Indian Journal of Geo Marine Sciences
Vol. 51 (05), May 2022, pp. 468-475
DOI: 10.56042/ijms.v51i05.65573

Sorption studies of divalent ions onto ternary beads of alginate, chitosan and carboxymethyl cellulose

B Mahalakshmi Devi[a], T Gomathi[b], K Vijayalakshmi[c], R Ramya[d], S Pavithra[b] & P N Sudha*[,b]

[a]Department of Chemistry, Bharathiar University, Coimbatore, Tamil Nadu – 641 046, India

[b]PG & Research Department of Chemistry, DKM College for Women, Vellore, Tamil Nadu – 632 001, India

[c]Department of Chemistry, Madras Christian College, Chennai, Tamil Nadu – 600 059, India

[d]Department of Chemistry, C. Kandaswami Naidu College for Women, Cuddalore, Tamil Nadu – 607 001, India

*[E-mail: drparsu8@gmail.com]

Received 05 February 2022; revised 10 May 2022

The potential of sodium alginate (AL)/ chitosan (CS)/ carboxymethyl cellulose (CMC) beads as an adsorbent for removing the divalent metal ions such as Cu (II) and Ni (II) ions from aqueous solution was assessed in the current work using a batch adsorption technique. FT-IR and XRD measurements were used to investigate the formation of the ternary beads. The percentage removal of metal ions was investigated in batch mode as a function of metal ion solution pH, initial metal ion concentration, adsorbent dosage, and contact time. The observed outcome shows that the best pH for removing both metal ions was reported to be 5.0. The incorporation of experimental data in theoretical modelling exhibits that the adsorption would be multilayer through pseudo-second order (R^2 > 0.9) kinetics. The removal efficiency of ternary beads reveals that copper ions (C_{max} = 203.69 mg/g) were removed better than nickel ions (C_{max} = 194.05 mg/g).

[**Keywords**: Batch adsorption, Copper (II), Divalent metal ions, Nickel (II), Ternary alginate beads]

Introduction

Water is the widely used natural resource on earth and is vital for all living things[1]. Such water becomes tainted with different pollutants, contributing to the global environmental issue[2]. Due to the massive expansion in the usage of heavy metals in the industries that have a significant impact on environmental contamination during the past few decades, there has unavoidably been an increase in the flux of metallic materials in aquatic environments[5]. Zn, Cu, Ni, Cr, Pb, Hg, Ni, and As are some of the dangerous heavy metals that come from the metal plating, mining, paint manufacturing, pesticides, pigment manufacturing, printing, and photographic industries[3]. Due to their tendency to bioaccumulate, even in small amounts, extremely poisonous heavy metals found in waste cause serious natural and health problems[4] and hence the heavy metal ions must be derived from wastewater streams and industrial effluents[5]. Copper (II) and Nickel (II) are such heavy metals which are widespread contaminants and most toxic to all the human beings and as well as other living organisms[6].

The adsorption process is a well-known, effective treatment around the globe[7,8] due to its adaptability, minimal chemical use, low waste sludge production, and affordability[9]. For the adsorption process, in recent years, various researchers point towards the naturally available biomaterials including agricultural products and by-products such as algae, bacteria, yeast, coir pith, sawdust, coconut husk, activated carbon, rice husk, egg shell which can accumulate high concentration of heavy metals. In addition to this some other sorbents which can be used for wastewater treatment includes activated carbon[10], carbon nanotubes[11], gelatin[12], lignocellulosic fibers[13], biopolymeric materials such as chitosan[14,15], sodium alginate[16], carboxymethyl cellulose[17], starch[18] and so on.

This work used low-cost adsorbents such chitosan, alginate, and CMC, a cellulose derivative, to remove the Cu(II) and Ni(II) ions from the synthetic wastewater solution[19,20]. Chitosan has higher adsorption properties[21] because of the free amino groups that are exposed. Biopolymeric polysaccharide alginate also has a very high affinity for metal ions[22]. CMC, a cellulose derivative shows amphiphilic characteristics due to its nontoxic, biocompatible, biodegradable and hydrophilic nature[23]. Gelation happens when an alginate solution interacts with divalent cations, and it is thought that this gelation

mostly takes place at junctions known as 'egg box junctions' in the sequence-rich chain area[24]. Cobalt (II) ion adsorption onto alginate beads was studied by Navarro and his co-workers in batch experiments at room temperature[25]. By employing sodium alginate/ fly ash beads as an adsorbent, Zn(II) ions may be successfully extracted from aqueous solutions[26].

Sodium alginate, chitosan, and carboxymethyl cellulose were combined to make beads are used to remove copper and nickel synthetic solution. Adsorbent dosage, pH of the solution, and duration spent in contact with the adsorbate are a few examples of the optimal parameters that affect metal ion uptakes.

Materials and Methods

Chitosan, which was 92 percent deacetylated, was purchased from Indian Sea Foods in Cochin. Thermo Fisher Scientific Private Ltd. and Nice Chemicals Private Ltd., respectively, provided the sodium alginate and carboxymethyl cellulose. Glutaraldehyde, the crosslinking agent, was purchased from SD-fine-chem.

