Journal of Dispersion Science and Technology

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/ldis20

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To cite this article: Muibat Diekola Yahya , Kehinde Shola Obayomi , Benjamin Adesina Orekoya , Adeola Grace Olugbenga & Benjamin Akoh (2020): Process evaluation study on the removal of Ni(II) and Cu(II) ions from an industrial paint effluent using kola nut pod as an adsorbent, Journal of Dispersion Science and Technology, DOI: 10.1080/01932691.2020.1822178

To link to this article: https://doi.org/10.1080/01932691.2020.1822178

JOURNAL OF DISPERSION SCIENCE AND TECHNOLOGY
https://doi.org/10.1080/01932691.2020.1822178

Process evaluation study on the removal of Ni(II) and Cu(II) ions from an industrial paint effluent using kola nut pod as an adsorbent

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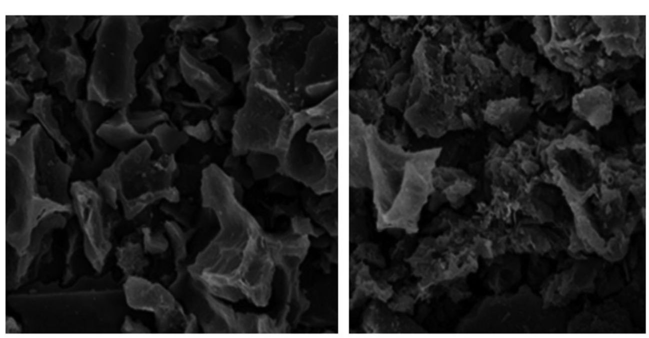
ABSTRACT

This study established the efficiency of a fixed bed column in the removal of Ni (II) and Cu (II) ions from an industrial paint effluent. The kola nut pod was characterized to identify functional groups, morphology, and porosity nature of the adsorbent. The appearance and shifts of some peaks in the Fourier transform infrared (FTIR) spectra revealed amide, carboxyl, and hydroxyl groups. The scanning electron microscopy (SEM) analysis revealed a non-cellulosic morphology with clear pore structure; the BET analysis gave a surface area and pore volume values of 225.0 m^2/g and 0.03949 cm^3/g, respectively. Surface area and pore volume of the loaded adsorbent decreased by 37.87 and 98.66%, respectively. Deposition and coverage of adsorptive sites were observed on the loaded adsorbent from the SEM results. Raw effluent from paint production industry was analyzed using the atomic absorption spectrophotometer (AAS). Results obtained indicated the presence of Ni(II) and Cu(II) at concentrations of 5.3747 mg/L and 35.6636 mg/L, respectively, among other heavy metals. Optimum values for an efficient column parametric study were obtained at a bed height of 10.0 cm, flow rate of 5.0 mL/min and at their respective initial concentrations. The percentage removal for Ni(II) and Cu(II) ions were 29.35 and 93.9%, respectively, with corresponding adsorption capacity of 12.841 and 6.100 mg/g. The range of values of the error functions obtained from the analysis on Thomas model for adsorption of both copper and nickel ions are SSE values range 0.0053–0.0928 and 0.0044–0.7491, HYBRID values of 0.0143–1.0999 and 0.0057–9.7006, MPSD values of 0.5193–5.4680 and 0.2260–30.0215 and R^2 values of 0.2720–0.8027 and 0.0008–0.5866, respectively. The kinetic isotherms revealed that the Thomas gave the lowest error between calculated and experimental values, coefficient of determination and thus can be used in describing the behavior of the adsorption process.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 6 April 2020
Accepted 6 September 2020

KEYWORDS
Kola nut pod; paint effluent; fixed bed; nickel; copper

Introduction

Biomass is the term used to refer to all organic matter which can be traced back to photosynthesis as their source.[1] Agricultural waste is a proven reserve of biomass which is a rich source of low-cost adsorbents besides industrial by-products and natural material. Low economic value of agricultural waste and search for alternatives for existing adsorbents are incentives for promoting biosorption as viable clean up technology for heavy metal pollution. Various biomaterials such as plant products (tree bark, peanut skin, saw dust, and plant weeds), rice husks,[2] and

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Supplemental data for this article is available online at https://doi.org/10.1080/01932691.2020.1822178

microbes (algae, fungi, bacteria) have been examined for their biosorptive properties.[3]

Kola nut is one of the most popular plantation crops in Nigeria. Kola is a member of the tropical family *sterculiaceae*, it grows into a tree of about 20 m high with long ovoid leaves pointed at both ends with a leathery texture. The nut is processed for sale as a cash crop while the pod is discarded and could pose an environmental threat due to the large volume of waste generated. Nigeria accounts for about 70% of the total world production of kola nut with an annual production capacity of 85,000 to 132,000 metric tonnes mostly from the South West, Nigeria. Statistics has shown that 90% of the kola produced is consumed within the country while 10% is exported.[4,5] This implies the sustainability of continuous supply of kola nut pod for adsorptive purposes with no harmful effect on the value chain. A novel biosorbent derived from kola nut pod (KNP), an abundant agricultural waste with good stability has several advantages as biosorbent which include wide availability, low cost, and high metal sorption capacity from aqueous solution and industrial waste effluents.[6]

Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another molecule, that is, onto a two-dimensional surface. In this case, the material accumulated at the interface is the adsorbate and the solid surface is the adsorbent.[7] Adsorption of heavy metal ions occur as a result of physicochemical interaction, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface. Column evaluation is used to optimize the parameters required to design industrial scale fixed bed adsorption columns. Fixed-bed column is the most effective configuration for operations such as adsorption and ion exchange; hence it is widely used in the chemical process industry.[8]

There are two major sources of release of heavy metals into wastewater effluents; either through natural or anthropogenic route.[9] Paint is a mixture of pigment, binder, additives, and solvent. The resulting solution consumes volumes of water and deposits large amount of effluent in little time through the cleaning operations of the reactors, mixers, fillers, packaging units, and floors. This effluents contain heavy metals such as nickel, copper, cadmium, lead, chromium, and other acidic and basic chemicals which are toxic, bioaccumulate, and are non-biodegradable.[10] Hence, there is a need to completely or reduce to permissible limit their effects on the environment.

Studies on the use of kola nut pods as a biosorbents are limited in literatures. Agarry and Ogunleye[11] have used kola nut pod under batch adsorption process for removal of organic pollutants and results obtained was promising, however its use in a fixed bed for treatment of large volume of contaminants in particular, multi mixtures heavy metals have not been done. The underutilized kola nut pod could serve as a viable material for industrial scale treatment plant as fewer researches are available on its adsorptive characteristics in continuous fixed bed operations.

In this study, kola nut pod was investigated as a potential adsorbent for continuous removal of Ni(II) and Cu(II) ions from a paint manufacturing effluent by identifying and optimizing the column parameter is most important to achieve the highest removal efficiency and which kinetic isotherm best described the adsorption process.

Material and method

Sample acquisition and preparation

Kola nut pod was separated from the fruits obtained from a farmland located in Sagamu, Ogun State, Nigeria. This sample was pretreated to remove impurities such as dirts, metal chips, and flakes. This was sundried and thereafter oven dried for 12 h at 60 °C to reduce moisture content. Treated pods were crushed and sieved into different particle sizes that ranged from 200 to 250 µm. Wastewater samples were collected from the effluent discharge points of Premier Paints Industry in Nigeria and digested according to United State Environmental Protection Agency (USEPA) method 3050B for vigorous digestion to ensure that all organometallic bonds are broken and organic impurities are removed to avoid interference during analysis.

Effluent sample digestion

The effluent sample was digested by adding 1 mL of HNO_3 into a 100 mL of the paint effluent in a 250 mL conical flask. The flask content was covered and heated on a hot plate at temperature of 95 ± 5 °C for 15 min without boiling and then allowed to cool. Further addition of 5 mL of concentrated HNO_3 was added to the cooled sample and again heated for 120 min with reflux for 30 min until no brown fumes are given off and allowed to cool. Two milliliter of deionized water and 3 mL H_2O_2 (30%) was added to the sample, covered and gently heated until effervescence subsides. This digesting solution was allowed to cool and subsequently heated at 95 ± 5 °C for further 2 h. The digested effluent was filtered using filter paper (Whatman No 40), the filtrate was collected and stored in a sterilized bottle, labeled, and ready for analysis. This digestion is to eliminate appreciable amounts of organic compound and other impurities that would interfere with the adsorption.

Continuous adsorption procedure

Fixed bed column adsorption experiments were conducted with raw effluent concentration using a glass tube of 3.0 cm diameter (I.D) and height of 30 cm. The column was filled to varying height of 4, 7, and 10 cm at known weights of kola nut pod on a glass-wool support. Paint effluent at initial concentration of 5.3 mg/L of Cu and 35 mg/L of Ni was fed to the column with the aid of Boarding Longer Peristaltic Precision Pump at flow rates of 5.0, 8.0, and 13.0 mL/min. The column was opened to the atmosphere in order to maintain the internal pressure in the column near atmospheric pressure.[12] The solution leaving the bottom of the column was collected at interval of 2 h for residual Cu and Ni ions concentration determination using atomic absorption spectrophotometer.

Characterization analysis

Physical characteristics of the raw and loaded adsorbent which include the surface morphology, functional groups, surface area and pore volume were carried out using scanning electron microscopy (SEM), Fourier transform infrared (FTIR), and Brauneur Emmet Teller (BET) analysis, respectively.

Surface morphology determination

The outer surface micro porosity and pore size of the raw and loaded kola nut pod sample was examined using a SEM EVO MA 10, Carl Zeiss (JSM-5600 Model) scanning electron microscope model spectrum. A thin layer of the adsorbent was mounted on the Al specimen holder by a double sided tape and coated with Au/Pb to a thickness of about 30 nm. The SEM micrographs of raw kola nut pod (KNP) and Ni-Cu-loaded KNP adsorbent were recorded at ×12000 and ×15000 magnifications.

Functional group determination

Kola nut pod sample was dried for 4 h and prepared with diluted KBr pellets (1:50, carbon to KBr) in a small agate mortar. Prepared sample was degassed to eliminate air and moisture afterward, compacted in a Perkin-Elmer manual hydraulic press operated at 10 tons for 3 min in a vacuum to produce pellet. The pellet was analyzed using a Schimadzu FT-IR-8400 operated at 10 nms^{-1} with spectra measured in the range of 4000 to 650 cm^{-1}. Infrared spectra of KNP before and after adsorption were recorded with the aid of Nicolet model 6000.

