Mathematical Modelling of Heavy Metal Biosorption in a Dynamic System

Felicia Omolara Afolabi[1], and Paul Musonge[2]

Abstract**—**Recently, biosorption has gained the interest of researchers due to the cost effectiveness and abundance of different biowastes. In this study, agricultural waste (orange peels) was used for the treatment of wastewater containing copper and lead ions in a dynamic system. The adsorbent was characterized before and after adsorption using Fourier Transform Infrared Spectroscopy to determine the functional groups present in the adsorbent. In the application of the bio-sorption process for industrial-scale treatment of wastewater, it is essential to apply the dynamic models to gain insight into the adsorption mechanism. Many operating parameters are important for industrial treatment application and scale-up. Therefore, in this study the existing mathematical models such as Thomas, Yoon Nelson and Adams Bohart models were applied to the experimental data obtained from the investigation of the effects of operating parameters (initial concentration, bed height and flowrate). The model results showed that Thomas and Yoon Nelson models performed well with a high coefficient of correlation ($R^2 > 0.9$).

Keywords**—**Bio-sorption, copper, lead, orange peels, breakthrough curve, modelling.

I. INTRODUCTION

Agricultural wastes have been proven to be efficient for the treatment of wastewater containing heavy metals. The treatment of wastewater is highly important because of increased water demand due to the increased population and urbanization. In addition, there is significant reduction in the annual rainfall patterns which has led to scarcity of water in some parts of the world. South Africa is a water scarce country which is evidence by the dwindling rainfall and the scarcity experienced in some parts of the country [1]. Furthermore, the increased industrial activities have led to the huge amount of wastewater in the industries which pollute the water bodies when discharged into the environment. The Environmental protection agencies (EPA) have rules and regulations governing the operations and management of wastewater in the industries to ensure that wastewater is treated to acceptable discharge limit. However, the industries find it difficult to conform to the rules due to the high cost of treatment hence the wastewater is discharged into the water bodies thus affecting the aquatic life and human health at the long run. Mostly, the wastewater contains hazardous substances that are dangerous to plant, animal and human being. Copper and lead ions are prevalent in the wastewater generated from industrial activities. These heavy metals are harmful to the environment and tend to hibernate in the food chain. Some of the effects of these metals on human health include dizziness, vomiting, cancer and damage to the central nervous system [2]. It is therefore imperative to remove these metals from wastewater to forestall the unrepairable damage to plant, animal and human health.

Biosorption is a process of utilizing materials of biological origin for the remediation of wastewater. Recently, researchers have focused on the use of biowastes derived from household wastes, agricultural wastes, fruit wastes and processing industries etc. for the removal of heavy metals from wastewater. These biowastes contain cellulose, hemicellulose, lignin and other molecular compounds that make them efficient for the adsorption of contaminants. Several biowastes have been reported for the removal of heavy metals from wastewater such as, apple pomace [3], banana peels [4], orange peels [5], sugarcane bagasse [6, 7], eggshell, mango peels [8], watermelon rind [9], rice husk [10], lemon peels [11], corn cob [12], moringa pods [13], water hyacinth [14], pine sawdust [15] etc. These are abundant in nature, low-cost and ecofriendly. These wastes can become nuisances and cause environmental pollution if not properly managed and disposed. These biomasses have been employed in adsorption studies either in the batch or dynamic mode.

In this study, orange peels were used for the adsorption of copper and lead ions in a dynamic mode. The effects of operating parameters such as initial concentration, bed height and flowrate were investigated. The most used dynamic models namely Thomas, Yoon Nelson and Bohart Adams models were employed to study the behaviour of the breakthrough curves obtained from the experimental data. For industrial treatment application of biosorbents, it is important to apply the models to gain insights into the adsorption mechanism and the efficiency of the adsorbent for large volume of wastewater treatment.

II. MATERIALS AND METHODS

A. Biosorbent preparation and characterization

The biosorbent used in this study for the remediation of Cu^{2+} and Pb^{2+} contaminated water was orange peel biomass. The biosorbent was prepared as stated in our previous published work [16, 17]. The surface functional groups on the biosorbent were investigated before and after adsorption using

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Fourier Transform Infrared spectroscopy (FT-IR) (Perkin Elmer, Frontier, Waltham, MA, USA).

B. Preparation of the metal solution

The stock solution of copper and lead was prepared using copper nitrate trihydrate (Cu $(NO_3)_2.3H_2O$) and lead nitrate $(Pb(NO_3)_2)$. The required salt was dissolved in deionized water in a 1000 mL volumetric flask while the different initial metal concentrations were prepared from the solution by serial dilution. All the adsorption experiments were conducted at a room temperature of 27^0C, and a constant pH of 5.

C. Fixed bed column study

Continuous adsorption studies were carried out at room temperature with a fixed bed column made of glass material. The column had an internal diameter of 2.3 cm and a height of 30 cm. The experiments were performed in a downward flow mode which provides maximum contact between the bio-sorbent and the adsorbates in the inlet stream. The column was packed with glass beads of 5 mm to a height of 1 cm at the top then followed by glass wool of 1 cm to make the bed compact and give mechanical support to the adsorbent bed. The desired amount of adsorbent was loaded, and 1 cm thick glass wool was placed at the bottom followed by a 1 cm glass bead to prevent adsorbent from been entrained in the solution. Each experimental run was carried out with an inlet feed of a determined volumetric flow rate, initial concentration, and pH. The pH of the solution was kept constant as already determined in the batch studies [16]. The flow rate was adjusted using a calibrated peristaltic pump (Flexflo A1N11E-4T). Samples were collected at the bottom of the column every 30 min for the first 5 h then at an hour interval and analyzed for metal ions concentration. The samples were filtered using Whatman filter paper (150 mm) and syringe filters (0.45 µm). The amount of Cu^{2+} and Pb^{2+} ions in the solution was analyzed using a micro-plasma atomic emission spectrophotometer (MP-AES, MY 18379001, Agilent, Santa Clara, CA, USA). The column experiments were carried out to investigate the effect of operating parameters such as initial metal ion concentration, bed height, and flow rate on the process efficiency. The maximum column capacity, q_{total} (mg/g) and the equilibrium metal uptake, q_{eq} (mg/g) are expressed in Equations (1) and (2) below.