Preparation of sodium alginate/ chitosan/ carboxymethyl cellulose (1:1:1) – glutaraldehyde beads

Ionic cross linking was used to prepare the sodium alginate/ chitosan/ carboxymethyl cellulose beads in a 1:1:1 ratio with the cross-linking chemical glutaraldehyde. In order to create chitosan solution, 0.5 g of chitosan was first mixed with 25 mL of glacial acetic acid. Under continuous magnetic stirring for about 30 minutes, both sodium alginate and CMC (each 0.5 g in 25 mL of water) solutions was added to this. The resulting mixture was uniform and free of bubbles. The mixture was injected into $CaCl_2$ solution. After setting up in $CaCl_2$ solution for 24 h, the produced beads were filtered. After three rounds of rinsing and washing with double-distilled water the beads were left to dry.

Metal ion removal

A conical flask containing 100 mL of separate solutions of copper sulphate and nickel ammonium sulphate (200 mg/L) was filled with about 1 g of prepared SA/CS/CMC bead (1:1:1-with glutaraldehyde). An orbital shaker was used to vigorously stir this solution for an hour at a constant speed of 160 rpm. To pH adjustment 0.1 N NaOH and HCl was added. The aforementioned combination was shaken, filtered via Whattmann filter paper, and then atomic absorption spectroscopy measurements were performed on the filtrate.

Results and Discussion

Characterization of ternary alginate beads

The sodium alginate with chitosan and carboxymethyl cellulose homogenous mixture was dropped in calcium chloride solution to get a ternary biopolymeric bead. The beads were created concurrently using an ionic cross-linking technique, and it is anticipated that the polymer chains' oppositely charged functional groups will limit one another's mobility during a gelation process by electrostatic interaction. Its formation is confirmed using FTIR and XRD analysis. The FTIR spectra of the sodium alginate /chitosan / carboxymethyl cellulose (1:1:1) ternary bead prepared with glutaraldehyde was shown in Figure 1. The prominent absorption peaks observed at 3626.32, 2930.52 and

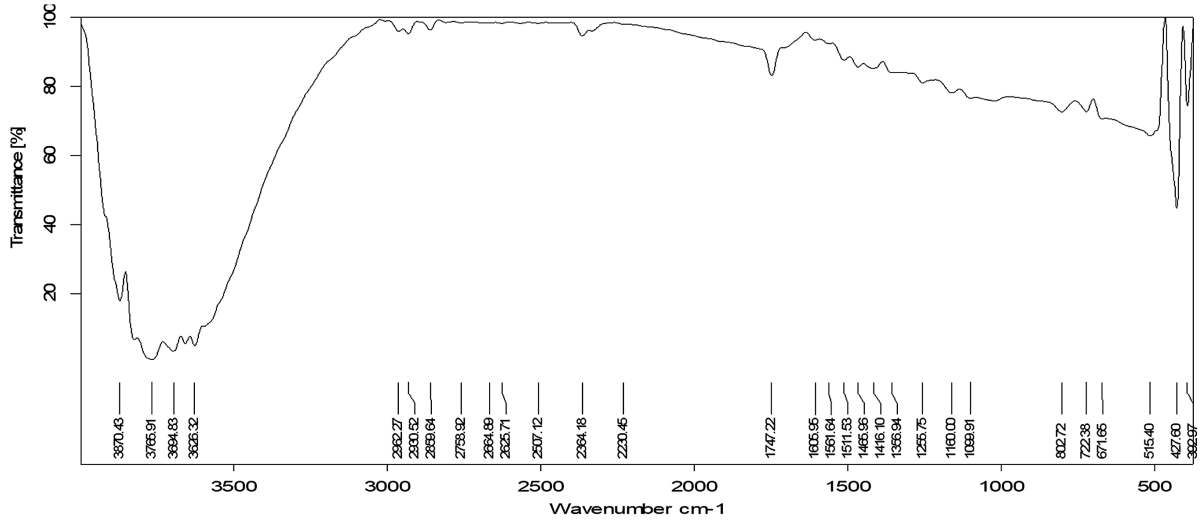

Fig. 1 — FTIR spectrum of chitosan /sodium alginate/ carboxymethyl cellulose (1:1:1) ternary bead – glutaraldehyde

2859.64 cm^{-1} was given to O-H, N-H, C-H stretching[27]. The peaks which were found at 1605.95, 1416.10 and 1356.94 cm^{-1} show the presence C=O, -C=N, OH, CH bending, respectively. The C-O, C-C stretching, N-H wagging and C-C corresponds to the peaks at 1160.00, 1099.91, 722.38 and 427.60 cm^{-1}, respectively. The observance of peaks due to various functional groups (OH, NH, COO^-) reveals that all the three added polymeric components chitosan, sodium alginate and carboxymethyl cellulose get blended effectively during the bead formation. The peak at 1605.95 cm^{-1} exhibit C=N stretching, also indicates that the glutaraldehyde is efficiently crosslinked with the added three polymeric components (CMC, CS and AL).

