Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25356

184 (2020) 199–213
April

Lignin/alginate/hydroxyapatite composite beads for the efficient removal of copper and nickel ions from aqueous solutions

Ayesha Naseer[a], Almas Hamid[a], Moinuddin Ghauri[b], Asma Nasrullah[c], Jibran Iqbal[d,*], Noor Samad Shah[e], Sikander Rafiq[f], Masooma Irfan[g], Nawshad Muhammad[h,*]

[a]*Department of Environmental Sciences/Chemistry, Kinnaird College for Women, Lahore, Pakistan, emails: ayeshanaseer29@hotmail.com (A. Naseer), almas209@yahoo.com (A. Hamid)*
[b]*Department of Chemical Engineering, COMSATS University Islamabad, Lahore Campus Defense Road, Lahore, Punjab 54000, Pakistan, email: drghauri@cuilahore.edu.pk (M. Ghauri)*
[c]*Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS (UTP), 31750 Tronoh, Perak, Malaysia, email: advent_chemist@yahoo.com (A. Nasrullah)*
[d]*College of Natural and Health Sciences, Zayed University, Abu Dhabi, United Arab Emirates, email: Jibran.Iqbal@zu.ac.ae (J. Iqbal)*
[e]*Department of Environmental Sciences, COMSATS University Islamabad, Vehari, 61100, Pakistan, email: noorsamad@cuivehari.edu.pk (N.S. Shah)*
[f]*Department of Chemical, Polymer & Composite Materials Engineering, University of Engineering and Technology, Lahore, KSK-Campus, Pakistan, email: sikanderafiq@gmail.com (S. Rafiq)*
[g]*Department of Chemistry, COMSATS University Islamabad, Defense Road, Lahore, Punjab 54000, Pakistan, email: masoomairfan@cuilahore.edu.pk (M. Irfan)*
[h]*Interdisciplinary Research Center in Biomedical Materials (IRCBM), COMSATS University Islamabad, Defense Road, Lahore, Punjab 54000, Pakistan, email: nawshadmuhammad@cuilahore.edu.pk (N. Muhammad)*

Received 27 May 2019; Accepted 14 December 2019

ABSTRACT

This study was conducted to analyze the adsorption efficiency of lignin/alginate/hydroxyapatite composite beads for the removal of copper Cu(II) and nickel Ni(II) ions from an aqueous solution. For this purpose, lignin, alginate and hydroxyapatite (HAp) composite was prepared in the form of lignin/alginate/hydroxyapatite composite beads. Adsorbents were synthesized in three different ratios by mixing lignin/alginate/hydroxyapatite and sodium alginate in distilled water (25–30 ml) which was then added dropwise to the calcium chloride ($CaCl_2$) solution to form its lignin/alginate/hydroxyapatite composite beads. Synthesized beads were characterized using X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis. The effect of various experimental parameters such as contact time, pH, the initial concentration of Cu(II) and Ni(II) and adsorbent dose on adsorption capacity was investigated. Kinetic and isotherm data confirmed that the pseudo-first-order model and Langmuir isotherm were best fitted to experimental data. An increase in the adsorption capacity of heavy metals from an aqueous solution was observed with the increase in lignin percentage in beads. The maximum adsorption capacity for Cu(II) and Ni(II) was 79.67 and 71.18 mg/g, respectively for C3 (60%) lignin. Reusability study of lignin/alginate/hydroxyapatite beads showed 79% removal efficacy after four successive adsorption-desorption cycles. The results showed that lignin/alginate/hydroxyapatite composite beads can be used as promising environmentally benign adsorbent for the removal of heavy metal ions from an aqueous solution.

Keywords: Lignin; Hydroxyapatite; Composite beads; Heavy metals; Wastewater treatment

---

* Corresponding authors.

1. Introduction

Global water demand has increased over the past many years. Increased population has created an imbalance in global water which has raised water withdrawal eight folds from 500 to 4,000 km^3/y since over the last 100 years [1]. According to an estimate, about sixty percent of the world population may experience water insufficiency issues by 2025 [2].

As the gap between water availability and water demand things, there is an urgent need to manage water resources. While on one hand there has been a rapid decline in water availability, on the other, the situation has further intensified due to pollution of water bodies as a result of the haphazard release of untreated industrial effluents in many areas of the world [3,4]. Industrial activities, uncontrolled traffic, and incineration activities are also responsible for this environmental issue. Surface and groundwater quality in Pakistan has deteriorated over the past many years due to untreated release of municipal, agricultural and industrial discharges [5]. According to the statistics, fast industrial growth has contributed significantly to water pollution issues. Every day approximately 2000 million gallons of sewage is released into surface water bodies in Pakistan [5].

Agricultural runoff, commercial and many industrial units (mining, electroplating, paper industry, fertilizers, and pesticides, etc.) discharge a significant amount of wastewater into the environment and/or water bodies, which contain a large variety of hazardous contaminants and toxic heavy metals [6]. Heavy metals constitute one of the major classes of water pollutants and in almost 85% of the industrial effluent. Heavy metals including chromium (Cr), manganese (Mn), nickel (Ni), iron (Fe), zinc (Zn), and cadmium (Cd) can cause water pollution [7]. Unlike organic pollutants, these metal ions do not degrade over a long period of time, thus, accumulate into the living tissues of human and cause severe physiological and psychological disorders if they exceeded their permissible limits [8,9]. Heavy metals can be removed using different techniques such as precipitation, chemical coagulation, adsorption, bio-sorption, electrodialysis, electro deionization, membrane separation, electrocoagulation, reverse osmosis and ionic-exchange [10]. These methods use different chemicals or bio-sorbents that are either synthetic or non-synthetic in nature. However, these methods have certain drawbacks such as high capital and operation cost, high skills, and technical knowledge for operation [11]. Among these available techniques, adsorption is an attractive separation technique due to its operation, fewer skill demands, insensitivity to adsorbents and cost-effectiveness [12,13]. Lignin is the second most abundantly available biomass after cellulose and covers about 20%–35% of the plant's structural arrangement [14]. It is a natural polymer present in cell walls of terrestrial plants that act as a binding agent for various fibrous materials. Structural analysis shows that it has a high molecular weight and surface area of 180 m^2/g. Its three-dimensional polymeric structure (which involves different functional groups hydroxyl, methoxyl, and phenolic groups) makes it a favorable material for the removal of heavy metals from wastewater [15–17]. Lignin can also be recovered from black liquor from the paper and pulp industry. It is a waste product and can be used as a fuel as well as for other productive applications [18]. Wastewater treatment approaches using this bio sorbent (lignin) with or without modifications have been reported [19]. Techniques for enhancing the reactivity involve methods in which hydroxyl content has been increased along with enhancement in mass transfer [20,21].

Hydroxyapatite (Hap) is a naturally occurring non-toxic inorganic material with a formula of ($Ca_{10}(PO_4)_6(OH)_2$). Along with HAp, several biomolecules have also been recommended for removing desired heavy metals [22–24]. Sodium alginate is a biopolymer that is used as a composite material and stabilizers in various applications [25]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is often used with sodium alginate as a biopolymer composite for various adsorption procedures [26]. A strong interaction between the positively charged calcium (Ca^{2+}) and the negatively charged carboxyl group (COO^-) has been shown in sodium alginate structure [25] forming inorganic/biopolymer composite. As stated, earlier lignin biopolymer is produced as a by-product from paper and pulp industry, fit perfectly to be used as an adsorbent. Lignin is an ideal candidate to be used as a hybrid material along with HAp in the form of beads. Lignin contains carboxylic and phenolic functional groups which make it an ideal adsorbent for selective adsorption of various toxic metals such as Cu(II), Cd(II), Ni(II), Pb(II), and Cu(II) [17]. Therefore, the development of lignin/alginate/hydroxyapatite sorbent from renewable resources will open new technology for wastewater treatment. In this study, composite beads were prepared using environment-friendly materials (lignin, HAp) by trapping them with sodium alginate. The prepared beads were applied to remove Cu(II) and Ni(II) from an aqueous solution. The adsorption capacity was investigated by varying different parameters such as solution pH, contact time, adsorbent dose, constituent's ratio in beads and the initial concentration of pollutants. The adsorption mechanisms were examined by studying kinetic and isotherm models [27]. The reusability of beads was also evaluated as a sustainable approach. The main objective of this study was to develop low-cost environmentally friendly composite beads for the removal of heavy metals from an aqueous solution.

2. Materials and methods

2.1. Materials

Lignin alkali was purchased from TCI America (CAS RN: 8068-05-1; Product Number: L0082), Sodium hydroxide (NaOH, CAS #: 1310-73-2, max. 0.02% K), hydrochloric acid (HCl 36%, product no #: 115186) and Calcium chloride ($CaCl_2$ anhydrous granules CAS #: 10043-52-4) were obtained from Merck, Germany). Sodium alginate was purchased from a local supplier. Hydroxyapatite (HAp CAS #: 12167-74-7), anhydrous ($NiCl_2$, CAS Number: 7718-54-9 and Copper(II) sulfate $CuSO_4$, 7758-98-7, ≥99.99% trace metals basis were purchased from Sigma-Aldrich (USA).

2.2. Preparation of lignin/alginate/hydroxyapatite beads

The lignin/alginate/hydroxyapatite beads were synthesized by mixing lignin, HAp and sodium alginate under controlled laboratory environment and protocols. These three materials were used in different ratios to form lignin/alginate/hydroxyapatite composite beads. Chemical ratios of these materials are given in Table 1.

The criteria for these adsorbent materials were to synthesize 5 g of adsorbent. Therefore, to prepare C1 composition, 1.5 g of sodium alginate, 1 g of hydroxyapatite and 2.5 g of lignin was dissolved in 25–35 ml of distilled water (more water can be added accordingly) to make a slurry-like suspension that was appropriate for bead formation. After the formation of a smooth mixture, an aliquot was taken out from the mixture and was added to a burette. The mixture was allowed dropwise into $CaCl_2$ solution to form beads. The beads were allowed to stir in $CaCl_2$ solution overnight to ensure complete gelation. In a similar way, C2 and C3 composition were prepared by mixing different ratios of sodium alginate, hydroxyapatite, and lignin.

2.3. Characterization of lignin/alginate/hydroxyapatite beads

Several characterization techniques were used to understand the potential behavior, physical and chemical properties of lignin beads in adsorption study. The PAN analytical X′pert PRO diffractometer (UK) using Cu Kα radiation (λ = 1.54 Å) at 40 KV and 30 mA with a scanning rate 0.01°/s and scan speed of 1°/min in a 2θ range of 10°–80° for analysis of the crystalline structure of lignin composites. Thermo Fisher Scientific Inc., MA, USA (Nicolet 6700) spectrometer with attenuated total reflection assembly was used for lignin composites in the range of wavenumber 600–4,000 cm^{-1}. Scanning electron microscopy (SEM-Philips XL-30, Eindhoven, The Netherlands) was used for the surface morphology of lignin composites. Thermal degradation (LECO's TGA701, USA) of developed beads was performed from 40°C to 600°C at the heating rate of 10°C/min under Nitrogen gas flow.