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=total} C_{ad}\, dt \qquad (1)$$

$$q_{eq} = \frac{q_{total}}{X} \qquad (2)$$

Where Q is the volumetric flow rate (mL/min^{-1}), A is the area under the curve, X is the mass of the adsorbent (g), t is the total flow time and C_{ad} is the adsorbed concentration (mg/L).

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III. DYNAMIC ADSORPTION MODELS

A. Thomas model

Thomas [18] is one of the most widely used to estimate the adsorptive capacity of adsorbents and to predict the breakthrough curve. This model assumes that adsorption kinetics follows pseudo-second order, which relates to Langmuir isotherm at equilibrium and a plug flow with no axial dispersion [19-21]. The non-linear form of the equation as stated below.

$$\frac{C_t}{C_o} = \frac{1}{1 + exp^{\left(\frac{K_{TH}}{Q}(q_o m - C_o V_{eff})\right)}} \qquad (3)$$

Where, K_{Th} is the Thomas constant (L/mg.min), q_0 is the maximum solid-phase concentration of the solute/equilibrium uptake of the metal ion (mg/g), V_{eff} is the effluent volume (L), m is the mass of the loaded adsorbent (g), Q is the flow rate (mL/min), C_0 is the influent concentration (mg/L), C_t is the effluent concentration at time t, (mg/L).

B. Adams Bohart Model

Bohart and Adams model was first applied to gas-solid systems and later extended to other kinds of systems [22]. This model is used to check the dynamic behavior of the column, it assumes irreversible adsorption; adsorption of solute is directly proportional to the concentration of solute in the bulk solution and residual adsorptive capacity of the adsorbent. Also, it assumes an ideal plug flow with no axial dispersion [19, 21, 23, 24]. The non-linear form of the equation is given below.

$$\frac{C_t}{C_o} = \frac{e^{K_{AB} C_o t}}{e^{(K_{AB} N_o Z / U_o)} - 1 + e^{K_{AB} C_o t}} \qquad (4)$$

Where K_{BA} is the kinetic constant in L/mg.min, N_0 is the maximum volumetric sorption capacity in mg/L, C_t is the solute concentration in the liquid phase at time t in min, C_0 is the initial concentration of the metal ion in solution in mg/L, U_0 is the superficial velocity in cm/min, Z is the bed depth/bed height in cm.

C. Yoon Nelson Model

Yoon and Nelson [25] established a model based on the adsorption of gases in activated coal. This model assumes that the decrease rate in the probability of adsorption of adsorbate molecule is directly proportional to the probability of adsorbate sorption as well as the probability of the sorbate breakthrough on the sorbent with no axial dispersion [23]. The non-linear form of the equation is represented in equation 5 below.

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$$\frac{C_o}{C_t} = \frac{1}{1 + e^{K_{YN}(\tau - t)}} \tag{5}$$

Where Y_{YN} is the Yoon-Nelson rate constant (min^{-1}) and τ is the time at which effluent concentration reaches 50 % of the initial concentration.

IV. RESULTS AND DISUSSION

A. FT-IR Spectroscopy Analysis

The functional groups present on the surface of the biosorbent before and after adsorption study were determined using FT-IR spectroscopy. The plot shows the percentage transmittance and the wavenumber in the range of 500 – 4000 cm^{-1} as represented in Figure 1. The natural orange peel (OP) revealed some notable peaks at 3330 cm^{-1}, 1316.4 cm^{-1} and 1015.7 cm^{-1} which correspond to the O-H group, hydroxylic stretching. The peak at 2920.4 cm^{-1} represents the C-H group signifying the presence of alkane sharp stretching band. The presence of carboxylic bond, C=O and the unsaturated bond, C=C which can be likened to aldehydes and ketones, are shown by the peaks 1734.4 cm^{-1} and 1607.03 cm^{-1} respectively. The presence of a high proportion of hydroxyl and carboxyl groups on the surface of the biosorbent indicates the potential of orange peels to remove cations from aqueous solutions. There is a tendency that the positively charged metal ions will have affinity for the functional groups during adsorption process thus leading to ion exchange.

The spectra of orange peel after the adsorption of Cu^{2+} (OP-Cu) and Pb^{2+} (OP-Pb) showed some significant shifts in the peaks of the functional groups on the surface of the biosorbent. These shifts occurred due to the interactions between the functional groups indicated on the surface of the biosorbent before adsorption and metal ions in the aqueous solution. These shifts occurred in the peaks corresponding to the O-H and C-O-H stretching as evident at wavenumbers 3330 cm^{-1}, 1316.4 cm^{-1}, and 1015.7 cm^{-1} where the peaks became less pronounced after adsorption of Cu^{2+} and Pb^{2+}.