Specific surface area and pore volume determination

Specific surface area and pore volume analysis of the adsorbent were carried out using BET surface area nitrogen adsorption procedure. The prepared adsorbent was out gassed under vacuum condition at 300 °C for 4 h. Out gassed carbon sample was tested for surface area (m^2/g) and pore volume (m^3/g) at 77 K using a 15-point BET NovaWinQuantachrome, 2013 version 11.03.

Modeling of column dynamic behavior

The effective design of a column adsorption process rests on appropriate prediction of the concentration-time profile or breakthrough curve for effluent concentrations. Several empirical models have been established for the application in the design of constant fixed bed columns. In this analysis, Thomas and Yoon–Nelson models were implemented to forecast the performance of the breakthrough curve and reported to adequately describe the fixed bed column performance analysis.[13,14]

Thomas model

Evaluation of a column adsorption process necessitates the prediction of the concentration-time profile for the effluent. The maximum adsorption capacity of a biosorbent is required in the analysis. In this work, the Thomas model is used to achieve this aim. The model has two forms, Equation (1) and its linearized form in Equation (2), respectively.[15]

$$\frac{C_e}{C_0} = \frac{1}{\left(1 + \exp\left[\frac{K_{TH}(q_0 m - C_0 V)}{\theta}\right]\right)} \tag{1}$$

where, K_{TH} is the Thomas rate constant (L/(min mg)) and θ is the volumetric flow rate (L/min). The linearized form of the Thomas model is given as Equation (1):

$$\ln\left(\frac{C_0}{C_e} - 1\right) = \frac{K_{TH} q_{0m}}{\theta} - K_{TH} C_0 t \tag{2}$$

The kinetic coefficient K_{TH} and the adsorption volume of the bed q_0 can be established from a plot of $\ln(C_0/C_e - 1)$ against t.

Yoon and Nelson model

The model is based on the hypothesis that the rate in reduction in the probability of adsorption for every of the adsorbate molecule is directly proportional to the probability of adsorbate adsorption and also to the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson model does not have complexities, but also require less data relating to the features of adsorbate, description of the adsorption bed, and the form of adsorbent. The Yoon and Nelson equation is given in Equation (3) and its linearized form by Equation (4).[16]

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp[K_{YN}(\tau - t)]} \tag{3}$$

where K_{YN} is the rate constant (min^{-1}), τ the time needed for 50% adsorbate breakthrough (min), while t is the breakthrough (sampling) time (min). The linearized form of the Yoon and Nelson model is indicated in Equation (9):

$$t = \tau + \frac{1}{K_{YN}} \ln\left(\frac{C_0}{C_e - C_0}\right) \tag{4}$$

The evaluation of hypothetical breakthrough curves for a single-constituent system necessitates the determination of the constant, k and τ for the adsorbate of interest. These rates could be determined from the experimental data. The derivation for Equation (4) was based on the fact 50% breakthrough of the adsorption process would happened at τ and that the bed should be totally saturated at 2τ. Owing to the proportionate characteristics of breakthrough curve, there is a partial quantity of metal adsorbed by the biosorbent of the cumulative metal ions going into the adsorption column within the 2τ duration. The adsorption volume could be established by means of Equation (5).[17]

$$q_{total} = \frac{1}{2} C_0 \theta (2\tau) = C_0 \theta \tau \tag{5}$$

where C_0 is the inlet concentration, θ liquid flow rate, and τ is the time to achieve 50% adsorbate breakthrough.

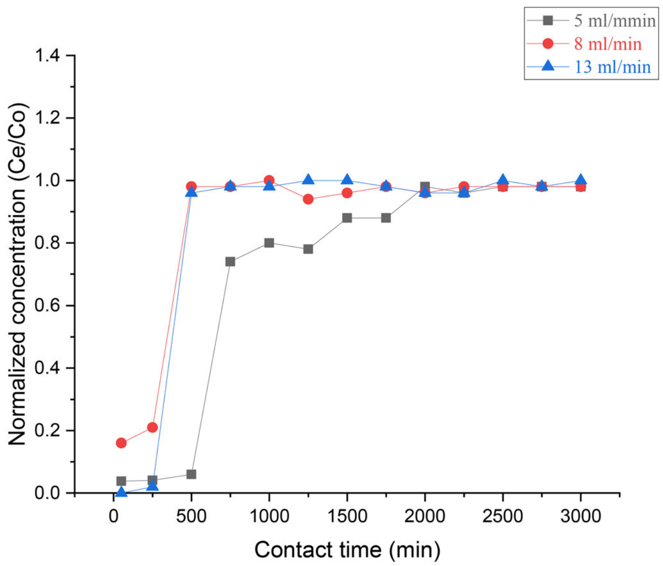

Figure 1. Breakthrough curves for adsorption of $Ni^{2+}$for different flow rates at bed height of 10.0 cm and concentration of 5.3747 mg/L.