2.4. Optimization of adsorption parameters

Synthesized adsorbent beads were used to remove heavy metals from the standard solution of known concentrations prepared in the laboratory. Adsorption parameters were optimized to attain high removal efficacy for metal ions. Parameters included pH of the solution, the initial concentration of adsorbate, contact time and adsorbent dosage. The above-mentioned parameters were varied for process optimization at room temperature. Metal salts were used to prepare a stock solution for Cu(II) and Ni(II).

2.5. Atomic absorption spectrophotometry

Standard solution of copper and nickel were prepared using $CuSO_4$ and $NiCl_2$ for standard calibration curve with metal concentrations as 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ppm. After all optimization studies, samples (filtrates) were stored in plastic bottles and were analyzed using AAS (Buck Scientific 210 VGP, USA) for the determination of residual metal ions in the solution.

The removal efficiency (%R) and adsorption capacity of metal ions were measured using Eqs. (1) and (2), respectively.

$$\%R = \left[\frac{C_0 - C_t}{C_0}\right] \times 100 \tag{1}$$

$$q_t = \left[\frac{\left(C_0 - C_t\right)}{M} \times V\right] \tag{2}$$

where C_0 (mg/L) and C_t (mg/L) are the concentrations before and after the adsorption of the pollutant, V (L) is the volume of sample and M (g) is the used mass of adsorbent.

2.6. Kinetic study

Kinetic study for adsorption of heavy metal ions on lignin/alginate/hydroxyapatite composite beads was investigated using pseudo-first-order [27] and pseudo-second-order [28] kinetic models. The mathematical expression for pseudo-first and pseudo-second-order kinetic models are given in Eqs. (3) and (4), respectively.

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303} t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e (mg/g) = amount of metals ions adsorbed at equilibrium; q_t (mg/g) = amount of metals ions adsorbed at time t; K_1 (s^{-1}) = rate constant for the pseudo-first-order kinetic model; K_2 (s^{-1}) = rate constant for the pseudo-second-order kinetic model.

2.7. Isotherm study of adsorption

2.7.1. Langmuir isotherm

The Langmuir isotherm equation is based on norms that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface. It uses two

Table 1
Chemical ratios for lignin/alginate/hydroxyapatite composite beads

Composition No	Identification No	Chemical ratios for beads		
		Sodium alginate	Hydroxyapatite	Lignin
1	C1	30% (1.5 g)	50% (2.5 g)	20% (1 g)
2	C2	30% (1.5 g)	30% (1.5 g)	40% (2 g)
3	C3	30% (1.5 g)	10% (0.5 g)	60% (3 g)

parameters, describes homogenous, monolayer adsorption on the adsorbent surface [29–32]. The Langmuir isotherm is defined as:

$$q_e = \frac{\left(K_a q_m C_e\right)}{\left(1 + K_a C_e\right)} \tag{5}$$

and in linearized form is:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_m}\right) + \frac{1}{\left(K_a q_m\right)} \tag{6}$$

where q_m and K_a are Langmuir constants that describe sorption capacity and sorption energy, respectively, C_e is the equilibrium concentration in mg/L, and q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). A plot of C_e/q_e vs. C_e should indicate a straight line with slope $1/q_m$ and an intercept of $1/K_a q_m$. Alternatively,

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) - \frac{1}{C_e} + \frac{1}{q_m} \tag{7}$$

where q_e (mg/g) and q_m (mg/g) are the equilibrium adsorption capacity and maximum monolayer adsorption capacity, respectively. C_e (mg/L) is the equilibrium sorbate concentration. K_a is constant and represents the affinity of binding sites. The influence of the shape of adsorption isotherm in terms of a dimensionless constant known as separation factor or equilibrium parameter (R_L) can be calculated using Eq. (8).

$$R_{L=}\frac{1}{1 + K_a^{*} C_i} \tag{8}$$

where K_a is the Langmuir constant and C_i (mg/L) is the initial adsorbate concentration. The value of separation factor (R_L) indicates favorability of adsorption such that when $R_L > 1$ (unfavorable), $R_L = 1$ (linear), $0 < R_L < 1$ (favorable) and $R_L = 0$ (irreversible).

2.7.2. Freundlich isotherm

Freundlich sorption isotherm is one of the most commonly used mathematical expressions, which gives an idea about surface heterogeneity and exponential distribution of active sites and their energy values respectively [31]. The Freundlich isotherm is defined as:

$$q_e = K_f C_e^{1/n} \tag{9}$$

In addition, in linearized form is:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e \tag{10}$$

where C_e the equilibrium concentration in mg/L, q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). "K_f" is a parameter related to temperature and "n" is a characteristic constant for the adsorption study. The only difference was that it represents multilayer heterogeneous adsorption. The affinity for bonding sites was not the same. This isotherm assumes that binding of metal ions and solute binding sites were non-identical.

3. Results and discussion

3.1. SEM analysis

The morphology of developed composite beads was analyzed using SEM. Fig. 1a–c shows the SEM images of different adsorbents under similar magnification. From the SEM images, it is clear that lignin/alginate/hydroxyapatite beads possess a rough surface having both large and small irregular pores. This porous structure provides a large surface area for efficient adsorption of heavy metals removal [33]. This increase in adsorption capacity with surface roughness has been reported in the literature [33]. SEM images also showed an increase in surface roughness of lignin/alginate/hydroxyapatite beads with an increase in lignin percentage from 20% to 60%. The increased lignin content enhances the porosity which ultimately increases the uptake of Cu(II) and Ni(II) from aqueous solution.

3.2. Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectroscopy analysis was performed to identify functional groups in lignin/alginate/hydroxyapatite beads. Adsorption performance of lignin/alginate/hydroxyapatite in aqueous solution depends on the interaction of these functional groups with heavy metals ions. Fig. 2 shows peaks of synthesized adsorbent having different functional groups of lignin as identified in different works of literature [34]. The broad peak around 3,340 cm^{-1} is assigned to stretching vibration of hydroxyl (–OH) groups present in all the constituents of beads (lignin, hydroxyapatite and sodium alginate) [35]. The peak located at 1,650 cm^{-1} is attributed to adsorbed O–H and conjugated C–O [25]. Some other characteristic peaks for lignin are C–H and O–CH at 1,464.29 cm^{-1} (C1), 1,465.72 cm^{-1} (C2) and 1,465.81 cm^{-1} (C3). The band located at 1,070 cm^{-1} is assigned to PO_4^{3-} group present in HAp [25].

3.3. X-ray diffraction analysis

The crystallinity and phase composition of the composite beads were analyzed with X-ray diffraction, shown in Fig. 3. The beads contain HAp; crystalline compound and lignin, and calcium alginate; amorphous compounds. The result demonstrated that the intensity of peaks assigned to HAp (002, 210, 112, 310, 222, 213, 004 and 304) increased with the increase of HAp content in the lignin/alginate/hydroxyapatite beads and vice versa.

3.4. Thermogravimetric analysis

The thermal degradation curves for all three compositions (C1, C2, and C3) of beads show similar thermal behavior as shown in Fig. 4. All lignin/alginate/hydroxyapatite showed a decrease in weight with increase in temperature. The weight loss up to 110°C is assigned to the loss of surface water [25]. Thermogravimetric analysis curve also shows

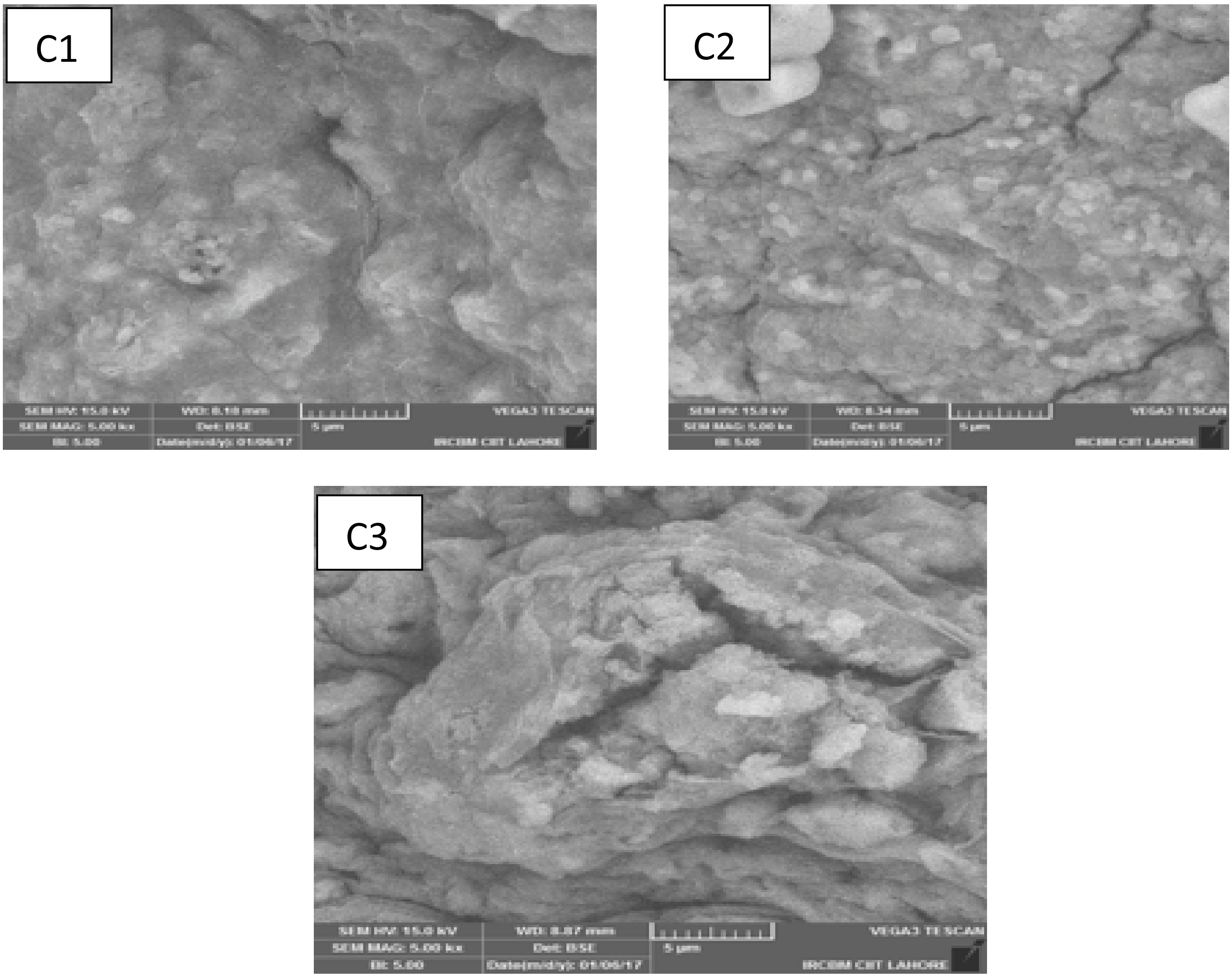

Fig. 1. SEM images of lignin/alginate/hydroxyapatite.

