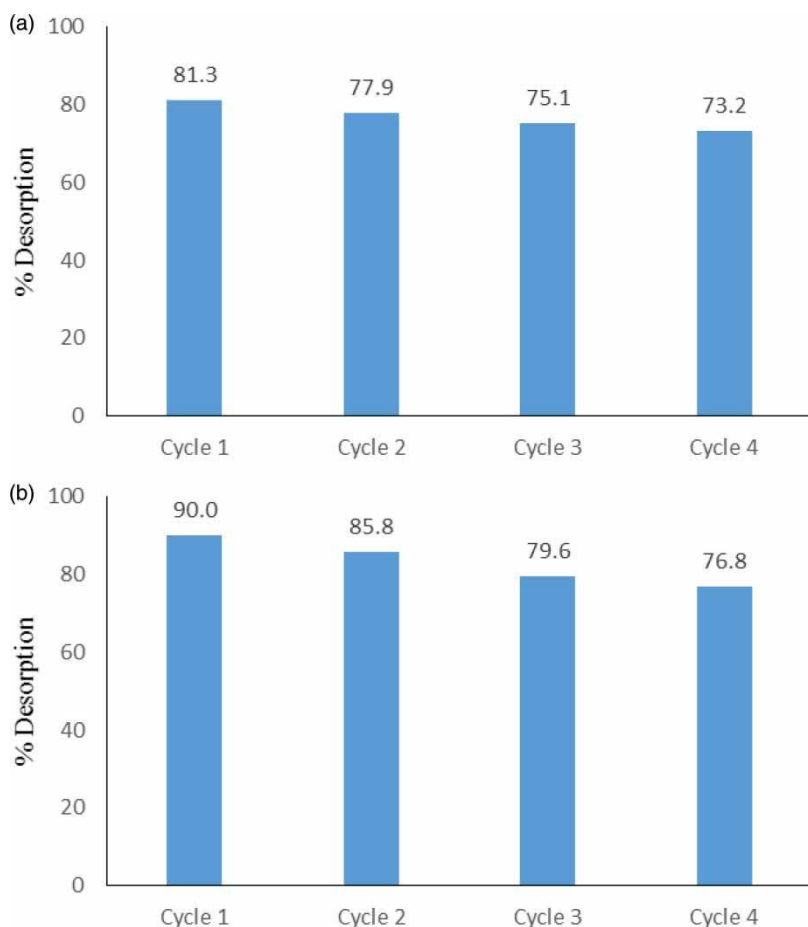


Figure 6 | Comparative desorption efficiency of 0.1 M HCl to elute Ni(II) ions from (a) CIF-R and (b) CIF-BC in consecutive cycles.

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