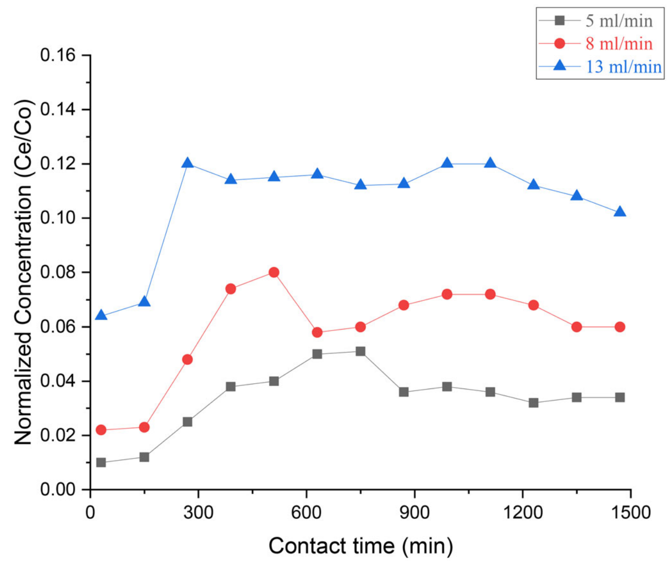

Figure 2. Breakthrough curves for adsorption of Cu^{2+} for different flow rates at bed height of 10.0 cm and concentration of 35.6636 mg/L.

Results and discussion

Effect of flowrate

The influence of flow rate on the breakthrough point of kola nut pod packed bed was shown in Figures 1 and 2. While maintaining initial metal ion concentration and bed height at constant values, varying the flow rate showed that the uptake of metal ions onto the kola nut pod decreases with increase in flow rate. An increase in the flow reduces the saturation adsorption capacity thereby, decreasing the service time of the bed. This is due to the decrease in contact time between the metal ions and the adsorbent at higher flow rates.[18] At lower flow rate much contact is achieved in little time leading to effective intra-particulate diffusion. This result was in agreement with the result obtained by Ref. [19]. As observed at 5 mL/min, the sorption of Ni and Cu increased gradually and there is delay in saturation of the sorbent. The results of the column efficiency evaluated as presented in Table 1 (see supporting document) revealed a total volume of 7350 mL was treated at flowrate of 5 mL/min out of which 38.96 mg of Cu (II) was sent into the column and 36.33 mg was adsorbed onto the kola nut pods giving 93.26% removal. Lower percentage removal was, however, observed at higher flowrate which is because of the short residence time for the mass transfer zone. A similar phenomenon was observed for Ni (II) ions, except for lower percentage removal.

Effect of bed height

The significance of bed height on the breakthrough point of kola nut pod packed bed was presented in Figures 3 and 4. The flow rate and initial metal ion concentration constant were kept constant at 5.0 mL/min and 5.3747 and 35.6636 mg/L for Ni (II) and Cu (II), respectively. Results showed that increase in bed heights increased the residence time, thus, allowing the metal ions to diffuse deeper inside the sorbent and hence reduces the breakthrough time. This can be explained by mass transfer phenomena on an increased surface area which provides more binding sites for the adsorption activities.[20,21] Moreover, increase in the bed adsorption capacity is observed at the breakthrough point with the increase in bed height as indicated on Table 2 (see supporting document).

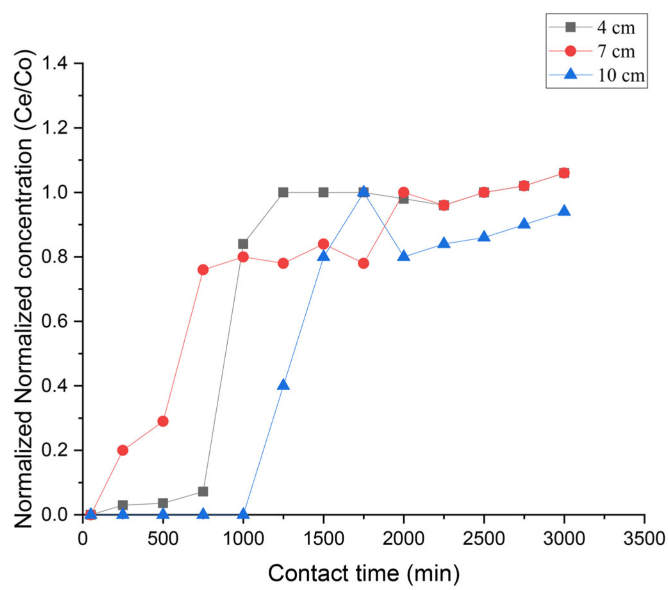

Figure 3. Breakthrough curve for adsorption of Ni^{2+} onto kola nut pods for different bed height at flow rate of 5.0 mL/min and concentration of 5.3747 mg/L.