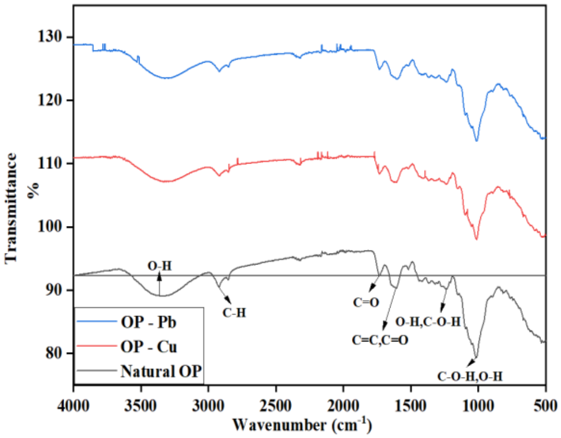


Fig. 1 FT-IR spectroscopy of natural orange peel (OP) before and after adsorption of Cu^{2+} and Pb^{2+}.

B. Thomas Model

The Thomas model is one of the widely used dynamic models for describing fixed-bed column performance and predicting the breakthrough curve operating parameters. The model constants K_{Th} and q_0 values calculated from the slope and intercepts of the linear graph of $\ln[(C_0/C_t)-1]$ against time obtained from the experimental data and representing the different operating parameters studied are summarized in Tables I and II for the biosorption of Cu^{2+} and Pb^{2+} respectively.

Flow rate: The values of K_{Th} and q_0 increased as the flow rate increased from 1 to 3 mL/min. The adsorption capacity is maximum at 3 mL/min, this is due to the increase in metal loading at the highest flow rate. A similar trend was reported by Ali Gh. Khamseh and Ghorbanian [26] during their study on the breakthrough modelling of thorium bio-sorption on orange peels in a fixed-bed column. The coefficient of correlation (R^2) values show that this model interpreted the experimental data well.

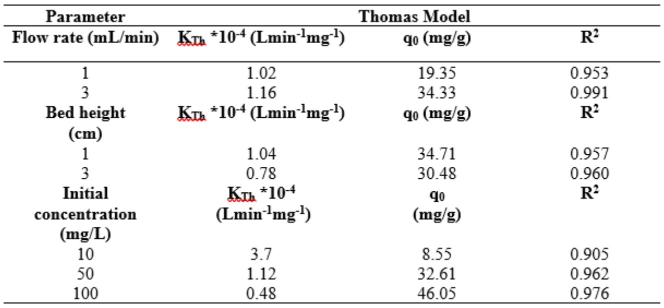
Bed height: An increase in bed height gave a corresponding decrease in the values of K_{Th} and q_0. However, the values of K_{Th} remained almost constant (1.94 – 1.9) for Cu^{2+} despite an increase in bed height. This might be because of the optimum utilization of the active sites. This result corresponds to what was obtained by other researchers [27, 28]. The correlation coefficient (R^2) values varied from 0.988 to 0.939 suggesting the relevance of this model in interpreting the adsorption behaviour.

Initial concentration: An increase in initial concentration resulted in a decrease in the value of K_{Th} and an increase in the values of q_0. This observation is in agreement with the results obtained by [27] who affirmed that this behaviour may be due to concentration difference which acted as the driving force for an improved adsorption process. The Thomas model parameters for the sorption of Cu^{2+} and Pb^{2+} onto orange peels followed the same trend. The high correlation coefficient R^2 values show that the Thomas model was well-fitted with the experimental data.

TABLE I
SUMMARY OF THOMAS MODEL PARAMETERS FOR CU^{2+} SORPTION USING ORANGE PEELS IN A FIXED BED COLUMN

Parameter	**Thomas Model**		
Flow rate (mL/min)	**K_{Th} *10^{-4} (Lmin^{-1}mg^{-1})**	**q_0 (mg/g)**	**R^2**
1	1.58	11.60	0.980
3	2.14	12.84	0.909
Bed height (cm)	**K_{Th} *10^{-4} (Lmin^{-1}mg^{-1})**	**q_0 (mg/g)**	**R^2**
1	1.94	14.02	0.988
3	1.9	13.34	0.939
Initial concentration (mg/L)	**K_{Th} *10^{-4} (Lmin^{-1}mg^{-1})**	**q_0 (mg/g)**	**R^2**
10	4.0	5.91	0.992
50	2.28	13.01	0.829
100	1.02	13.85	0.913

TABLE II
SUMMARY OF THOMAS MODEL PARAMETERS FOR PB^{2+} SORPTION USING ORANGE PEELS IN A FIXED BED COLUMN



Parameter	Thomas Model		
Flow rate (mL/min)	**K_{Th} *10^{-4} (Lmin^{-1}mg^{-1})**	**q_0 (mg/g)**	**R^2**
1	1.02	19.35	0.953
3	1.16	34.33	0.991
Bed height (cm)	**K_{Th} *10^{-4} (Lmin^{-1}mg^{-1})**	**q_0 (mg/g)**	**R^2**
1	1.04	34.71	0.957
3	0.78	30.48	0.960
Initial concentration (mg/L)	**K_{Th} *10^{-4} (Lmin^{-1}mg^{-1})**	**q_0 (mg/g)**	**R^2**
10	3.7	8.55	0.905
50	1.12	32.61	0.962
100	0.48	46.05	0.976

C. Yoon Nelson Model

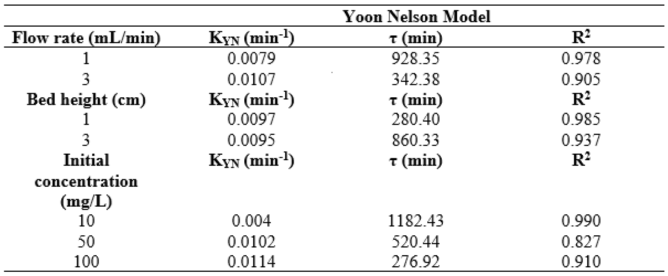
Yoon Nelson model is regarded as a simplified model because it does not require data like characteristics of adsorbate, type of adsorbent, and the physical properties of the bed. The assumption of this model is based on the rate of decrease in the adsorption probability of each adsorbate which is proportional to the adsorbate adsorption probability and the probability of adsorbate breakthrough on the adsorbent [29].