Figure 2 shows the XRD diffractogram of sodium alginate /chitosan /carboxymethyl cellulose (1:1:1) ternary bead. Two broad peaks were observed at various 2θ values such as 29° and 41°. By disrupting amino, carboxylate ion, and -OH groups, the crosslinking agent glutaraldehyde caused the increased packing of chitosan, sodium alginate, and CMC chains, which led to deformation of the crystalline regions and a broadening of the peaks. The synthesized bead was significantly amorphous, as indicated by the calculated values for the reduced percentage degree of crystallinity, making it suitable for adsorption.

The proposed binding mechanism for the metal ions onto AL/CS/CMC ternary beads produced with glutaraldehyde based on the findings of several research (Fig. 3).

Influence of contact time

Figure 4 demonstrated that, with increasing contact time, the percent removal of both Cu and Ni metal ions increased. The percentage of elimination by the adsorbent was high throughout the first 60 min. This can be because of the sizeable surface of the adsorbent and the length of time required for the metal ions to successfully make contact with the beads employed. After some time, equilibrium was attained, and because there were fewer active sites available on the sorbent's surface, the uptake of metal ions remained stable.

Effect of pH

The pH has an impact on the proportion of heavy metals removed and metal sorption[29]. The results show that as the pH rises from 4 to 5 (Fig. 5), the percentage of nickel and copper metal ions eliminated increases, but after that, it decreases.

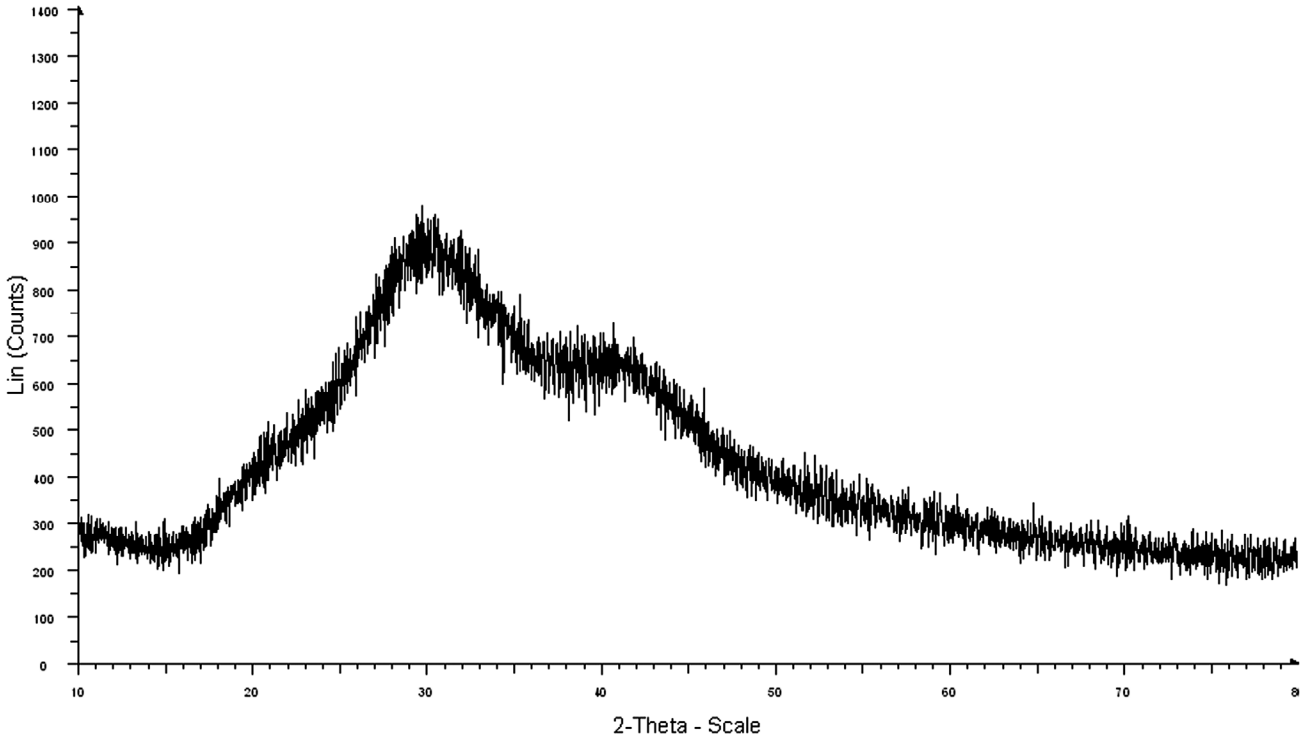

Fig. 2 — X-ray diffractogram of chitosan /sodium alginate/ carboxymethyl cellulose (1:1:1) ternary bead – glutaraldehyde