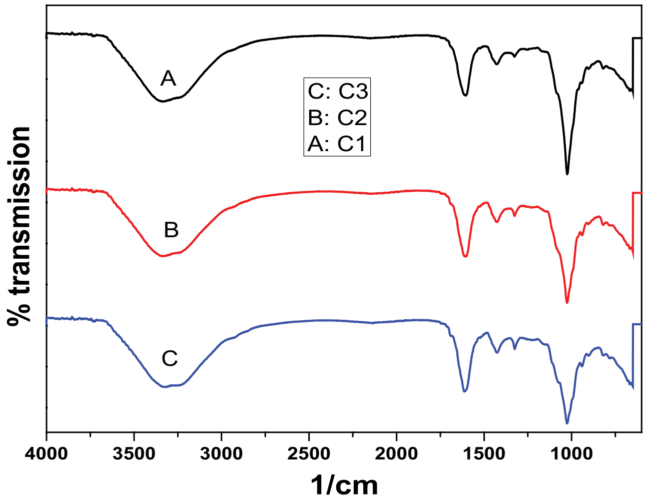

Fig. 2. Fourier transform infrared spectra lignin/alginate/hydroxyapatite.

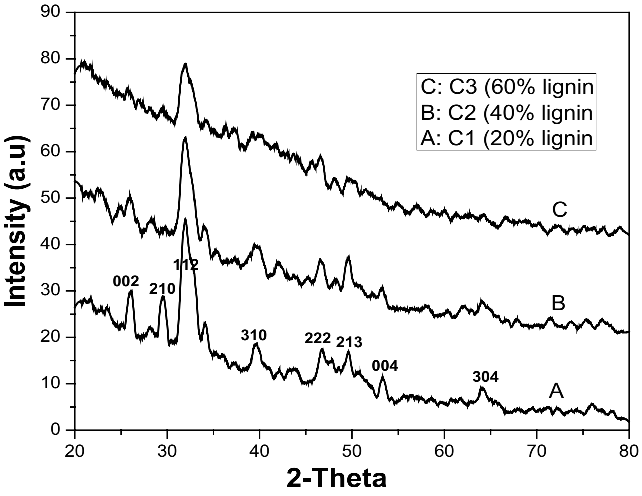

Fig. 3. X-ray diffraction spectra of lignin/alginate/hydroxyapatite.

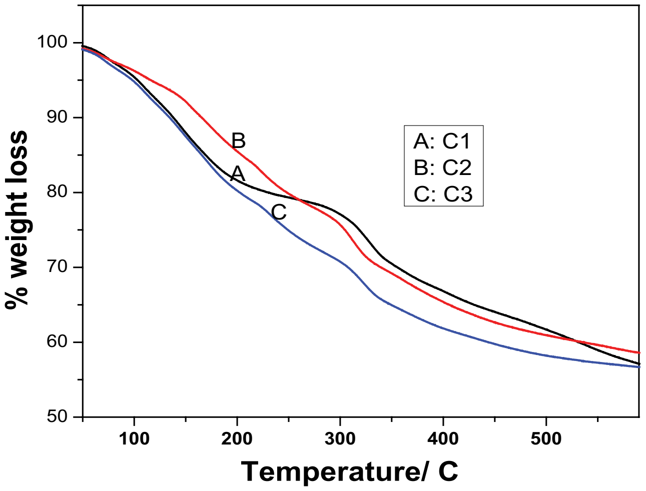

Fig. 4. Thermal degradation analysis of lignin/alginate/hydroxyapatite.

that an increase in lignin amount caused a relative decrease in the thermal stability of beads. According to Fig. 4, the loss in weight can be seen at 375.16°C for C1, 325.74°C for C2 and 307.4°C for C3. The weight loss is in the order of C1 > C2 > C3 with a weight loss of 74.13%, 69.26%, and 59.54% respectively.

3.5. Batch adsorption studies

3.5.1. Effect of contact time

Optimum contact time is needed for maximum metal uptake on the adsorbent. Fig. 5 illustrates a graphical trend of the effect of contact time for percentage removal of Cu(II) and Ni(II) using lignin/alginate/hydroxyapatite beads. The optimum time is referred to as the total amount taken for metal adsorption at the equilibrium point which showed the maximum efficiency of the process under given conditions [36]. The experimental result shows that the adsorption of Cu(II) and Ni(II) is rapid and increases with the increase contact time. For all three compositions, the adsorption of Cu(II) and Ni(II) reached equilibrium in almost 30 min. At this point, maximum removal was observed and above this time no significant increase in adsorption occurred.

3.5.2. Effect of pH

Another dominant factor that largely affects adsorption efficiency is the pH of the solution as it also directly affects the adsorption capacity and controls the adsorption process. The activity of different functional groups and speciation in metals depends extremely on the pH of the solution [36]. To optimize the pH of a solution, adsorption was carried out within pH range from 3–7 with an initial concentration of Cu(II) and Ni(II) as 100 ppm and an adsorbent dose of 0.4 g (Fig. 6). The adsorption increased with the increase in pH with maximum removal observed at pH 5 for Cu(II) and at pH 6 for Ni(II). This is due to the fact that at lower pH, H^+ concentration is high and this higher concentration of H^+ ions leads to competition between metal ions and H^+ ions for active sites on biosorbent surface. Hence pH optimization showed pH 5 as optimum pH for Cu(II) below which no significant adsorption occurred while for Ni(II), optimum pH was found at pH 6 above which precipitation occurs (at pH 7).

3.5.3. Effect of initial concentration of nickel and copper ions

The results show that at the equilibrium point, adsorption of Cu(II) and Ni(II) ions onto adsorbent was directly proportional to the initial concentration of sample solution and resulted in the increase of equilibrium loading [36]. The initial concentration of metal ions in an aqueous solution as a function of adsorption rate which is also shown in Fig. 7. In the present study, 10, 25, 50, and 100 mg/L solution of Cu(II) and Ni(II) were prepared to study the effect of initial concentration on sorption kinetics. Until 100 mg/L, a linear trend was observed as adsorption increases with an increase in the initial concentration. As shown in Fig. 7,

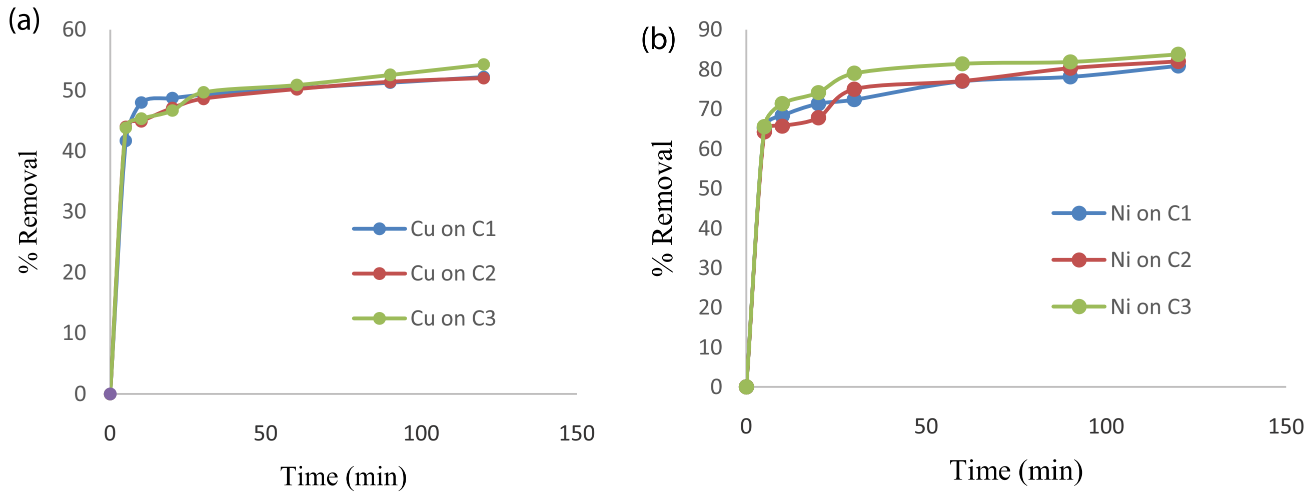

Fig. 5. Percentage removal of (a) Cu(II) and (b) Ni(II).

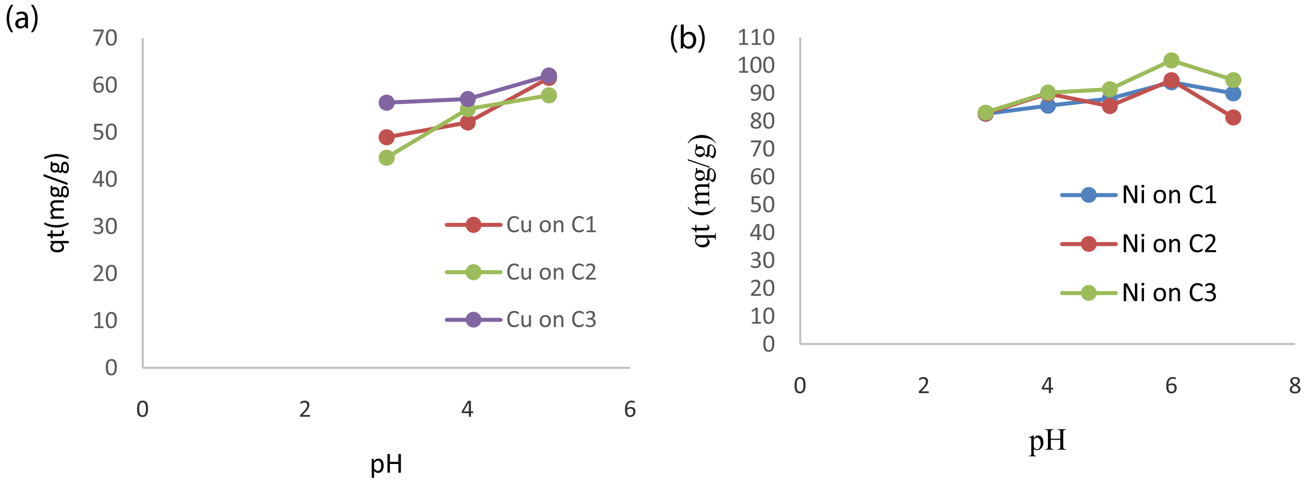

Fig. 6. Effect of pH on adsorption capacity of (a) Cu(II) and (b) Ni(II).