Flow rate: Yoon Nelson model estimates the time it takes to obtain 50% of the inlet concentration (τ) in the effluent. The plot of $\ln(C_t/C_0-C_t))$ against time helped to calculate the constants K_{YN} and τ. An increase in the flow rate gave an increase in the values of K_{YN} and a decrease in the value of τ which may be due to the fast saturation of the bed at a higher flow rate. A similar result was reported by Basu, Guha [30] who used a fixed-bed column bioreactor for the adsorption of lead using lentil husk as a bio-sorbent.

Bed height: The application of the Yoon Nelson model to the experimental data showed that an increase in the bed height resulted in a decrease in the values of K_{YN} and an increase in the value of τ. The adsorption capacity increased with increasing bed height for both metal ions. The bed height delayed 50 % adsorbate breakthrough time τ increased with increasing bed height since the metal ions had more access to a greater number of active sites at higher bed height. The finding is in agreement with the report of Alalwan, Kadhom [31]. The coefficient of correlation (R^2) values showed a good fitting of this model to the experimental data.

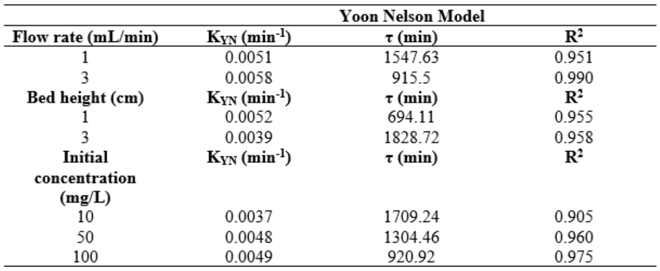
Initial concentration: An increase in initial concentration resulted in an increase in the values of K_{YN} and a decrease in the values of τ. This result is similar to the findings reported by Aranda-Garcia and Cristiani-Urbina [32]. The results for the biosorption of Cu^{2+} and Pb^{2+} showed that increasing the bed height, decreasing the flow rate and the initial concentration improved the removal capacity of the bio-sorbent. The values of the correlation coefficient R^2 as shown in Table III and IV are close to 1, this suggests that the experimental data are well-fitted with the Yoon Nelson model.

TABLE III
SUMMARY OF YOON NELSON MODEL PARAMETERS FOR CU^{2+} SORPTION USING ORANGE PEELS IN A FIXED BED COLUMN.



Yoon Nelson Model			
Flow rate (mL/min)	**K_{YN} (min^{-1})**	**τ (min)**	**R^2**
1	0.0079	928.35	0.978
3	0.0107	342.38	0.905
Bed height (cm)	**K_{YN} (min^{-1})**	**τ (min)**	**R^2**
1	0.0097	280.40	0.985
3	0.0095	860.33	0.937
Initial concentration (mg/L)	**K_{YN} (min^{-1})**	**τ (min)**	**R^2**
10	0.004	1182.43	0.990
50	0.0102	520.44	0.827
100	0.0114	276.92	0.910

TABLE IV
SUMMARY OF YOON NELSON MODEL PARAMETERS FOR PB^{2+} SORPTION USING ORANGE PEELS IN A FIXED BED COLUMN



Yoon Nelson Model			
Flow rate (mL/min)	**K_{YN} (min^{-1})**	**τ (min)**	**R^2**
1	0.0051	1547.63	0.951
3	0.0058	915.5	0.990
Bed height (cm)	**K_{YN} (min^{-1})**	**τ (min)**	**R^2**
1	0.0052	694.11	0.955
3	0.0039	1828.72	0.958
Initial concentration (mg/L)	**K_{YN} (min^{-1})**	**τ (min)**	**R^2**
10	0.0037	1709.24	0.905
50	0.0048	1304.46	0.960
100	0.0049	920.92	0.975

D. Adams Bohart Model

This model is based on assumption that equilibrium is not instantaneous, which implies that the adsorption rate is proportional to the adsorbent residual capacity and the concentration of the dissolved species [22]. The values of K_{BA} and N_0 were obtained from the linear plot of $\ln(C_t/C_0)$ against time while the different operating parameters studied are summarized in Table V and VI for biosorption of Cu^{2+} and Pb^{2+} respectively. The trends observed by the model parameters are the same for both metal ions.

Flow rate: An increase in flow rate increased correspondingly with an increase in the values of both K_{BA} and N_0.

Bed height: In this case, an increase in bed height increased K_{BA} whereas N_0 followed the opposite trend. These observations are in agreement with the findings of Basu, Guha [30].

Initial concentration: The model parameters showed that K_{BA} values representing the Bohart-Admas constant decreased with an increasing initial concentration while the values of N_0 increased at a higher concentration as shown in Tables 5 and 6. The low correlation coefficient (R^2) values obtained for the Adams Bohart model show that the Thomas model and Yoon Nelson model best fitted the experimental data for the adsorption process.

TABLE V
SUMMARY OF BOHART-ADAMS MODEL PARAMETERS FOR CU^{2+} SORPTION USING ORANGE PEELS IN A FIXED BED COLUMN.