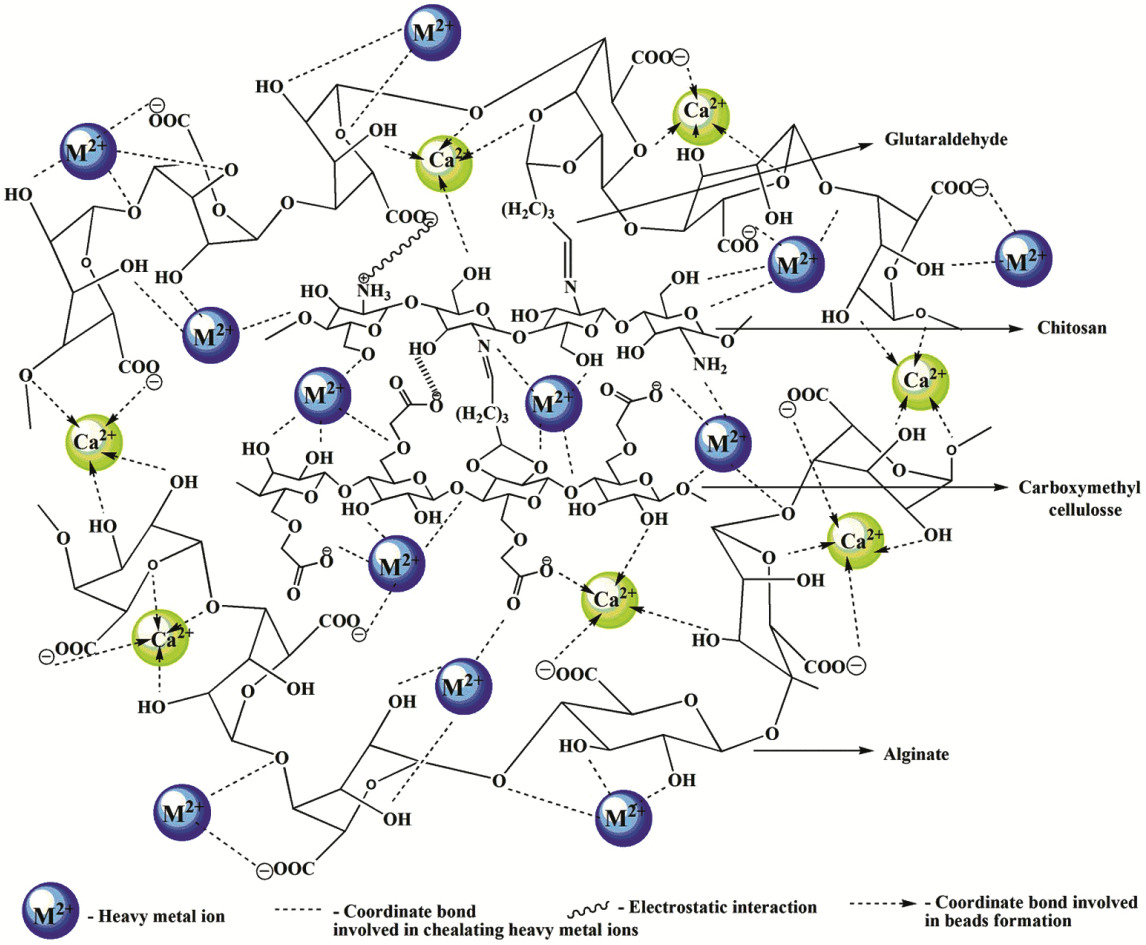

Fig. 3 — Proposed mechanism of binding of metal ion onto CS/AL/CMC (1:1:1) ternary bead – glutaraldehyde

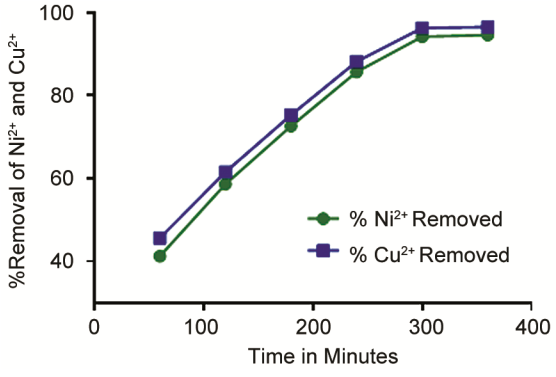

Fig. 4 — Effect of contact time on adsorption of Cu(II) and Ni(II) ions by CS/AL/CMC (1:1:1) - ternary bead – glutaraldehyde

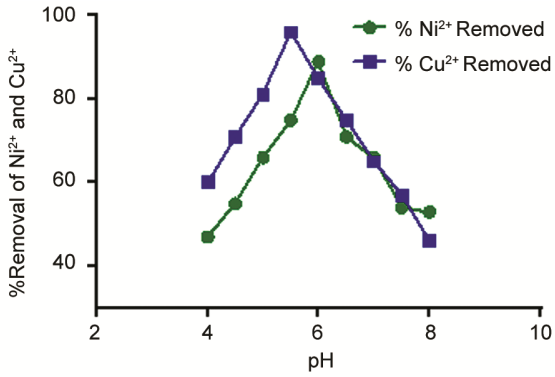

Fig. 5 — Effect of pH on the adsorption of Cu(II) and Ni(II) ions using CS/AL/CMC (1:1:1) - ternary bead- glutaraldehyde

Low pH values inhibit adsorption because protons and metal ions compete for same functional groups (OH, NH_2, COO^-) in the AL/CS/CMC bead. Also, the bulk of functional groups are protonated at low pH levels, which decreases the number of binding sites available for metal ion[30]. Optimum pH was 5.5 and 6 for Cu and Ni.