Effect of concentration

Effect of initial metal ion concentration was depicted in Figures 5 and 6 on the breakthrough curve of kola nut pod packed bed. Increased Ni^{2+} and Cu^{2+} ions percentage removal was observed at higher concentrations which were due to the increased driving force of concentration gradient. At concentration of 22.4 mg/L for $Cu^{2+}$and 1.43 mg/L for

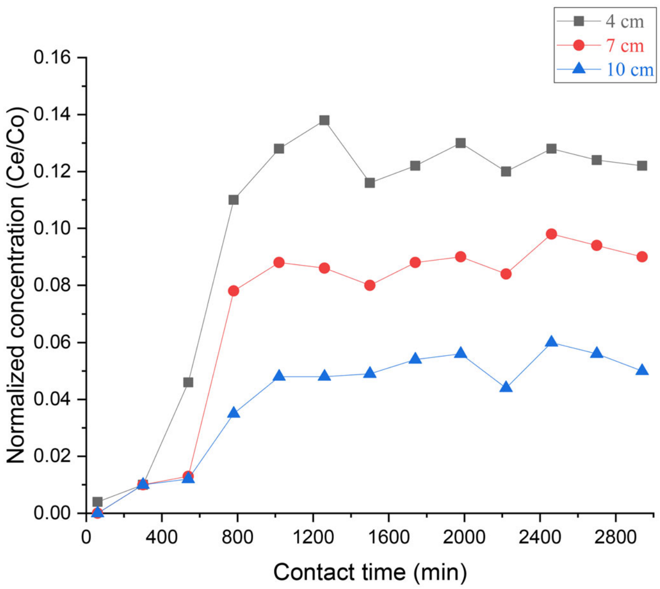

Figure 4. Breakthrough curves for adsorption of Cu^{2+} for different bed heights at flow rates of 5.0 mL/min and concentration of 35.6636 mg/L.

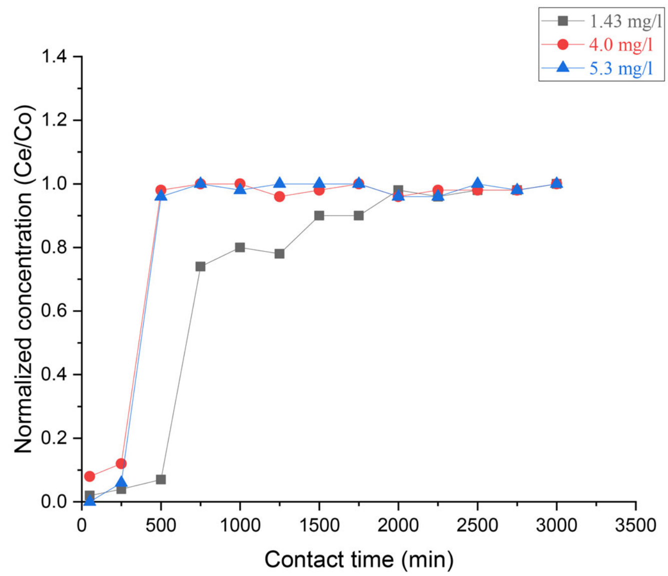

Figure 6. Breakthrough curve for adsorption of Ni^{2+} onto kola nut pods for different concentrations at bed height of 10.0 cm and flow rate of 5.0 mL/min.

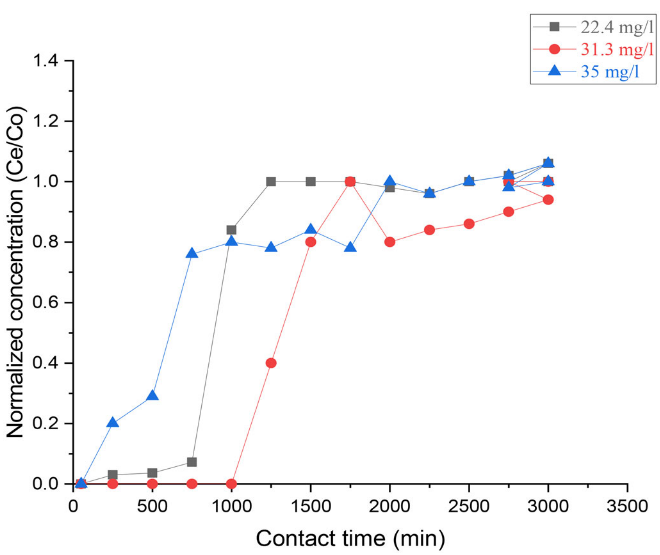

Figure 5. Breakthrough curves for adsorption of Cu^{2+} onto kola nut pods for different concentrations at bed height of 10.0 cm and flow rate of 5.0 mL/min.

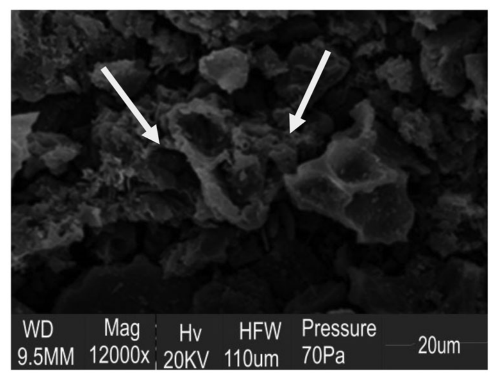

Figure 7. SEM image of raw KNP adsorbent ×12,000.

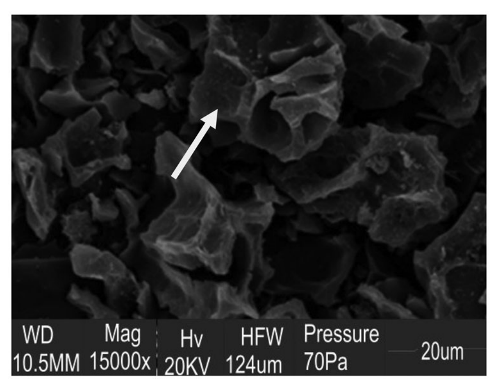

Figure 8. SEM image of KNP adsorbent at ×15,000.