Adams Bohart Model			
Flow rate (mL/min)	**K_{BA}*10-4 ($Lmin^{-1}mg^{-1}$)**	**N_0 (mg/L)**	**R^2**
1	1.12	7102.10	0.901
3	0.62	13854.83	0.668
Bed height (cm)	**K_{BA}*10-4 ($Lmin^{-1}mg^{-1}$)**	**N_0 (mg/L)**	**R^2**
1	0.3	23923.82	0.561
3	1.3	8962.79	0.812
Initial concentration (mg/L)	**K_{BA}*10-4 ($Lmin^{-1}mg^{-1}$)**	**N_0 (mg/L)**	**R^2**
10	2.2	4483.53	0.894
50	1.3	9164.32	0.598
100	0.25	17727.24	0.556

TABLE VI
SUMMARY OF BOHART-ADAMS MODEL PARAMETERS FOR PB^{2+} SORPTION USING ORANGE PEELS IN A FIXED BED COLUMN

Adams Bohart Model			
Flow rate (mL/min)	**K_{BA}*10-4 ($Lmin^{-1}mg^{-1}$)**	**N_0 (mg/L)**	**R^2**
1	0.68	12331.81	0.905
3	0.7	23711.51	0.914
Bed height (cm)	**K_{BA}*10-4 ($Lmin^{-1}mg^{-1}$)**	**N_0 (mg/L)**	**R^2**
1	0.56	26581.51	0.884
3	0.6	17680.02	0.948
Initial concentration (mg/L)	**K_{BA}*10-4 ($Lmin^{-1}mg^{-1}$)**	**N_0 (mg/L)**	**R^2**
10	2.8	5091.72	0.945
50	0.82	19579.23	0.938
100	0.25	36218.79	0.871

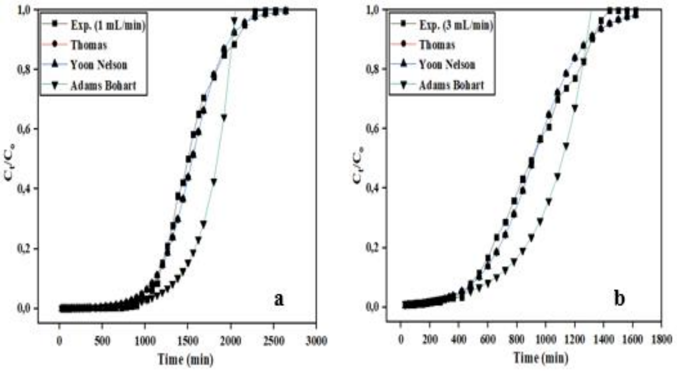


Fig. 2 Modeling of Thomas, Yoon Nelson and Adams Bohart models on the effect of flowrate of Pb^{2+} (a) 1 mL/min (b) 3 mL/min

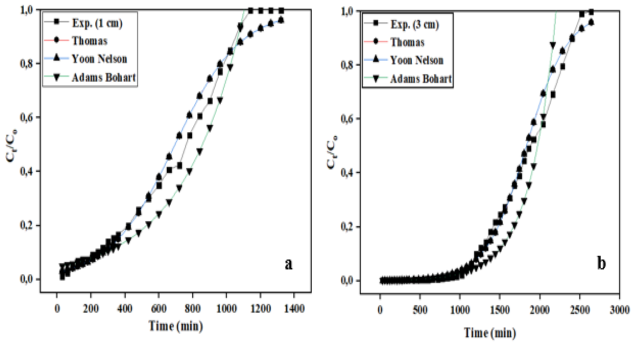


Fig. 3 Modeling of Thomas, Yoon Nelson and Adams Bohart models on the effect of bed height of Pb^{2+} (a) 1cm (b) 3cm

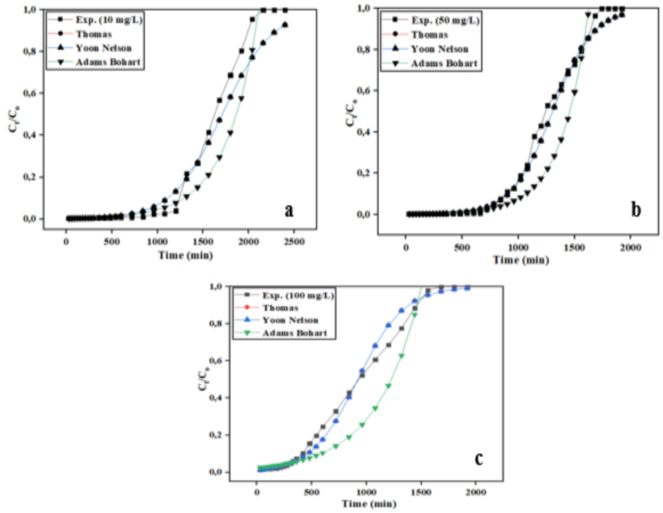


Fig. 4 Modeling of Thomas, Yoon Nelson and Adams Bohart models on the effect of initial metal ion concentration of Pb^{2+} (a) 10 mg/L (b) 50 mg/L (c) 100 mg/L

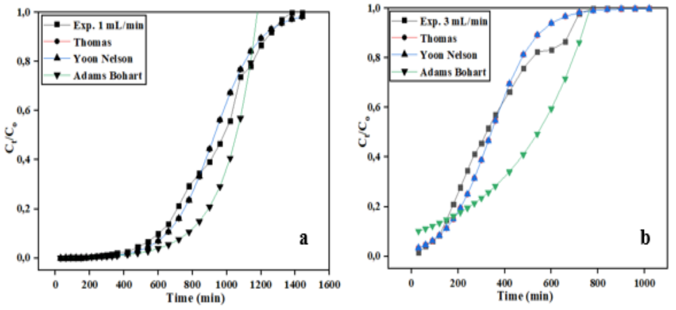


Fig. 5 Modeling of Thomas, Yoon Nelson and Adams Bohart models on the effect of flowrate of Cu^{2+} (a) 1 mL/min (b) 3 mL/min