Effect of adsorbent dose

Figure 6 clearly shows that as adsorbent dosage is increased, the adsorption efficiency also raises noticeably[32]. An improvement in removal efficiency resulted from the greater adsorbent dose increasing the quantity of adsorbent surface that was available for the solute to be adsorbed.

To put it in another way, the higher removal rates of Cu(II) and Ni(II) ions can be due to the larger dosage's increased surface and binding sites[33]. The saturation of active sites may be the reason why there was no noticeable improvement in the elimination of either metal ion after 5 g of adsorbent dose.

Adsorption isotherm

Langmuir isotherm

The Langmuir isotherm follows[33,34]:

$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L$

$C_{max} = K_L/b$

C_{ads} = amount of metal ion adsorbed (mg/g)

C_{eq} = equilibrium concentration of metal ion (mg/dm^3)

K_L = Langmuir constant (dm^3/g)

b = Langmuir constant (dm^3/mg)

C_{max} = maximum metal ion adsorbed[35]

Figure 7(a, b) illustrates the Langmuir plot for Cu(II) and Ni(II) ions onto AL/CS/CMC beads synthesized in the presence of the glutaraldehyde; whereas Table 1 displays the Langmuir constants. The essential characteristic of Langmuir isotherm[36] was given by the separation factor (R_L) (Table 2).

The Langmuir isotherm was used to determine whether or not an adsorption process is favorable. Since the computed values of R_L (Table 2) in the current investigation were found to be more than 0 and less than 1, it was decided that the adsorption process is thought to be advantageous.

Freundlich isotherm

The Freundlich equation is:

$$\log Y_e = \log K_f + 1/n \log C_e \quad \ldots (1)$$

Figure 8(a, b) shows the Freundlich adsorption isotherm plots of Cu (II) and Ni (II) onto CS/AL/CMC beads and Table 3 displays the Freundlich constants[37].

The findings showed that the Freundlich better suits well the experimental value than the Langmuir, indicating that multilayer sorption.

Adsorption kinetics

The rate of adsorption site occupation is primarily taken into account in this model, and it is assumed that it is proportionate to the number of vacant sites[38-40]. Pseudo-first-order model's is:

$$\log (q_e\text{-}q_t) = \log q_e - k_1 t / 12.303 \quad \ldots (2)$$

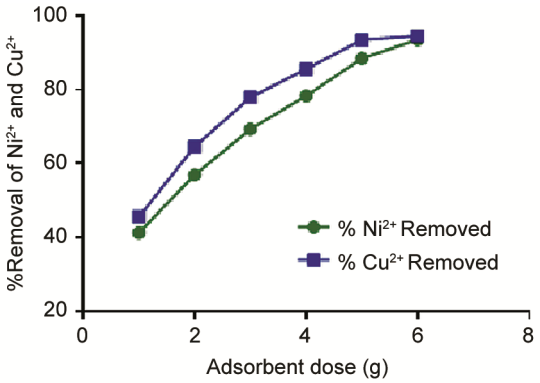

Fig. 6 — Effect of adsorbent dose on the adsorption of Cu(II) and Ni(II) ions using CS/AL/CMC (1:1:1) - ternary bead-glutaraldehyde

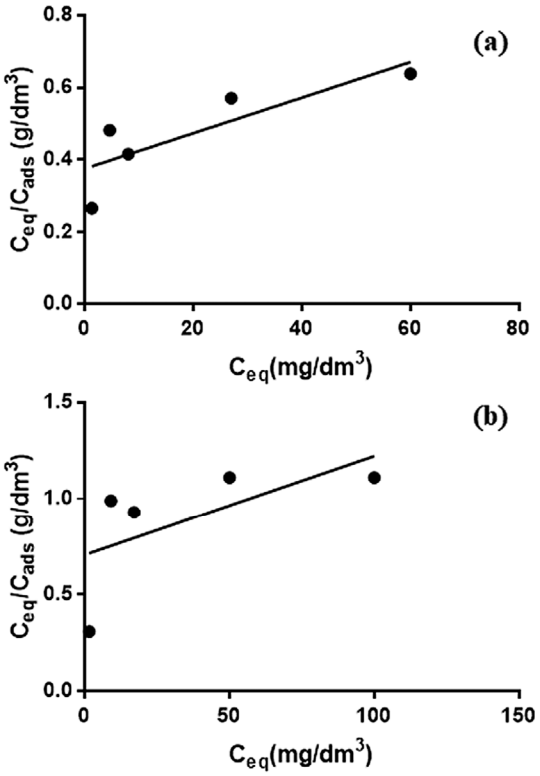

Fig. 7 — Langmuir plot for the adsorption of Cu(II) ion (a); and Ni(II) ion (b) onto CS/AL/CMC-(1:1:1) - ternary bead-glutaraldehyde