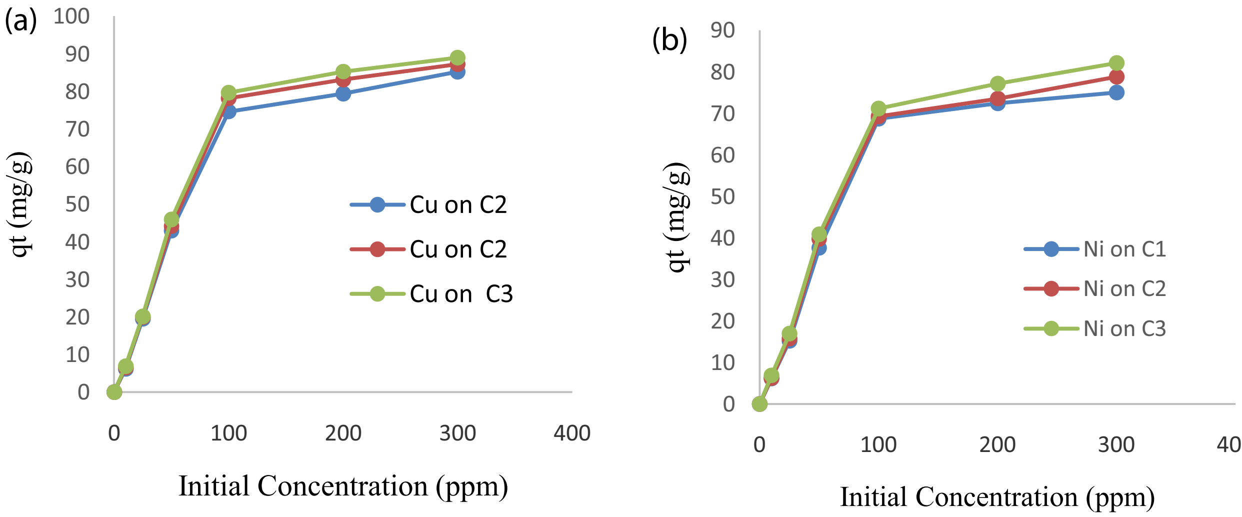

Fig. 7. Effect of initial concentration of (a) Cu(II) and (b) Ni(II) on adsorption capacity.

after 100 mg/L, no significant increase occurred therefore optimized concentration achieved at 100 mg/L.

3.5.4. Effect of adsorbent dosage

The adsorbent amount can significantly affect the removal efficiency of metals from an aqueous solution. Fig. 8 shows the effect of adsorbent dose 0.1, 0.2 and 0.4 g. Adsorption of metal ions increased with an increase in adsorbent dose as shown in Fig. 8 and percentage removal of both metal ions increased with an increase in adsorbent dose. At a low adsorbent dose, for example, 0.1 g, the available sorption sites were quite insufficient compared with the high adsorbent dose, hence, percentage removal was low at this point as compared to 0.4 g. Wu et al. [37] carried out a study using lignin to remove Cr(III) from water. After following the optimization of different parameters, it appeared that Cr(III) adsorption clearly depended on the adsorbent. Results showed a higher lignin dose was the best option that results in 90% removal efficiency. The result also demonstrated that the adsorption capacity decreases with the increase of adsorbent dose for the adsorbent. This decrease is due to the inverse relation of adsorption capacity with adsorption dose.

3.5.5. Role of lignin in the adsorption of metal ions

The results from AAS analysis showed that an increase in lignin content in beads resulted in enhanced removal efficiency for both Cu(II) and Ni(II) (Fig. 9). This increase in removal efficiency can be attributed to the functional group moieties of lignin that provides more active sites with the addition of more lignin in lignin/alginate/hydroxyapatite composites beads.

3.6. Isotherm study

Langmuir plots for the adsorption of Cu(II) and Ni(II) are shown in Figs. 10 and 11. Isotherms constant for both

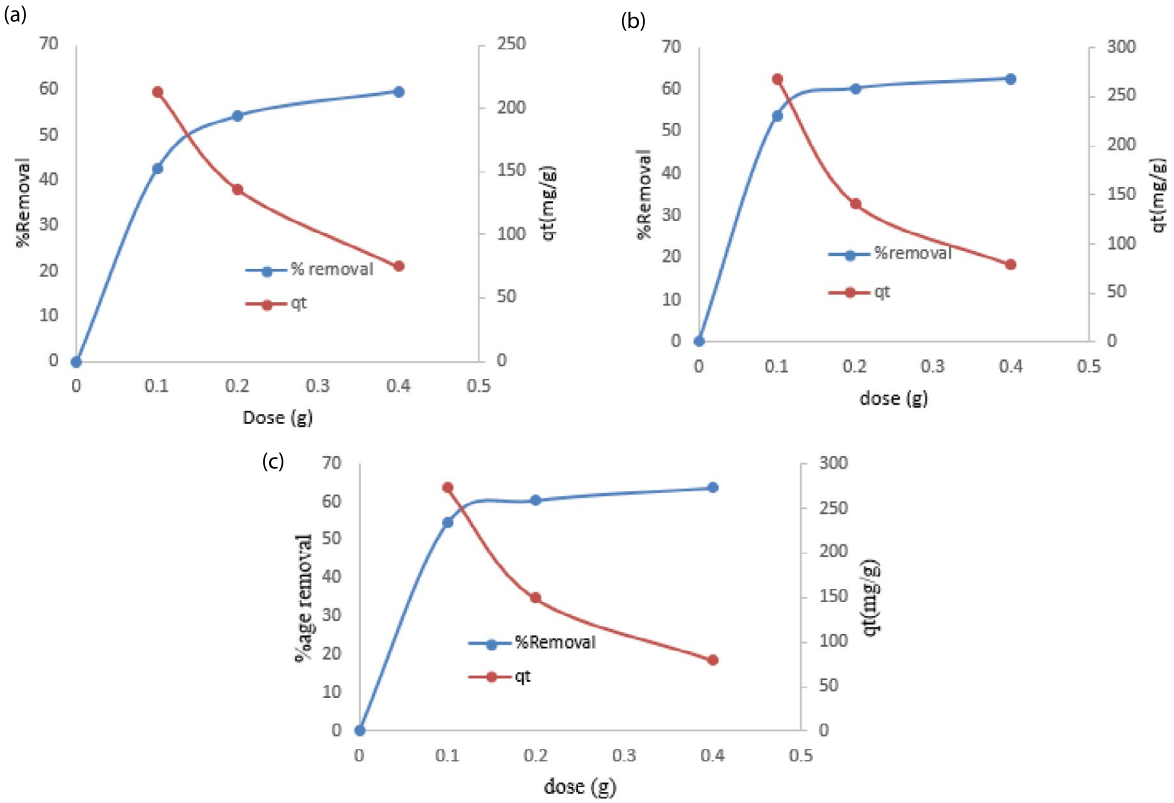

Fig. 8. Effect of beads dose on the removal of Cu(II) on (a) C1, (b) C2, and (c) C3.

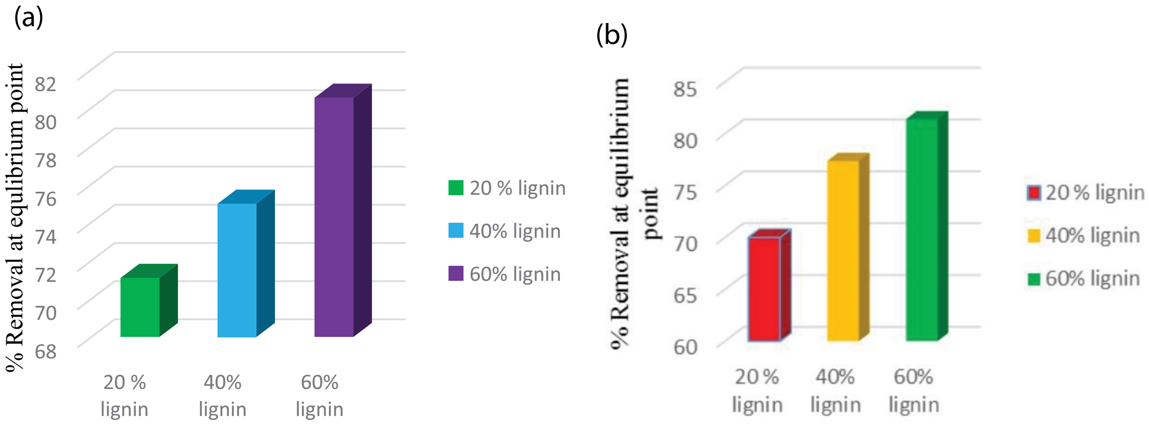

Fig. 9. Lignin role on the adsorption of (a) Cu(II) and (b) Ni(II).

Cu(II) and Ni(II) are shown in Table 3. The plot shows that Langmuir isotherm is applicable for adsorption of Cu(II) and Ni(II). The Langmuir isotherm was found to be linear over the entire study's concentration range, that is, (10, 25, 50, and 100 ppm) with high R^2 values. The R^2 values for both copper and nickel showed the best applicability of this isotherm. The values of both isotherms showed that adsorbed metal ions formed a monolayer on the adsorbent surface [25]. The results showed R_L values between 0.2–0.7 for Cu(II), while for Ni(II) it was between 0.4–0.9, indicating the favorability of adsorption (Table 2). Freundlich isotherm for adsorption of Cu(II) and Ni(II) are shown in Figs. 12 and 13 and the isotherm constants are given in Table 3. It was observed that the correlation factor R^2 of the Freundlich model ($R^2 = 0.9906$) was less compared with Langmuir Model. The results indicate that Langmuir isotherm was best fitted to the experimental data which means monolayer adsorption on the surface of beads.

3.7. Adsorption kinetics

The kinetics of Cu(II) and Ni(II) ions adsorption on lignin/alginate/hydroxyapatite beads was analyzed using pseudo-first-order and pseudo-second-order kinetic models.