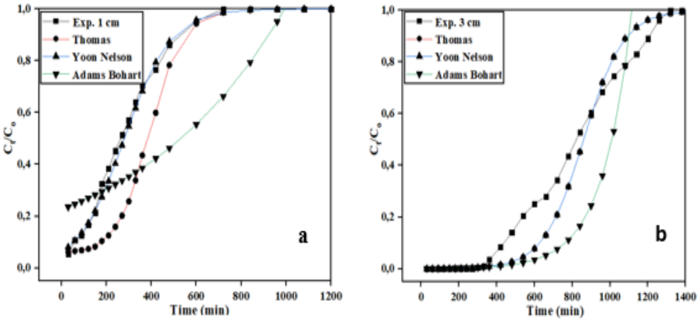


Fig. 6 Modeling of Thomas, Yoon Nelson and Adams Bohart models on the effect of bed height of Cu^{2+} (a) 1cm (b) 3cm

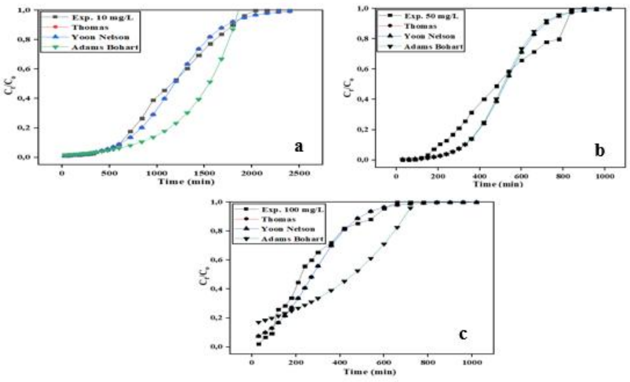


Fig. 7 Modeling of Thomas, Yoon Nelson and Adams Bohart models on the effect of initial metal ion concentration of Cu^{2+} (a) 10 mg/L (b) 50 mg/L (c) 100 mg/L

E. Statistical Validation

Statistical validation is significant for evaluating the performance of dynamic adsorption models. The purpose is to evaluate the statistical and mathematical features of the applied models and compare the error values obtained to determine the best model that fits the experimental data the most. Three different error functions were examined in this study namely: mean absolute error, root mean square error, and the coefficient correlation as represented in Table VII below.

TABLE VII
ERROR FUNCTIONS USED TO STATISTICALLY VALIDATE THE PERFORMANCE OF THE MODELS

Error function	Abbreviation	Equation
Mean absolute error	MAE	$MAE = \frac{1}{n}\sum_{i=1}^{n}\lvert y_{e,exp} - y_{e,pred}\rvert$
Root mean square error	RMSE	$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(y_{e,exp} - y_{e,pred}\right)^2}$
Coefficient of correlation	R^2	$R^2 = \frac{\Sigma\left(y_{e,exp} - y_{e,pred}\right)^2}{\Sigma\left(y_{e,exp} - y_{e,pred}\right)^2 + \left(y_{e,exp} - y_{e,pred}\right)^2}$

From Tables VIII and IX, the error functions showed good agreement between the experimental and predicted values for the three models with RMSE and MAE < 1 in most cases. The highest values of R^2 and lowest values of RMSE and MAE were obtained. The best model chosen had the highest value of R^2 and lowest values of RMSE and MAE, which suggests that the Thomas and Yoon Nelson models performed well for the biosorption of Cu^{2+} and Pb^{2+}.

TABLE VIII
BREAKTHROUGH CURVES REGRESSION AND ERROR ANALYSIS FOR CU^{2+} SORPTION

Parameters	**Thomas**			**Yoon Nelson**			**Adams Bohart**		
single solute Cu	**RMSE**	**MAE**	**R^2**	**RMSE**	**MAE**	**R^2**	**RMSE**	**MAE**	**R^2**
Flow rate (mL/min)									
1	0.037	0.024	0.980	0.037	0.024	0.978	0.754	0.296	0.901
3	0.055	0.040	0.909	0.055	0.040	0.905	0.368	0.254	0.668
Bed height (cm)									
1	0.023	0.016	0.988	0.023	0.016	0.985	0.323	0.246	0.561
3	0.075	0.049	0.939	0.075	0.049	0.937	1.662	0.661	0.812
Concentration (mg/L)									
10	0.029	0.018	0.992	0.030	0.019	0.990	0.539	0.245	0.894
50	0.088	0.067	0.829	0.088	0.066	0.827	1.130	0.522	0.598
100	0.062	0.045	0.913	0.062	0.045	0.910	0.359	0.275	0.556

TABLE IX
BREAKTHROUGH CURVES REGRESSION AND ERROR ANALYSIS FOR PB^{2+} SORPTION

Parameters	**Thomas**			**Yoon Nelson**			**Adams Bohart**		
single solute Pb	**RMSE**	**MAE**	**R^2**	**RMSE**	**MAE**	**R^2**	**RMSE**	**MAE**	**R^2**
Flow rate (mL/min)									
1	0.027	0.017	0.953	0.028	0.018	0.951	1.242	0.422	0.905
3	0.028	0.020	0.991	0.028	0.020	0.990	0.470	0.227	0.914
Bed height (cm)									
1	0.045	0.035	0.957	0.045	0.035	0.955	0.208	0.111	0.884
3	0.030	0.018	0.960	0.031	0.019	0.958	0.501	0.168	0.948
Concentration (mg/L)									
10	0.065	0.039	0.907	0.065	0.040	0.905	0.266	0.114	0.945
50	0.034	0.021	0.962	0.035	0.021	0.960	0.511	0.215	0.938
100	0.040	0.027	0.976	0.040	0.027	0.975	0.438	0.203	0.871