Table 1 — Adsorption isotherm constant, C_{max} and correlation coefficients

Metal ion	Langmuir constants			
	K_L (dm^3/g)	b (dm^3/mg)	C_{max} (mg/g)	R^2
Ni(II)	1.4146	0.00729	194.05	0.3911
Cu(II)	2.6602	0.01306	203.69	0.6944

The mathematical expression of the pseudo-second-order is:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad \ldots (3)$$

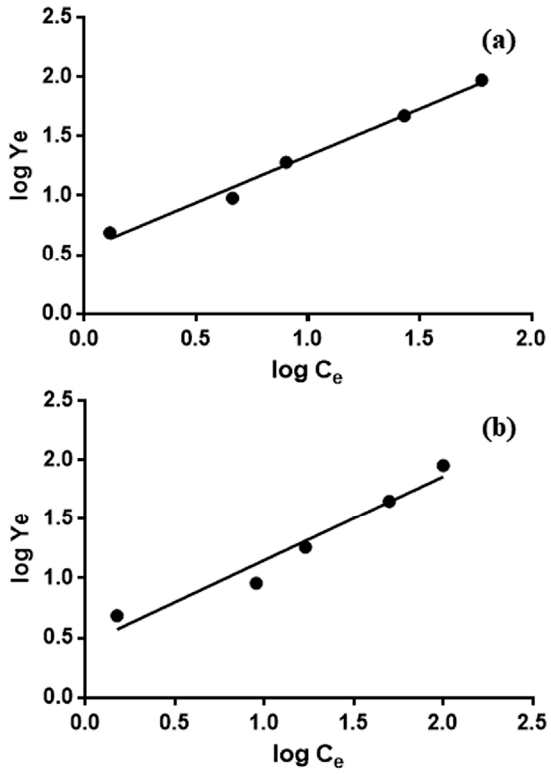

Fig. 8 — Freundlich plot for the adsorption of Cu(II) ion (a); and Ni(II) ion (b) onto CS/AL/CMC (1:1:1) - ternary bead- glutaraldehyde

Table 2 — R_L values based on Langmuir adsorption

Metal ions	Initial concentration C_0 (mg/dm^3)	Final concentration C_f (mg/dm^3)	R_L values
Ni(II)	1000	100	0.578369
	500	50	0.732869
	200	17	0.889735
	100	9	0.93843
	50	1.5	0.989183
Cu(II)	1000	60	0.695701
	500	27	0.835541
	200	8	0.944894
	100	4.6	0.967554
	50	1.3	0.990612

Where, q_e and q_t are the amounts of metal adsorbed (mg/g) at time t (min).

Figures 9 & 10 shows first and second order plots and Table 4 shows the values obtained. The correlation coefficients were recognized as very low.

The results demonstrated that the generated adsorbent was found to follow a pseudo-second order based on their observed (R^2 > 0.98) values for both metal ions[41].

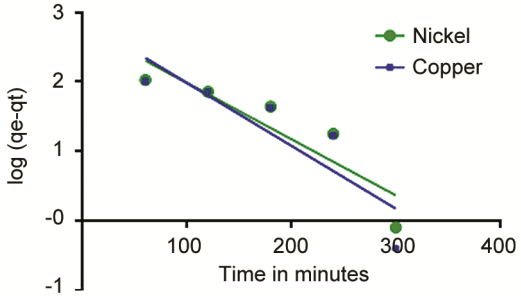

Fig. 9 — Pseudo-first-order kinetics for Cu(II) and Ni(II) ions onto CS/AL/CMC (1:1:1) - ternary bead- glutaraldehyde

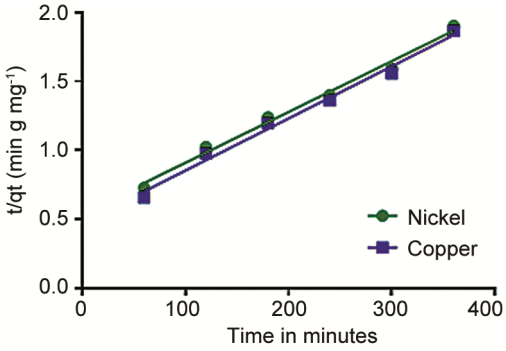

Fig. 10 — Pseudo-second-order kinetics for Cu(II) and Ni(II) ions onto CS/AL/CMC (1:1:1) - ternary bead- glutaraldehyde

Table 3 — Freundlich isotherm constants for the adsorption of Ni(II) and Cu(II) ions onto AL/CS/CMC (1:1:1) - ternary bead- glutaraldehyde

Metal ion	Freundlich constants		
	K_f (dm^3/g)	n (dm^3/mg)	R^2
Ni (II)	2.7990	1.4160	0.9512
Cu (II)	3.5294	1.2666	0.9889

Table 4 — Comparison between Lagergren pseudo-first-order and pseudo second-order kinetic models for Cu (II) and Ni (II) sorption by AL/CS/CMC (1:1:1) - ternary bead- glutaraldehyde

Metal ion	Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
	q_e(mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	q_e (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2
Ni(II)	345.11	0.008096	0.8119	194	146.70	0.003685	0.9898
Cu(II)	319.06	0.009061	0.7805	194.8	125.20	0.003785	0.9894

Conclusion

The ternary biopolymeric beads were created by combining chitosan, alginate, and carboxymethyl cellulose in a 1:1:1 ratio with the cross-linking agent glutaraldehyde. Chitosan, alginate, and carboxymethyl cellulose were successfully combined to form beads using the cross-linking agent glutaraldehyde, according to FT-IR studies. An XRD study explains the decrease in crystalline behaviour (amorphous nature) of the prepared AL/CS/CMC beads, making them suitable for the adsorption process. The optimum pH for metal ions was discovered to be 5.5 in investigations on the effects of different parameters of the adsorption of hazardous metal ions onto beads.