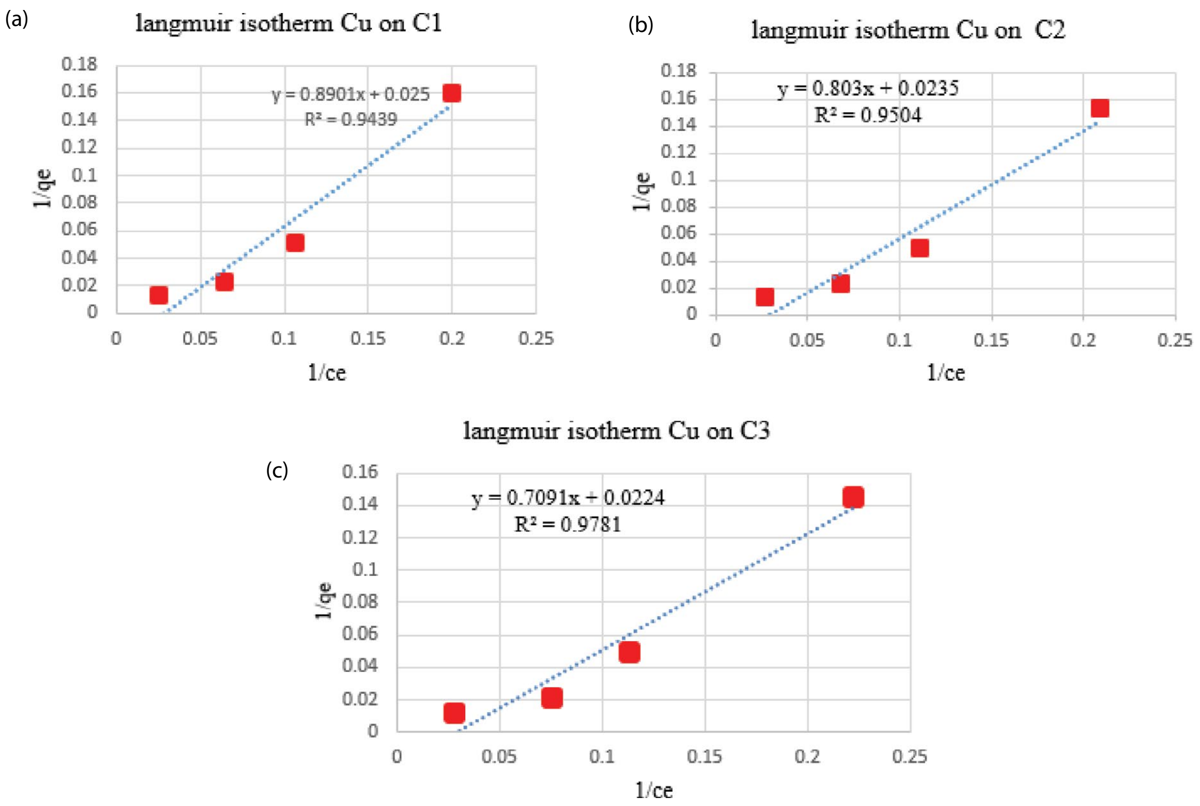

Fig. 10. Langmuir isotherm model for Cu(II) adsorption.

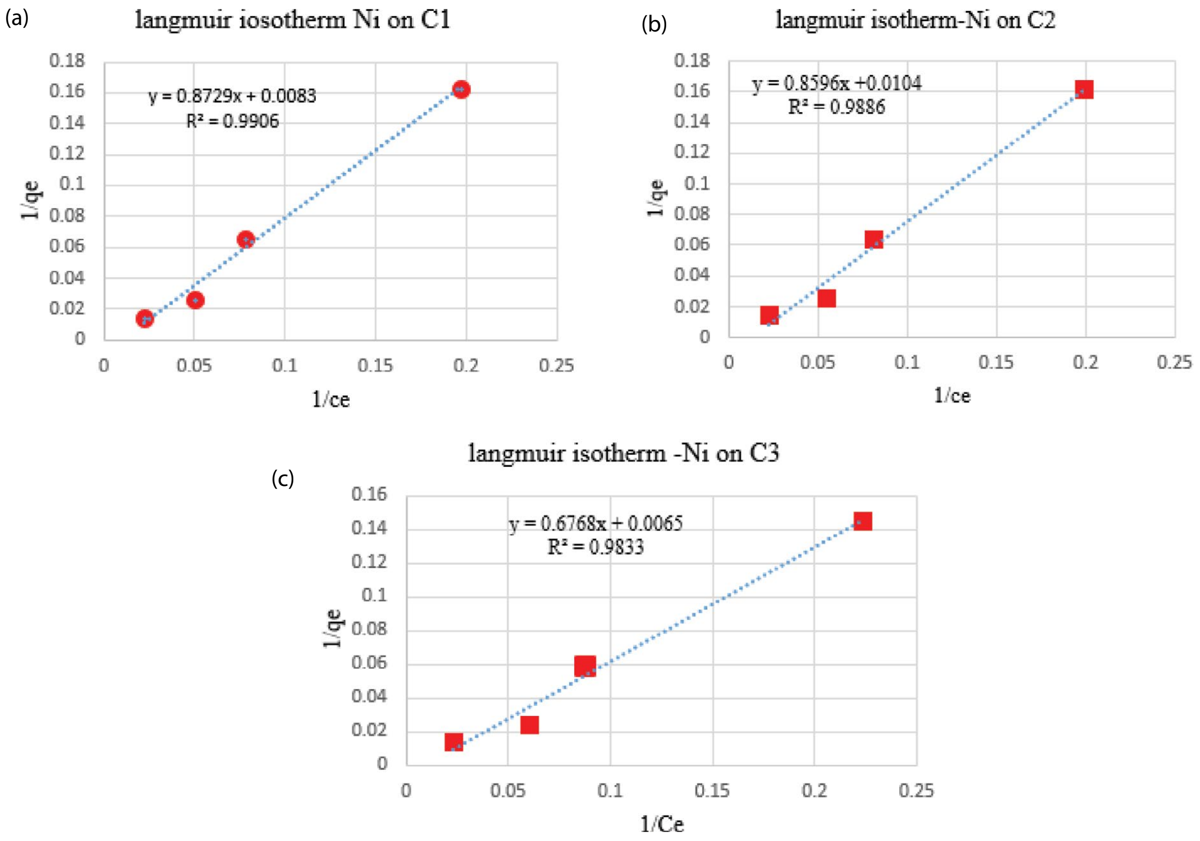

Fig. 11. Langmuir isotherm model for Ni(II) adsorption.

Table 2
R_L values for isotherm model

C_i	Cu-C1	Cu-C2	Cu-C3	Ni-C1	Ni-C2	Ni-C3
	R_L (for Langmuir constant)					
10	0.787	0.781	0.763	0.9174	0.892	0.917
25	0.597	0.588	0.563	0.8163	0.769	0.816
50	0.425	0.416	0.392	0.689	0.625	0.689
100	0.270	0.263	0.243	0.5263	0.454	0.526

Figs. 14 and 15 show the pseudo-first-order kinetic model plot for adsorption and Figs. 16 and 17 show a pseudo-second-order kinetic model plot. The less value of R^2 for the pseudo-first-order model shows that this model is not applicable to experimental kinetic data compared to the pseudo-second-order model value which was closed to regression factor 1. On the basis of these model results, it can be concluded that adsorption of lignin/alginate/hydroxyapatite beads did not follow the pseudo-first-order kinetics. Therefore, the adsorption system under study can be defined by the pseudo-second-order kinetic model. A similar

Table 3
Results of applied isotherm models

Isotherm model and parameters	Copper			Nickel		
	C1	C2	C3	C1	C2	C3
Experimental q_e (mg/g)	74.64	78.11	79.67	68.7004	69.2791	69.2791
Langmuir isotherm						
q_m (mg/g)	41.6	43.47	45.45	120.48	96.15	153.84
K_a (L/mg)	0.027	0.028	0.031	0.009	0.012	0.009
R^2	0.9469	0.9504	0.9371	0.9906	0.9886	0.9835
Freundlich isotherm						
K_f (mg/g)	1.19	1.267	1.614	1.049	4.779	1.452
R^2	0.928	0.934	0.9217	0.9275	0.9673	0.9607
$1/n$	0.846	0.8025	0.8525	0.8722	0.5375	0.9375

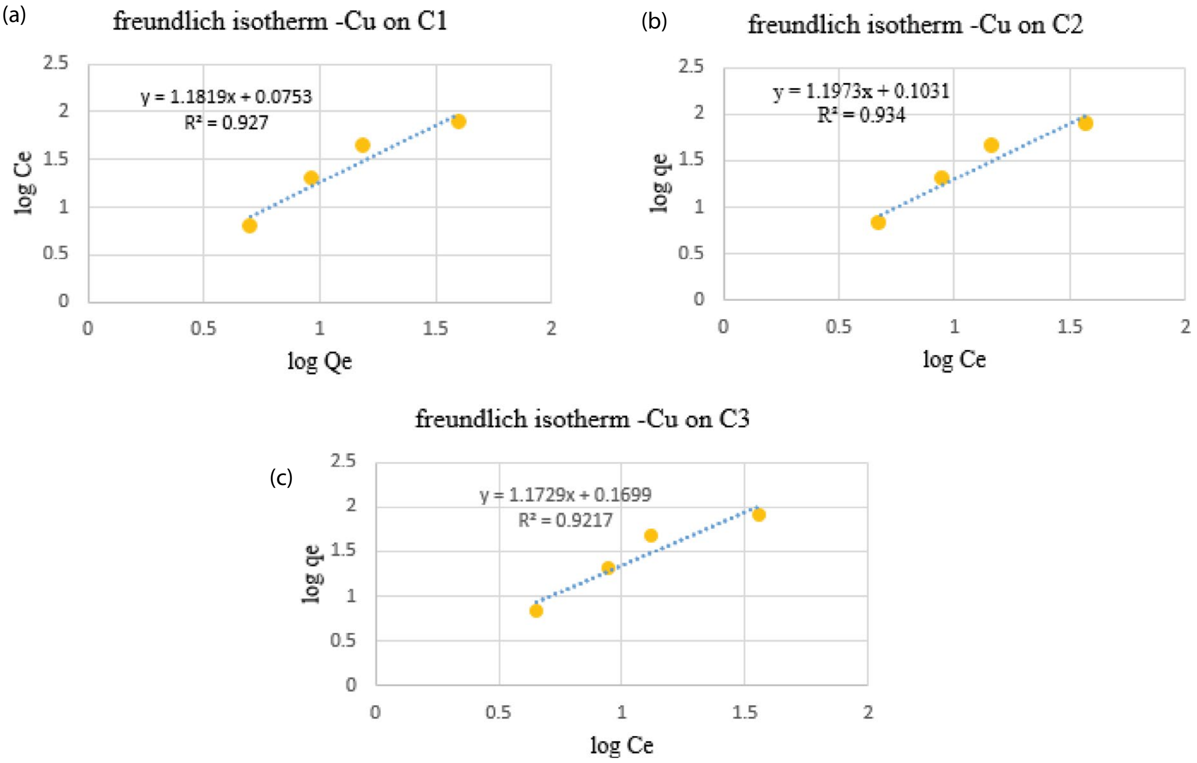

Fig. 12. Freundlich isotherm model for Cu(II) adsorption.