Ni^{2+}, breakthrough occurred lately because lower concentration gradient caused a slower mass transfer owing to reduction in diffusion coefficient or mass transfer.[21] At normalized concentration, the breakthrough time was approximately 300 min at 35 mg/L Cu^{2+} and about 60 min at 5.3 mg/L Ni^{2+} as shown in Figures 5 and 6. It was observed that increased in the inlet metal concentration resulted into decrease in the volume of effluent treated before the packed bed gets saturated. The results indicated that increase in the concentration modifies the adsorption rate through the bed and increases the bed adsorption capacity.[22]

Characterization of the adsorbent

The SEM images of kola nut pods adsorbent was shown in Figure 7 at ×12,000 magnification clearly revealed that wide varieties of pores are present in the raw adsorbent. There is no cellulosic structure form on the surface but there exist very small cavities on the surface.[23] Adsorption of any heavy metal depends upon the pore size of the adsorbent. The entrapment of the accumulated Ni(II) and Cu(II) ions after the adsorption process can easily be entrapped in the cavities as indicated in Figures 7 and 8.

Spectra characteristics of functional groups present on the kola nut pod adsorbent before and after adsorption are

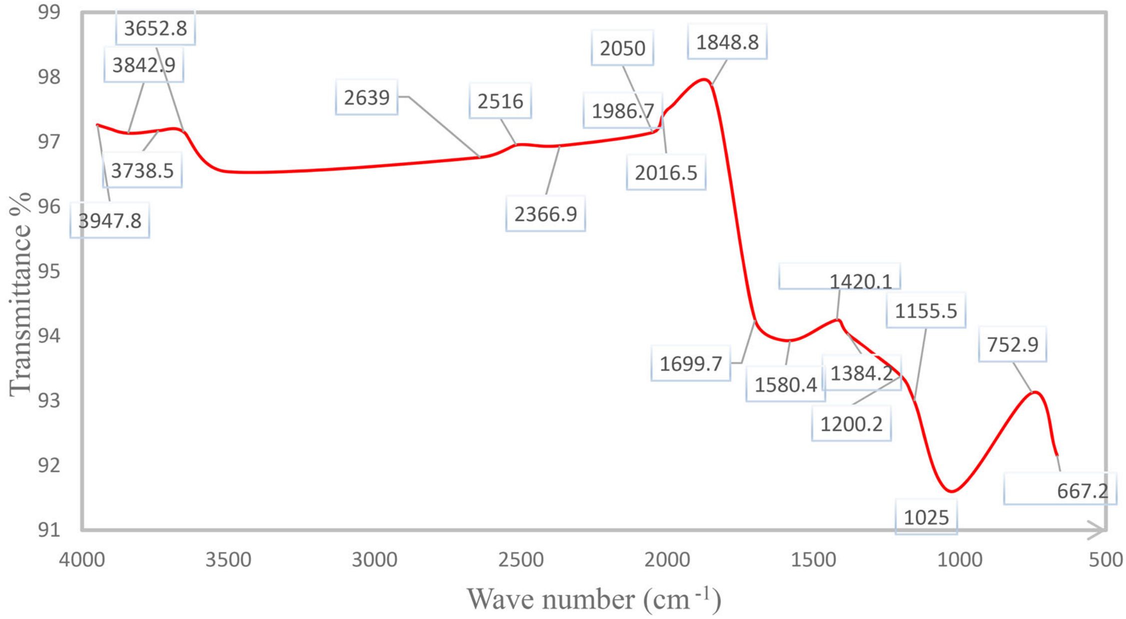

Figure 9. FTIR spectra of raw kola nut pods.