Acknowledgements

The authors would like to thank the management of DKM College for Women, Vellore for extending the DST-FIST facility to carry out this research.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Statement

This work was not published in any mean and no endangered species are being used in this study.

Author Contributions

BMD: Experimental data analysis and manuscript writing; TG: Manuscript formatting and result interpretation; KV: Data interpretation; RR: Data analysis; SP: Plagiarism and reference formatting; and PNS: Conceptualization and editing the manuscript.

References

1 Yasmin R M, Saraswathy S, Kamal B, Karthik V & Muthukumaran K, Removal of nickel (ii) ions from waste water using low cost adsorbents: a review, *J Chem Pharm Sci*, 8 (2015) 1-6.

2 Mudasir A, Shakeel A, Babu L S & Saiqa I, Adsorption of heavy metal ions: role of chitosan and cellulose for water treatment, *Int J Pharmacogn*, 2 (2015) 280-289.

3 Mukesh P & Lokendra S T, Adsorption of Heavy Metal (Cu^{2+}, Ni^{2+} and Zn^{2+}) from Synthetic Waste Water by Tea Waste Adsorbent, *J Chem Pharm Sci*, 2 (2013) 6-19.

4 Umran T U & Sadettin E O, Removal of Heavy Metals (Cd, Cu, Ni) by Electrocoagulation, *Int J Environ Sci Development*, 6 (2015) 425-429.

5 Gotoh T, Matsushima K & Kikuchi K I, Preparation of alginate–chitosan hybrid gel beads and adsorption of divalent metal ions, *Chemosphere*, 55 (2004) 135-140.

6 Theophanides T & Anastassopoulou J, Copper and Carcinogenesis, Copper and Carcinogenesis, *Oncology/ Haematology*, 42 (2002) 57-64.

7 Akhtar M, Iqba S, Kausar A, Bhanger M I & Shaheen M A, An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk, *Coll Surf B: Biointerf*, 75 (2010) 149–155.

8 Moreno J C, Gomez R & Giraldo L, Removal of Mn, Fe, Ni and Cu ions from waste water using cow bone charcoal, *Open access J Mat*, 3 (2010) 452-466.

9 Pandharipande S L & Kalnake R P, Tamarind fruit shell synthesis, Charecterization studies for the removal of Cr (IV) and Ni (II) ions from aqueous solution, *Int J Eng Sci Emerg Technol*, 4 (2013) 83-89.

10 Renukadevi C, Santhi T & Makeswari, Equilibrium and kinetics study for the removal of copper from aqueous solution by activated carbon derived from *Annona squamosa* seed, *J Chem Pharm Res*, 7 (2015)732-740.

11 Ashish G & Jyotsna W, Removal of heavy metal ions from wastewater by carbon nanotubes (CNTS), *Int J Chem Sci Appl*, 5 (2014) 56-67.

12 Asma S, Anita C, Leena R & Bajpai A K, Biopolymer Based Nanomaterials as Potential Biosorbents for Toxic Metal Ions, *Chem Proc Eng Res*, 11 (2013) 7-10.

13 Hajeeth T, Sudha P N, Vijayalakshmi K & Gomathi T, Sorption studies on Cr (VI) removal from aqueous solution using cellulose grafted with acrylonitrile monomer, *Int J Biol Macromol*, 66 (2014) 295–301.

14 Saifuddin M, Nomanbhay & Kumaran P, Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal, *Electronic J Biotechnol*, 8 (2005) 43-53.

15 Zuo X & Balasubramanian R, Evaluation of a novel chitosan polymer-based adsorbent for the removal of chromium (III) in aqueous solutions, *Carbohydr Polym*, 92 (2013) 2181–2186.

16 Marwa M E-T, El-Shafei M M & Mahmoud M, The Role of Alginate as Polymeric Material in Treatment of Tannery Wastewater, *Int J Sci Technol*, 2 (2013) 218-224.

17 Xuemei H, Huidong X & Hui L, Cr(VI) Removal from Aqueous Solution by Chitosan/ Carboxylmethyl Cellulose/ Silica Hybrid Membrane, *World J Eng Technol*, 3 (2015) 234-240.

18 Ramasubramaniam S, Govindarajan C, Nasreen K & Sudha P N, Removal of cadmium (II) ions from aqueous solution using chitosan/starch polymer blend, *Composite Interfaces*, 21 (2014) 95-109.

19 Bailey S E, Olin T J, Bricka R M & Adrian D D, A review of potentially low costs sorbents for heavy metals, *Water Res*, 33 (1999) 2469- 2479.