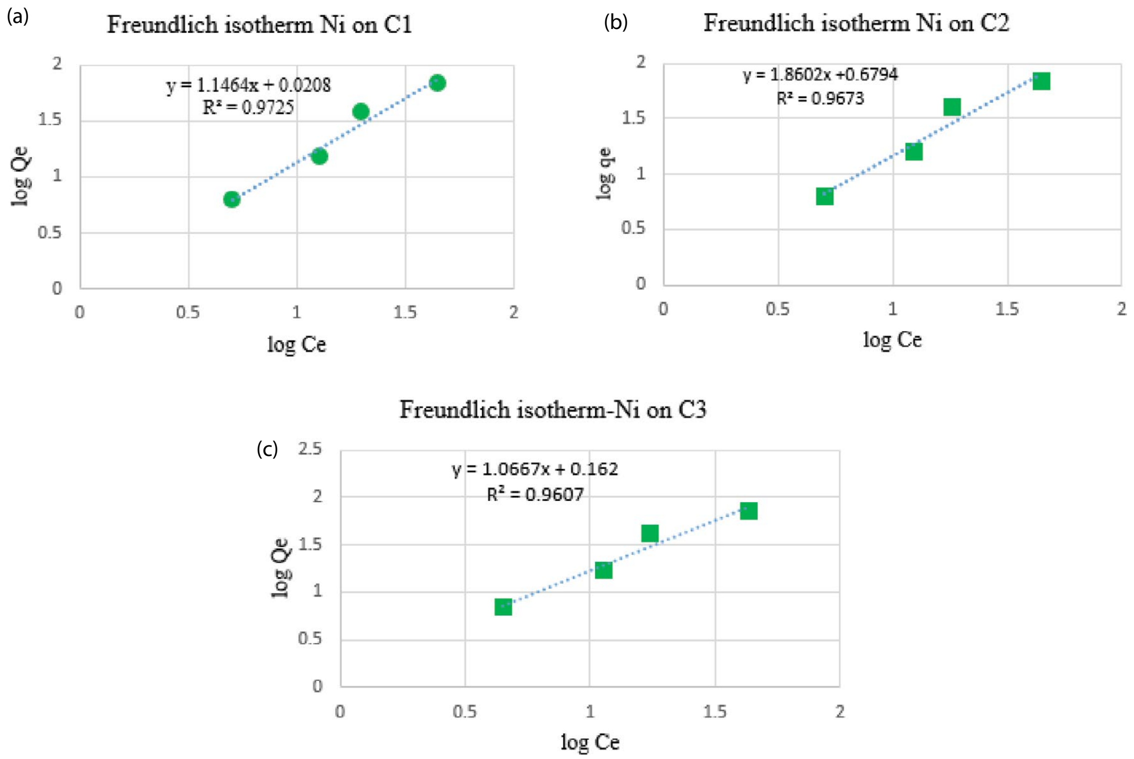

Fig. 13. Freundlich isotherm model for Ni(II) adsorption.

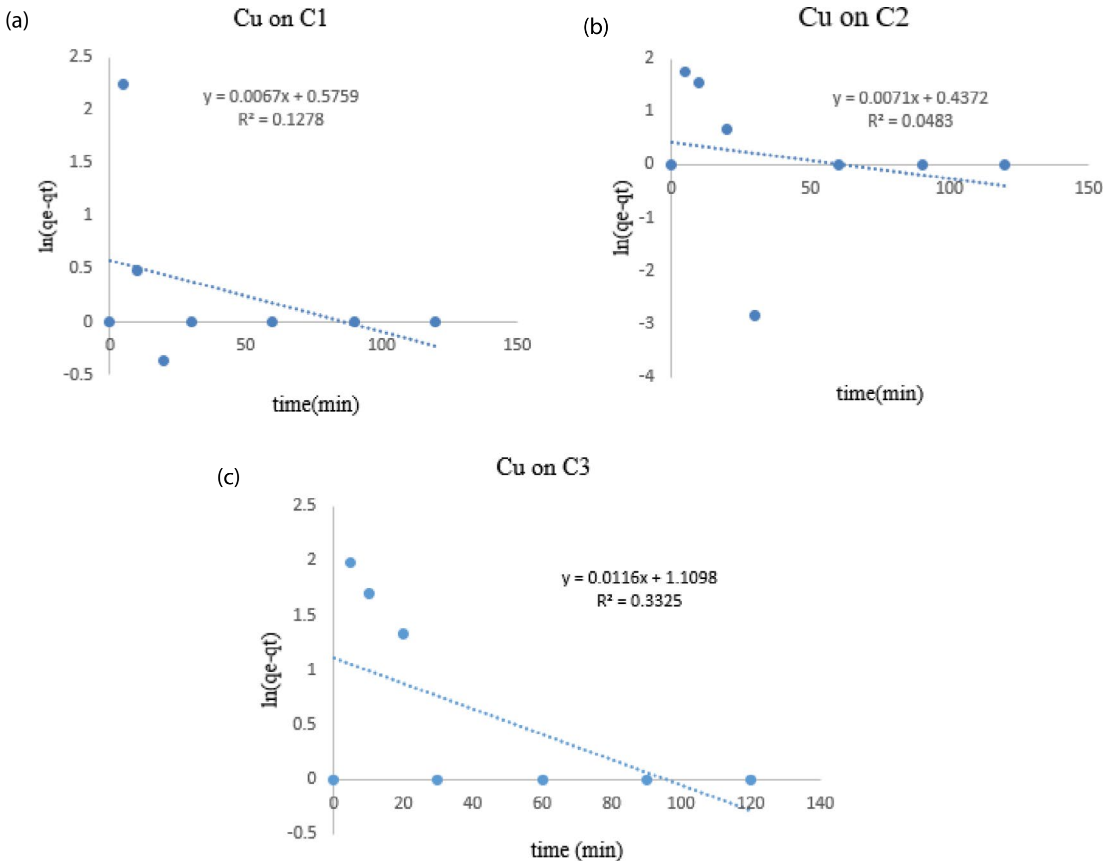

Fig. 14. Pseudo-first-order kinetic model for Cu(II) adsorption.

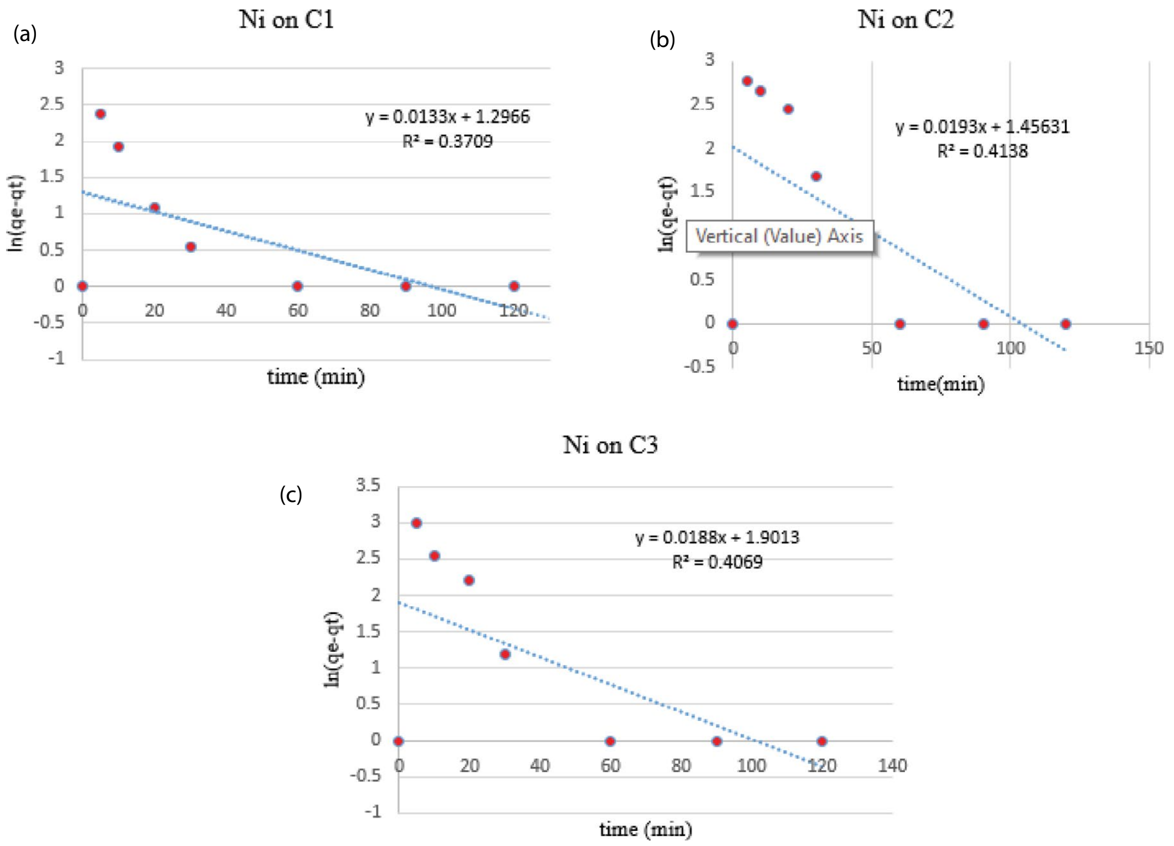

Fig. 15. Pseudo-first-order kinetic model Ni(II) adsorption.