V. CONCLUSION

The major aim of this study was to evaluate the performance of natural orange peels in the removal of Cu^{2+} and Pb^{2+} in a fixed-bed column. The FT-IR analysis of the biosorbent revealed the presence of pronounced peaks corresponding to O-H, C-H and C=O which further suggest a significant amount of carbon and oxygen on the surface of the biosorbent, thereby enhancing the adsorption of copper and lead ions. The experimental results showed that the performance of the bed was improved with an increase in bed height, the quantity adsorbed increased from 2.65 mg/g to 16.67 mg/g for Pb^{2+} and from 0.75 mg/g to 5.68 mg/g for Cu^{2+} as the bed height increased from 1 cm to 3 cm. The volume of solutions treated at breakthrough decreased with an increase in flow rate for both metals. The volume treated at breakthrough for Pb^{2+} decreased from 0.928 to 0.831 L and Cu^{2+} decreased from 0.360 to 0.108 L when the flow rate was increased from 1 to 3 mL/min. The significant factors used to measure the performance of an adsorbent such as breakthrough adsorption capacity (Q_b) and the breakthrough time (t_b) were analyzed for both metal ions. However, similar trends were observed for both metals though Pb^{2+} performance was better than Cu^{2+} with all the parameters. The Q_b and t_b decreased with an increase in flow rate while it increased with an increase in bed height for both metal ions. Also, the Q_b increased with an increase in the initial metal ion concentration and a consequent decrease in t_b for both metal ions. The quantity adsorbed for Pb^{2+} increased from 4.13 to 15.83 mg/g and 2.05 to 3.83 mg/g for Cu^{2+} as the initial concentration increased from 10 to 100 mg/L. The experimental data obtained were fitted into the Thomas, Yoon Nelson, and the Bohart-Adams models to determine the best fit and the well-performed model. For all the parameters considered, the Thomas and Yoon Nelson models performed well with a high coefficient of correlation ($R^2 > 0.9$). The models were also validated using some statistical error analysis, which showed that the Thomas and Yoon Nelson models fitted the experimental data

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

REFERENCES

[1] I. Moodley, et al., "*Environmentally sustainable acid mine drainage remediation: Research developments with a focus on waste/by-products,"* Miner. Eng., vol. 126, pp. 207-220, 2018. https://doi.org/10.1016/j.mineng.2017.08.008

[2] S.K, Guna., "*Methods of Removing Heavy Metals from Industrial Wastewater,"* J. multidiscip. eng. sci. studi. (JMESS), vol. 1, no. 1, pp. 12-18, 2015.

[3] Y. Gomravi, A. Karimi, and H. Azimi, "*Adsorption of heavy metal ions via apple waste low-cost adsorbent: Characterization and performance*," Korean J. Chem. Eng., vol. 38, no. 9, pp. 1843-1858, 2021. https://doi.org/10.1007/s11814-021-0802-8

[4] A.S. Adesanmi, et al., "*Utilization of waste in solving environmental problem: Application of banana and orange peels for the removal of lead (II) ions from aqueous solution of lead nitrate,"* Nig. J. Eng. Sci. Technol. Res., vol. **6, no.** 1, pp. 18-33, 2020.

[5] B.P. Mora, et al., "*Batch and fixed-bed column studies of selenite removal from contaminated water by orange peel-based sorbent*," Water Sci. Eng., vol. **13, no.** 4, pp. 307-316, 2020. https://doi.org/10.1016/j.wse.2020.12.003

[6] L.M. vera, et al., "*Fixed bed column modeling of lead (II) and cadmium (II) ions biosorption on sugarcane bagasse*," Environ. Eng. Res., vol. 24, no. 1, pp. 31-37, 2018. https://doi.org/10.4491/eer.2018.042

[7] A.L.P. Xavier, et al., "*Modeling adsorption of copper(II), cobalt(II) and nickel(II) metal ions from aqueous solution onto a new carboxylated sugarcane bagasse. Part II: Optimization of monocomponent fixed-bed column adsorption*," J. Colloid. Interface Sci., vol. 516, pp. 431-445, 2018. https://doi.org/10.1016/j.jcis.2018.01.068

[8] M.A. Ashraf, et al., "*Removal of heavy metals from aqueous solution by using mango biomass*," Afr. J. Biotechnol., vol. **10, no.** 11, pp. 2163-2177, 2011.

[9] R. Lakshmipathy and N.C. Sarada, "*A fixed bed column study for the removal of Pb^{2+} ions by watermelon rind*," Environ. Sci.: Water Res. & Technol., vol. **1, no.** 2, pp. 244-250, 2015. https://doi.org/10.1039/C4EW00027G

[10] H. Ahmad, C.J. Ee, and N.S. Baharudin, "*A preliminary study for removal of heavy metals from acidic synthetic wastewater by using pressmud-rice husk mixtures,*" IOP Conference Series: Environ. Earth Sci., vol. 36, pp. 1-8, 2016. https://doi.org/10.1088/1755-1315/36/1/012031

[11] A. Bhatnagar, A.K. Minocha, and M. Sillanpää, "*Adsorptive removal of cobalt from aqueous solution by utilizing lemon peel as biosorbent,"* Biochem. Eng. J., vol. 48, no. 2, pp. 181-186, 2010. https://doi.org/10.1016/j.bej.2009.10.005

[12] M.A. Mahmoud, "*Kinetics studies of uranium sorption by powdered corn cob in batch and fixed bed system*," J Adv Res, vol. 7, no. 1, pp. 79-87, 2016. https://doi.org/10.1016/j.jare.2015.02.004