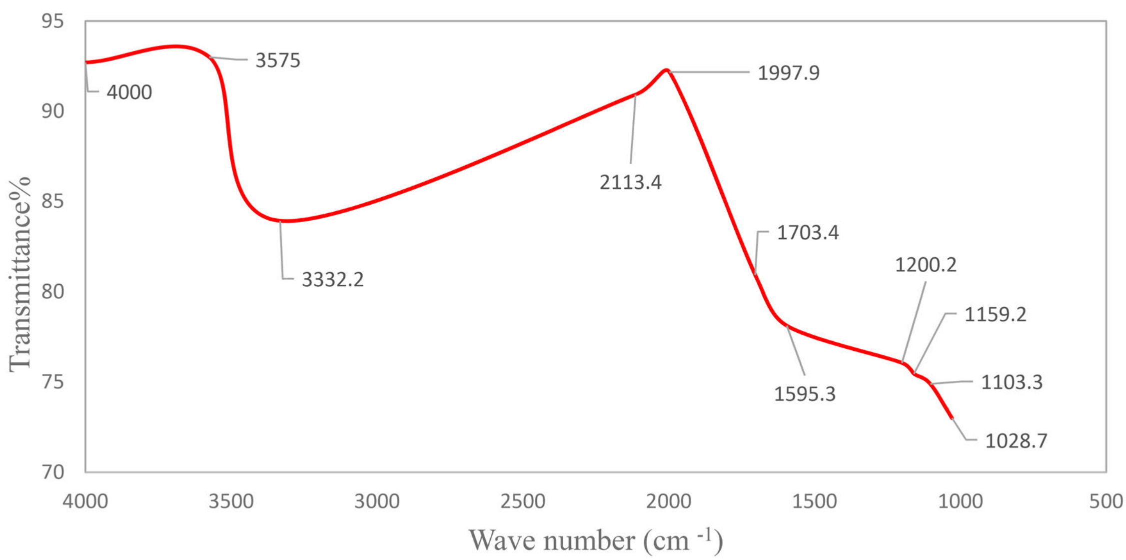

Figure 10. FTIR spectra of Ni(II) and Cu(II) ions bound kola nut pods.

shown in Figures 9 and 10. The FTIR spectrum of unloaded KNP biosorbent showed several distinct and sharp adsorption bands of different wavelength. However, the FTIR spectra of loaded KNP adsorbent indicated some shifts in some of characteristic bands and decrease in intensity of bands. These shifts in absorbance observed implied that there were metal binding processes taking place on the active sites. The very strong adsorption band of 3950–3500 cm^{-1} recorded for samples may be due to presence of –NH stretching of amines and amides group and –OH polymeric association. The adsorption band observed around 2600–2500 cm^{-1} could be assigned to –CH stretching of aliphatic–CH_2 group.[24] The peak observed near 2350–2000 cm^{-1} was due to stretching vibration of $–NH^{2+}$ as well as $–NH^{3+}$while the band present at 1840–1695 cm^{-1} corresponds to –C = O (band from carboxylic group or ester group). The peak at 1620 cm^{-1} indicating the –C = O (amide band—primarily a stretching band). The band at 1550–1360 cm^{-1} corresponds to –C = O stretching of carbonyl group. The peak near 1200 cm^{-1}which is related to –C-O stretching in –COOH group. The peak shift from 1020 to 1150 cm^{-1} could be due to the involvement of the –C-O polysaccharides. Two weak absorption bands at 750 and 660 cm^{-1}could be attributed to O-C-O scissoring and –C = O bending vibrations was due to lipids. Similar change in assignation had also been observed by Areif et al.[25]

The cumulative surface area, pore volume, and pore size of loaded adsorbent results showed that the surface area decreased to 139.8 m^2/g from an initial value of 225.0 m^2/g which represent 37.86% reduction while pore volume decreased by 98.66% to 0.03948 cm^3/g at correlation coefficient R^2 of 0.9999 (see supporting document for Table 2).

Table 1. Thomas model parameters using linear regression analysis for Cu adsorption under various operating conditions.

Q (mL/min)	L (cm)	C_0 (mg/L)	K_{TH} (mL/min.mg)	R^2	$q_{e(cal)}$ (mg/g)	$q_{e(expl)}$ (mg/g)
5	4	35	$4.571E^{-02}$	0.70820	5.2849	5.6383
8	4	35	$2.2857E^{-02}$	0.27200	5.1465	3.6787
13	4	35	$5.1429E^{-02}$	0.45250	4.8859	6.0080
5	7	35	$6.5714E^{-02}$	0.61350	5.2487	9.1123
5	10	35	$1.000E^{-03}$	0.80270	2.9086	3.2221
5	4	22.4	$1.5625E^{-03}$	0.80703	5.9651	8.2866
5	4	31.3	$9.5847E^{-02}$	0.51910	9.0507	6.7286

Table 2. Thomas model parameters using linear regression analysis for Ni adsorption under various operating conditions.

Q (mL/min)	L (cm)	C_0 (mg/L)	K_{TH} (mL/min.mg)	R^2	$q_{e(cal)}$ (mg/g)	$q_{e(expl)}$ (mg/g)
5	4	5.3	$1.6981E^{-02}$	0.1672	10.8361	4.1479
8	4	5.3	$3.7736E^{-02}$	0.0008	5.3056	6.9462
13	4	5.3	3.7736^{-02}	0.0181	6.0556	11.1221
5	7	5.3	$5.6604E^{-02}$	0.3355	11.3389	10.2400
5	10	5.3	$5.6604E^{-02}$	0.2325	10.2540	8.1479
5	4	1.43	0.13986	0.1809	3.9312	1.0763
5	4	4.00	0.12500	0.5866	7.1518	3.2863

Table 3. Comparison of Cu(II) and Ni(II) ions adsorption capacity of kola nut pod with other low-cost adsorbents.

Metal/organic compound	Adsorbent	q (mg/g)	References
Cu (II)	Almond shell	2.41	[8]
Cu(II)	Algal cells entrapped in beads.	0.997 mmol/g	[34]
Cd(II)		0.724 mmol/g	
Cu(II)	Corncob char waste	23.584	[35]
Cu (II)	Grape stalk	42.92	[36]
Ni(II)		38.31	
Cu (II)	Zeolite	8.13	[37]
Pd(II)	Commercial activated carbon	27	[38]
Rh(III)		15	
Ru(III)		4	
Pb(II)	Lignin	1293.75	[39]
Cu(II)		22.86	
Cd(II)		25.43	
Zn(II)		11.18	
Ni(II)		6.018	
Ni (II)	Chitosan-coated magnetic nano particles in a fixed bed	0.09-1	[40]
Ni (II)	Granulated activated carbon	2.88	[41]
Cu(II)	Kola nut pod in a fixed bed	6.81	This study
Ni (II)	Kola nut pod in a fixed bed	12.841	This study

This reduction could be attributed to the deposition and coverage of adsorptive sites of the adsorbent by Ni(II) and Cu(II) ions.