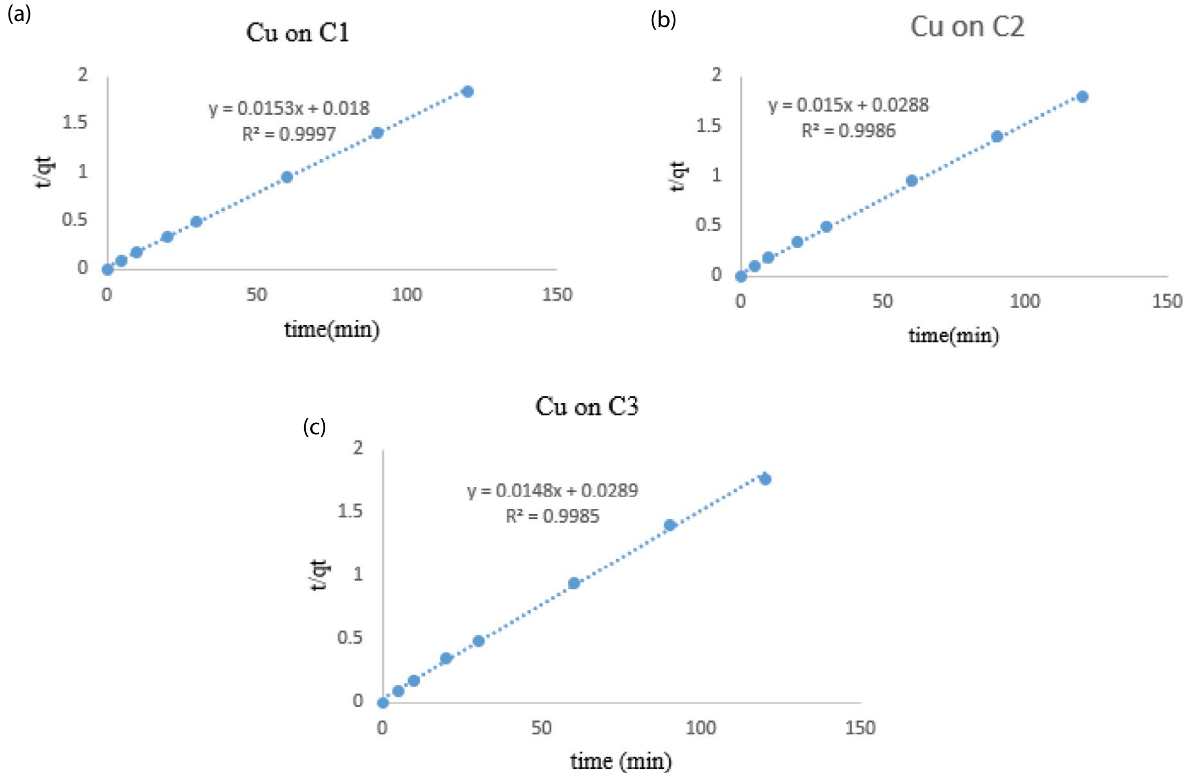

Fig. 16. Pseudo-second-order kinetic model for Cu(II) adsorption.

trend was observed by Seyedvakili and Samipoorgiri [45], during a thermo-kinetic study of heavy metal ions adsorption onto lignin. The present study was also supported by adsorption studies conducted at different temperatures, at which, lignin particle sizes, pH and solid to liquid ratios were calculated. The maximum lignin adsorption capacities at 25°C were 87.05 mg/g (1.37 mmol/g). Adsorption of Cu(II) (68.63 mg/g at 10°C and 94.68 mg/g at 40°C) at 10°C increased with an increase in temperature. Copper adsorption followed the pseudo-second-order rate kinetics. In present study, a linear plot of t/q_t vs. t (Figs. 16a–c) showed R^2 value of closer to 1 as compared with R^2 values obtained from the pseudo-first-order model (Fig. 14). Therefore, it was evident that the pseudo-first-order model is not applicable for modeling the adsorption of Cu(II) and Ni(II) on lignin/HA beads. The results given in Table 4 suggest that the pseudo-second-order model fitted well with data with R^2 value of 0.9990.

3.8. Reusability studies

The reusability of an adsorbent is an important characteristic for its use in industrial applications considering cost-benefit relationships alongside its efficiency.

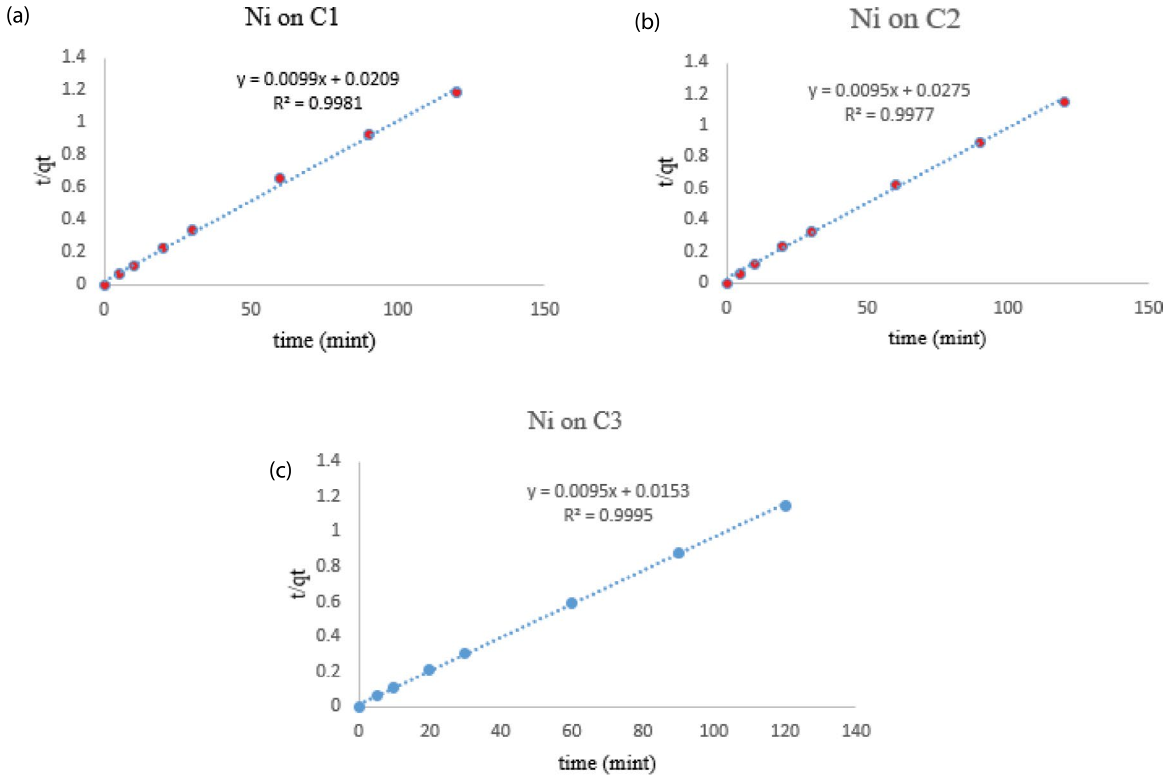

Fig. 17. Pseudo-second-order kinetic model for Ni(II) adsorption.

Table 4
Kinetic model and parameters for Cu(II) and Ni(II)

Kinetic model	Copper			Nickel		
	C1	C2	C3	C1	C2	C3
Experimental q_e (mg/g)	74.64	78.11	79.67	68.7004	69.2791	69.2791
Pseudo-first-order						
q_e (mg/g)	3.7661	2.976	15.516	19.79	28.57	153.84
K_1 (1/min)	0.027	0.028	0.0116	0.0133	0.0193	0.0188
R^2	0.1278	0.0483	0.3325	0.9906	0.4138	0.4069
Pseudo-second-order						
q_e (mg/g)	65.35	66.66	67.56	101.01	105.26	105.263
R^2	0.999	0.998	0.998	0.998	0.997	0.999
K_2 (g/mg min)	0.013	0.0078	0.0075	0.0046	0.0032	0.0058

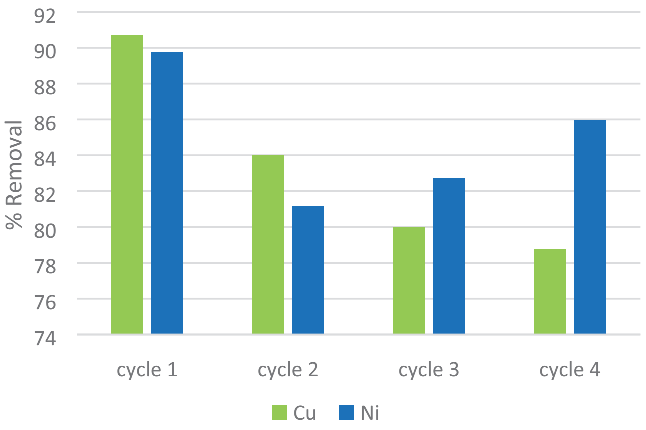

Fig. 18. Regeneration cycle efficiency of adsorbent.

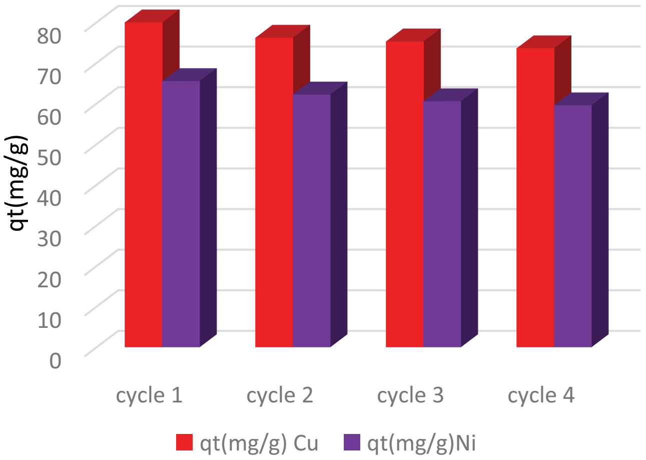

Fig. 19. Regeneration cycle efficiency of adsorbent on adsorption.

The reusability of lignin/alginate/hydroxyapatite beads was examined by adsorption-desorption experiments. Desorption experiments were carried out in 0.1 M NaOH solution as eluent. A mixture of NaOH and metal ions loaded adsorbent was kept in an orbital shaker at room temperature till equilibrium was reached. Filtered solutions were analyzed with an atomic adsorption spectrometer for residual metal ions concentration. The results from four consecutive adsorption-desorption experiments showed that the developed beads can be used multiple times without considerable loss in adsorption efficiency. The removal efficiency remained above 79% after four successive cycles. For regeneration study optimized parameters of Cu(II) and Ni(II) were taken with initial concentration 100 ppm; C3 ratio for lignin composite beads; time 30 min and pH 5. Figs. 18 and 19 show the change in % adsorption efficiency and adsorption capacity with increased in the regeneration cycle, which showed that % removal and q_t (mg/g) slightly decreased with the increase in adsorption–desorption cycle.

4. Conclusion

The present study focused on the development of eco-friendly lignin/alginate/hydroxyapatite beads as an adsorbent for the efficient removal of Cu(II) and Ni(II) ions from an aqueous solution. Results showed that the removal efficiency of adsorbent was dependent on contact time, pH, initial concentration and adsorbent dose. The adsorption of Cu(II) and Ni(II) ions of lignin/alginate/hydroxyapatite beads followed the pseudo-second-order kinetic model and Langmuir isotherm model. The adsorption capacity was enhanced with the increase of lignin content in beads. The maximum adsorption capacity for Cu(II) at pH 5 with initial concentration 100 ppm at equilibrium time of 30 min was 79.67 mg/g while for Ni(II) it was 71.18 mg/g at pH 7 with an initial concentration 100 ppm at equilibrium time of 60 min on C3 (60% lignin). The reusability of lignin/alginate/hydroxyapatite beads showed 79% removal efficiency after four successive cycles. Results showed that lignin/alginate/hydroxyapatite composite beads have good potential as an adsorbent material for the removal of heavy metal ions from an aqueous solution.