[13] M. Matouq, et al., "*The adsorption kinetics and modeling for heavy metals removal from wastewater by Moringa pods*," J. Environ. Chem. Eng., vol. 3, no. 2, pp. 775-784, 2015. https://doi.org/10.1016/j.jece.2015.03.027

[14] S.A. Sadeek, et al., "*Metal adsorption by agricultural biosorbents: Adsorption isotherm, kinetic and biosorbents chemical structures*," Int. J. Biol. Macromol., vol. 81, pp. 400-409, 2015. https://doi.org/10.1016/j.ijbiomac.2015.08.031

[15] L. Semerjian, "*Removal of heavy metals (Cu, Pb) from aqueous solutions using pine (Pinus halepensis) sawdust: Equilibrium, kinetic, and thermodynamic studies*," J. Environ. Technol. Innov, vol. 12, pp. 91-103, 2018. https://doi.org/10.1016/j.eti.2018.08.005

[16] F.O. Afolabi, P. Musonge, and B.F. Bakare, "*Application of the Response Surface Methodology in the Removal of Cu^{2+} and Pb^{2+} from Aqueous Solutions Using Orange Peels*," Sci. Afr., vol. 13, 2021. https://doi.org/10.1016/j.sciaf.2021.e00931

[17] F.O. Afolabi, P. Musonge, and B.F. Bakare, "*Adsorption of Copper and Lead Ions in a Binary System onto Orange Peels: Optimization, Equilibrium, and Kinetic Study*," Sustain., vol. 14, no. 17, 2022. https://doi.org/10.3390/su141710860

[18] H.C. Thomas, "*Heterogeneous ion exchange in a flowing system*," J. Am. Chem. Soc., vol. 66, no. 10, pp. 1664-1666, 1944. https://doi.org/10.1021/ja01238a017

[19] A. Chatterjee, and S. Schiewer, "*Biosorption of Cadmium(II) Ions by Citrus Peels in a Packed Bed Column: Effect of Process Parameters and Comparison of Different Breakthrough Curve Models*," CLEAN - Soil, Air, Water, vol. 39, no. 9, pp. 874-881, 2011. https://doi.org/10.1002/clen.201000482

[20] Z. Aksu, and F. Gönen, "*Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves*," Process Biochem., vol. 39, no. 5, pp. 599-613, 2004. https://doi.org/10.1016/S0032-9592(03)00132-8

[21] S. Chatterjee, S. Mondal, and S. De, "*Design and scaling up of fixed bed adsorption columns for lead removal by treated laterite*," J. Clean. Prod., vol. 177, pp. 760-774, 2018. https://doi.org/10.1016/j.jclepro.2017.12.249

[22] G. Bohart, and E. Adams, "*Adsorption in columns*," J. Am. Chem. Soc, vol. 42, pp. 523-544, 1920. https://doi.org/10.1021/ja01448a018

[23] M. calero, et al., "*Study of Cr (III) biosorption in a fixed-bed column,*" J Hazard Mater, vol. 171, no. 1-3, pp. 886-93, 2009. https://doi.org/10.1016/j.jhazmat.2009.06.082

[24] K.H. Chu, "*Fixed bed sorption: setting the record straight on the Bohart-Adams and Thomas models*," J Hazard Mater, vol. 177, no. 1-3, pp. 1006-12, 2010.

[25] Y.H. Yoon, and J.H. Nelson, *"Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life,"* Am Ind Hyg Assoc J, vol. 45, no. 8, pp. 509-516, 1984. https://doi.org/10.1016/j.jhazmat.2010.01.019

[26] Ali Gh. Khamseh and S.A. Ghorbanian, *"Experimental and modeling investigation of thorium biosorption by orange peel in a continuous fixed-bed column,"* J. Radioanal. Nucl. Chem., vol. 317, pp. 871-879, 2018. https://doi.org/10.1007/s10967-018-5954-6

[27] M. Amin, A. Alazba, and M. Shafiq, *"Batch and fixed-bed column studies for the biosorption of Cu (II) and Pb (II) by raw and treated date palm leaves and orange peel,"* Global Nest J., vol. 19, pp. 464-478, 2017. https://doi.org/10.30955/gnj.002294

[28] H. Muhamad, H. Doan, and A. Lohi, "*Batch and continuous fixed-bed column biosorption of Cd^{2+} and Cu^{2+},"* Chem. Eng. J., vol. 158, no. 3, pp. 369-377, 2010. https://doi.org/10.1016/j.cej.2009.12.042

[29] S. Afroze, and T.K. Sen, *"A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents,"* Water, Air, & Soil Pollut, vol. 229, no. 7, pp. 1-50, 2018. https://doi.org/10.1007/s11270-018-3869-z

[30] M. Basu, A.K. Guha, and L. Ray, *"Adsorption of Lead on Lentil Husk in Fixed Bed Column Bioreactor,"* Bioresour Technol, vol. 283, pp. 86-95, 2019. https://doi.org/10.1016/j.biortech.2019.02.133

[31] H.A. Alalwan, M.A. Kadhom, and A.H. Alminshid, *"Removal of heavy metals from wastewater using agricultural byproducts,"* J. Water Supply Res. Techn., vol. 69, no. 2, p. 99-112, 2020. https://doi.org/10.2166/aqua.2020.133

[32] E. Aranda-Garcia, and E. Cristiani-Urbina, *"Hexavalent chromium removal and total chromium biosorption from aqueous solution by Quercus crassipes acorn shell in a continuous up-flow fixed-bed column: Influencing parameters, kinetics, and mechanism,"* PLoS One, vol. **15, no.** 1, pp. e0227953, 2020. https://doi.org/10.1371/journal.pone.0227953