Application of Thomas model

Linear regression results and values of R^2 obtained from Thomas model are listed in Tables 1 and 2. Experimental data fitted into the Equation (2) shows that adsorption capacities, q_e, were quite high at higher bed heights, lower solute concentrations and at lower flow rates. The kinetic constant, K_{TH}, decreased with increase in flow rate from 5 mL/min to 13 mL/min which implies that the breakthrough curve is favorable at lower flow rate. The K_{TH} values decreased with increase in influent concentration, which also indicated that sorption is favored at lower concentration as there is delay in the saturation of the sorbents which thus offers better interactions between the sorbates and sorbents.[18,26] However, the Thomas kinetic coefficient, K_{TH} fluctuates on the amount of the pods in the bed. The rate of transfer increases from $4.571E^{-02}$ to $6.5714E^{-02}$ as the height increases from 4 to 7 cm but dropped to $1.00E^{-03}$ at 10 cm. This is also noticeable on the adsorption capacity.[27] A considerable increase in the adsorption capacity of the bed at various solutions ionic strengths indicate that ion exchange may be a possible adsorption mechanism.[21] The values of R^2 ranged from 0.27200 to 0.80703 for both ions, hence, the experimental data and theoretical results differ marginally and thus, it fits the adsorption of the ions as reported by other researchers.[28,29]

Application of Yoon-Nelson model

The linear regression results and values of R^2 obtained from Yoon Nelson model was given in Tables 4 and 5 (see supporting document). The kinetic constants, K_{YN} and τ were evaluated from the linear plots of (C_t/C_o-C_t) versus t (min) at different flow rates, bed heights, and initial metal ions concentration. The values of $K_{YN}$and τ for 50% breakthrough time (min) showed that as the flow rate increased, the rate constant (K_{YN}) increased while the τ decreased. This indicates earlier breakthrough at higher flow rate and shorter travel time for the sorbate through the column length. The time required for 50% adsorbate breakthrough

(τ) decreased with increase in flow rate and inlet solute concentration due to lesser residence time of metal ions interaction with the kola nut pods in bed height.[30] At increased initial metal ions concentration, the values of K_{YN} decreases which is an indication of saturations of pores of the kola nut pods and subsequent removal of the metals ions becomes almost impossible.[31] The time needed for 50% exhaustion of column, τ (min) reduced with the increase in the flow rate and initial concentration but rose with increase in bed height. This agrees with the outcomes gotten by Ref. [32]. The values of R^2 ranges from 0.2720 to 0.8703 for Cu(II) and 0.008–0.0598 for Ni(II). However, the $\tau_{(cal)}$ values obtained theoretically differed marginally as compared with the $\tau_{(expl)}$ experimental data. The low R^2 values reveal that the model is unfit to describe the adsorption of the ions.

Error analysis

Thomas and Yoon Nelson models used to investigate the removal of copper ion and nickel ion from industrial wastewater by kola nut pod were verified by analyzing the correlation between the models by using error analysis functions SSE, HYBRID, and MPSD. These values are presented in Table 6 through to Table 9 (see supporting documents). The range of values of the error functions obtained from the analysis on Thomas model for adsorption of both copper and nickel ion are SSE values range 0.0053–0.0928 and 0.0044–0.7491, HYBRID values of 0.0143–1.0999 and 0.0057–9.7006, MPSD values of 0.5193–5.4680 and 0.2260–30.0215 and R^2 values of 0.2720–0.8027 and 0.0008–0.5866, respectively, at various bed heights. From the results obtained for the both models, the Thomas model is suitable for the adsorption of the both heavy metals from the industrial wastewater since low values of the error functions were obtained from the model.[29,33]

Comparison with other adsorbents

In comparison with other adsorbents as indicated on Table 3, most of the adsorption technique was carried out in batch processes and not in a continuous fixed bed as this study indicated.

Conclusion

The use of kola nut pod in a fixed bed as an adsorbent for the removal of Cu (II) and Ni (II) from a paint effluent was successful. The characterization of the adsorbent revealed the presence of carboxylic, amide, and hydroxyl groups for the capturing of the Cu(II) and Ni(II) ions. The SEM clearly indicated morphology of the raw kola nut pods by depicting the pores and active sites. The BET results showed a reduction in the surface area from 225 to 138 m^2/g, thereby proving the coverage of the adsorptive sites of the metallic ions. The column evaluation revealed that bed heights, flowrate, and initial metal ion concentrations are important parameters to metal ions removal. Highest removal efficiency of Ni(II) and Cu(II) was obtained at bed height of 10.0 cm, flow rate of 5.0 mL/min, and respective concentration of 35 mg/L and 5.3 mg/L. Conclusively, Thomas and Yoon-Nelson models can be used to describe the behavior of the adsorption process with the former providing results that marginally approached experimental data.

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