Acknowledgment

The research was supported by Kinnaird College for Women, Lahore, Pakistan and the research cluster grant (R18029) from Zayed University, Abu Dhabi, United Arab Emirates.

References

[1] Y. Wada, M. Flörke, N. Hanasaki, S. Eisner, G. Fischer, S. Tramberend, Y. Satoh, M.T.H. van Vliet, P. Yillia, C. Ringler, P. Burek, D. Wiberg, Modeling global water use for the 21st century: the water futures and solutions (WFaS) initiative and its approaches, Geosci. Model Dev., 9 (2016) 175–222.

[2] T. Sato, M. Qadir, S. Yamamoto, T. Endo, A. Zahoor, Global, regional, and country level need for data on wastewater generation, treatment, and use, Agric. Water Manage., 130 (2013) 1–13.

[3] D. Lakherwal, Adsorption of heavy metals: a review, Int. J. Environ. Res. Dev., 4 (2014) 41–48.

[4] S. Pandey, Water pollution and health, Kathmandu Univ. Med. J., 4 (2006) 128–134.

[5] A. Nasrullah, B. Saad, A.H. Bhat, A.S. Khan, M. Danish, M.H. Isa, A. Naeem, Mangosteen peel waste as a sustainable precursor for high surface area mesoporous activated carbon: characterization and application for methylene blue removal, J. Cleaner Prod., 211 (2019) 1190–1200.

[6] Environment SA, Unit SD, Region SA, Pakistan Strategic Country Environmental Assessment (In Two Volumes) Volume I: Main Report South Asia Environment and Social Development Unit South Asia Region Pakistan Strategic Country Environmental Assessment Volume I, 2006, I (36946). Available at: http://siteresources.worldbank.org/SOUTHASIAEXT/Resources/Publications/448813-1188777211460/pakceavolume1.pdf

[7] A. Aeisyah, M.H.S. Ismail, K. Lias, S. Izhar, Adsorption process of heavy metals by low-cost adsorbent: a review, Res. J. Chem. Environ., 18 (2014) 91–102.

[8] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater., 97 (2003) 219–243.

[9] M.K. Daud, M. Nafees, S. Ali, M. Rizwan, R.A. Bajwa, M.B. Shakoor, M.U. Arshad, S.A.S. Chatha, F. Deeba, W. Murad, I. Malook, S.J. Zhu, Drinking water quality status and contamination in Pakistan, Biomed Res. Int., 2017 (2017) 18p.

[10] A. Farooqi, H. Masuda, N. Firdous, Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan, and possible contaminant sources, Environ. Pollut., 145 (2007) 839–849.

[11] E.T. Igunnu, G.Z. Chen, Produced water treatment technologies, Int. J. Low-Carbon Technol., 9 (2014) 157–177.

[12] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - a review, Bioresour. Technol., 99 (2008) 6017–6027.

[13] A. Jamshaid, A. Hamid, N. Muhammad, A. Naseer, M. Ghauri, J. Iqbal, S. Rafiq, N.S. Shah, Cellulose-based materials for the removal of heavy metals from wastewater–an overview, ChemBioEng Rev., 4 (2017) 240–256.

[14] Z. Shirani, C. Santhosh, J. Iqbal, A. Bhatnagar, Waste *Moringa oleifera* seed pods as green sorbent for efficient removal of toxic aquatic pollutants, J. Environ. Manage., 227 (2018) 95–106.

[15] S.O. Lesmana, N. Febriana, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Studies on potential applications of biomass for the separation of heavy metals from water and wastewater, Biochem. Eng. J., 44 (2009) 19–41.

[16] T. Hatakeyama, H. Hatakeyama, Lignin structure, properties, and application, biopolymers, Adv. Polym. Sci., 232 (2009) 1–63.

[17] A. Demirbas, Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignication, J. Hazard. Mater., 109 (2004) 221–226.

[18] A. Naseer, A. Jamshaid, A. Hamid, N. Muhammad, M. Ghauri, J. Iqbal, S. Rafiq, S. Khuram, N.S. Shah, Lignin and lignin based materials for the removal of heavy metals from waste water – an overview, Z. Phys. Chem., 233 (2019) 315–345.

[19] S.K. Srivastava, A.K. Singh, A. Sharma, Studies on the uptake of lead and zinc by lignin obtained from black liquor–a paper industry waste material, Environ. Technol., 15 (1994) 353–361.

[20] A. Agarwal, B. Kapil, Removal of lead from aqueous solution using black liquor – a pulp mill waste, Int. J. Sci. Res., 3 (2014) 2047–2050.

[21] D. Stewart, Lignin as a base material for materials applications: chemistry, application and economics, Ind. Crops Prod., 27 (2008) 202–207.

[22] R.M. Rowell, Removal of Metal Ions from Contaminated Water Using Agricultural Residues, 2nd International Conference on Environmentally-Compatible Forest Products, Fernando Pessoa University, Oporto, Portugal, 2006, pp. 20–22.

[23] S. Lin, R. Huang, Y. Cheng, J. Liu, B.L.T. Lau, M.R. Wiesner, Silver nanoparticle-alginate composite beads for point-of-use drinking water disinfection, Water Res., 47 (2013) 3959–3965.

[24] M. Rajkumar, N. Meenakshisundaram, V. Rajendran, Development of nanocomposites based on hydroxyapatite/sodium alginate: synthesis and characterization, Mater. Charact., 62 (2011) 469–479.

[25] Suhas, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Lignin–from natural adsorbent to activated carbon: a review, Bioresour. Technol., 98 (2007) 2301–2312.

[26] A. Jamshaid, J. Iqbal, A. Hamid, M. Ghauri, N. Muhammad, A. Nasrullah, S. Rafiq, N.S. Shah, Fabrication and evaluation of cellulose-alginate-hydroxyapatite beads for the removal of heavy metal ions from aqueous solutions, Z. Phys. Chem., 233 (2018) 1351–1375.

[27] W. Zheng, X.-m. Li, Q. Yang, G.-m. Zeng, X.-x. Shen, Y. Zhang, J.-j. Liu, Adsorption of Cd(II) and Cu(II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste, J. Hazard. Mater., 147 (2007) 534–539.

[28] A. Nasrullah, A.H. Bhat, M.H. Isa, M. Danish, A. Naeem, N. Muhammad, T. Khan, Efficient removal of methylene blue dye using mangosteen peel waste: kinetics, isotherms and artificial neural network (ANN) modeling, Desal. Wat. Treat., 86 (2017) 191–202.

[29] S. Lagergren, About the theory of so-called adsorption of solid substance, Handlinger, 24 (1898) 1–39.

[30] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[31] X. Chen, Modeling of experimental adsorption isotherm data, Information, 6 (2015) 14–22.

[32] J. Iqbal, N.S. Shah, M. Sayed, M. Imran, N. Muhammad, F.M. Howari, S.A. Alkhoori, J.A. Khan, Z. Khan, A. Bhatnagar, K. Polychronopoulou, I. Ismail, M.A. Haija, Synergistic effects of activated carbon and nano-zerovalent copper on the performance of hydroxyapatite-alginate beads for the removal of As3+ from aqueous solution, J. Cleaner Prod., 235 (2019) 875–886.

[33] Q. Zhang, S. Dan, K. Du, Fabrication and characterization of magnetic hydroxyapatite entrapped agarose composite beads with high adsorption capacity for heavy metal removal, Ind. Eng. Chem. Res., 56 (2017) 8705–8712.

[34] C. Ren, X. Ding, W. Li, H. Wu, H. Yang, Highly efficient adsorption of heavy metals onto novel magnetic porous composites modified with amino groups, J. Chem. Eng. Data, 62 (2017) 1865–1875.

[35] A. Dutta, Y. Diao, R. Jain, E.R. Rene, S. Dutta, Adsorption of cadmium from aqueous solution onto coffee grounds and wheat straw: equilibrium and kinetic study, J. Environ. Eng., 142 (2015) 1–6.

[36] L. Li, J. Iqbal, Y. Zhu, P. Zhang, W. Chen, A. Bhatnagar, Y. Du, Chitosan/Ag-hydroxyapatite nanocomposite beads as a potential adsorbent for the efficient removal of toxic aquatic pollutants, Int. J. Biol. Macromol., 210 (Pt B) (2018) 1752–1759.

[37] Y. Wu, S. Zhang, X. Guo, H. Huang, Adsorption of chromium(III) on lignin, Bioresour. Technol., 99 (2008) 7709–7715.

[38] N. Mahmood, Z. Yuan, J. Schmidt, C.C. Xu, Hydrolytic depolymerization of hydrolysis lignin: effects of catalysts and solvents, Bioresour. Technol., 190 (2015) 416–419.

[39] P. Senthil Kumar, K. Ramakrishnan, S. Dinesh Kirupha, S. Sivanesan, Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk, Braz. J. Chem. Eng., 27 (2010) 347–355.

[40] R. Rostamian, H. Behnejad, Insights into doxycycline adsorption onto graphene nanosheet: a combined quantum mechanics, thermodynamics, and kinetic study, Environ. Sci. Pollut. Res., 25 (2018) 2528–2537.

[41] M. Irani, M. Amjadi, M.A. Mousavian, Comparative study of lead sorption onto natural perlite, dolomite and diatomite, Chem. Eng. J., 178 (2011) 317–323.

[42] A. Ahmadi, S. Heidarzadeh, A.R. Mokhtari, E. Darezereshki, H.A. Harouni, Optimization of heavy metal removal from aqueous solutions by maghemite (γ-Fe_2O_3) nanoparticles using response surface methodology, J. Geochem. Explor., 147 Part B (2014) 151–158.

[43] A. Tripathi, M. Rawat Ranjan, Heavy metal removal from wastewater using low cost adsorbents, J. Bioremed. Biodegrad., 6 (2015) 1–5.

[44] B.G. Lee, R.M. Rowell, Removal of heavy metal ions from aqueous solutions using lignocellulosic fibers, J. Nat. Fibers, 1 (2004) 97–108.

[45] F. Seyedvakili, M. Samipoorgiri, Thermo-kinetic investigation of heavy metal ions adsorption onto lignin considering coupled adsorption–desorption mechanisms: modeling and experimental validation, Int. J. Model. Simul. Sci. Comput., 9 (2018) 1850014.