20 Deshpande M V, Enzymatic degradation of chitin and its biological applications, *J Sci Ind Res*, 45 (1986) 277- 281.

21 Yang T C & Zall R R, Adsorption of metals by natural polymers generated from sea food processing waste, *Indus Eng Chem Produc Res Development*, 23 (1984) 168-172.

22 Sudha V J, Madhusudhna R, Siva G R K & Krishna R K S V, Synthesis and Characterization of Sodium Carboxy Methyl Cellulose/Poly (Acrylamide) Magnetic Nano Composite Semi Ipn's for Removal of Heavy Metal Ions, *World J Nano Sci Tech*, 2 (2013) 33-41.

23 Kong A, Yanhong J, Huanhuan M, Yunfei S, Benqiao H, *et al.*, A novel route for the removal of Cu(II) and Ni(II) ions via homogeneous adsorption by chitosan solution, *J Clean Prod*, 192 (2018) 801-808.

24 Rees D A & Welsh E J, Secondary and tertiary structure of polysaccharides in solutions and gels, Angew *Chem Int Edit Engl*, 16 (1977) 214–224.

25 Navarro A E, Musaev H, Serrano K & Masud M E, Adsorption Kinetics of Cobalt (II) Ions onto Alginate Beads from Aqueous Solutions, *J Earth Sci Clim Change*, 5 (2014) 1-5.

26 Uzma N & Monika D, Adsorption studies of zinc(II) ions on biopolymer composite beads of alginate-fly ash, *Eur Chem Bull*, 3 (2014) 682-691.

27 Bhosale R S, Hajare K Y, Mulay B, Mujumdar S & Kothawade M, Biosynthesis, Characterization and Study of Antimicrobial Effect of Silver Nanoparticles by *Actinomycetes spp*., *Int J Curr Microbiol App Sci*, Special Issue 2 (2015) 144-151.

28 Hameed B H & Ahmad A A, Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, *J Hazard Mater*, 164 (2009) 870-875.

29 Wiwid P P, Azlan K, Siti N M Y, Che Fauziah I, Azmi M, *et al.*, Biosorption of Cu(II), Pb(II) and Zn(II) Ions from Aqueous Solutions Using Selected Waste Materials: Adsorption and Characterisation Studies, *J Encapsul Adsorp Sci*, 4 (2014) 25-35.

30 Zvinowanda C M, Okonkwo J O, Shabalala P N & Agyei N M, A novel adsorbent for heavy metal remediation in aqueous environments, *Int J Environ Sci Tech*, 6 (2009) 425-434.

31 Al-Jariri J S & Khalili F, Adsorption of Zn(II), Pb(II), Cr(III) and Mn(II) from Water by Jordanian Bentonite, *Desaln Water Treat*, 21 (2012) 308-322.

32 Reddy D, Seshaiah K, Reddy A V R & Lee S M, Optimization of Cd(II), Cu(II) and Ni(II) Biosorption by Chemically Modified *Moringa oleifera* Leaves Powder, *Carbohyd Polym*, 88 (2010) 1077-1086.

33 Aziza R, Rachid M, Nabil S, Abdellatif L, Said G, *et al.*, Removal of Carbofuran pesticide from aqueous solution by adsorption onto animal bone meal as new low cost adsorbent, *Chem Proc Eng Res*, 28 (2014) 32-44.

34 Orodu V E, Olisedeme S & Okpu R C, Removal of Heavy Metals from Aqueous Solutions using Snail Shell Powder as available Adsorbent, *Int J Sci Technol*, 3 (2014) 422-428.

35 Sureshkumar M K, Das D, Mallia M B & Gupta P C, Adsorption of Uranium from aqueous solution using chitosan-tripolyphosphate (CTPP) beads, *J Hazard Mater*, 184 (2010) 65–72.

36 Hall K R, Eagleton L C, Acrivos A & Vermeulen T, Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions, *Industrial Eng Chem Fundamentals*, 5 (1966) 212-223.

37 Ramya R, Sankar P, Anbalagan S & Sudha P N, Adsorption of Cu (II) and Ni (II) ions from metal solution using crosslinked chitosan-g-acrylonitrile copolymer, *Intl J Environ Sci*, 1 (6) (2011) 1323-1338.

38 Kadirvelu K, Thamaraiselvi K & Namasivayam C, Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, *Bioresour Technol*, 76 (2001) 63–65.

39 Zhu H Y, Fu Y Q, Jiang R, Yao J, Xiao L, *et al.*, Novel magnetic chitosan/poly(vinyl alcohol) hydrogel beads: Preparation, characterization and application for adsorption of dye from aqueous solution, *Bioresour Technol*, 105 (2012) 24–30.

40 Khaled A, Nemr A Z, El Sikaily A & Abdelwahab O, Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon, *Desalination*, 238 (2009) 232- 210.

41 Chou W L, Wang C T, Huang K Y, Chang Y C & Shu C M, Investigation of indium ions removal from aqueous solutions using spent coffee grounds, *Int J Phys Sci*, 7 (2012) 2445–2454.