Fixed-Bed Column Biosorption of Cu^{2+} and Pb^{2+} Using Green Adsorbent

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

***Abstract*—**Many studies on adsorption have focused on batch experiments. However, a laboratory-scale fixed-bed column study is important to describe the breakthrough curve behaviour which is typical of an industrial treatment plant. In this study, the performance of orange peels was investigated for the removal of copper and lead ions from wastewater in a fixed-bed column. The fixed bed experiments were conducted to investigate the effect of column parameters; flow rate (1 and 3 mL/min), initial concentration (10, 50, and 100 mg/L), and bed height (1 and 3 cm). The experimental results showed that the performance of the bed was improved with an increase in the bed height, the quantity adsorbed increased from 0.75 mg/g to 5.68 mg/g for Cu^{2+} and 2.65 mg/g to 16.67 mg/g for Pb^{2+} as the bed height was increased from 1 cm to 3 cm. The volume treated at breakthrough for Cu^{2+} decreased from 0.360 to 0.108 L and Pb^{2+} decreased from 0.928 to 0.831 L when the flow rate was increased from 1 to 3 mL/min. 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.

***Keywords*—**Breakthrough curve, Fixed-bed, Wastewater, heavy metals.

I. Introduction

The quest to enrich the life of mankind through scientific and technological know-how has caused a lot of damage to valuable natural resources and the environment. Modern industrialization and urbanization are factors that impose huge costs upon the global environment. However, sustainability and development should be considered concurrently to make the environment safe for every living species.

Water pollution is one of the major environmental challenges caused by various industries through the discharge of wastewater containing toxic pollutants such as heavy metals into water bodies. Heavy metals are metals with a density higher than 5 kg/m^3, which are hazardous to human health. The level of harm depends on how toxic the metal is and how much of it a person is exposed to. Copper and lead are the most common heavy metals found in wastewater. The presence of lead and copper ions in water at low concentrations is a risk to human life. Copper is one of the heavy metals polluting water bodies, it is a threat to human and aquatic life when in high concentration. The industrial activities involving the application of copper include; electrolysis deposition, pesticides, electroplating, and mining [1]. On the other hand, lead (Pb) is one of the most toxic heavy metals commonly produced from metal plating and galvanising, paint, laundry process, mining, battery manufacturing and steel industries. Generally, heavy metals are detrimental to human health, however the toxicity and exposure level to each heavy metal determine its effect on vital organs and systems. According to the World Health Organization (WHO) reports, long-term exposure to copper and lead causes fatigue, insomnia, osteoporosis, heart disease, cancer, migraine headaches, and seizures [2].

The treatment of effluents before disposal has become a global concern which has led to the formulation of rules and guidelines by various International Environmental Authorities. However, many industries do not obey the proposed guidelines precisely and consequently pollute both fresh and marine water resources. The primary reasons for non-compliance as highlighted in the literature include the high cost of treatment, lack of proper knowledge and awareness, and failure of existing conventional wastewater treatment technologies [3]. In addition, the existing treatment methods which include electrolytic extraction, chemical precipitation, ion exchange, reverse osmosis, coagulation, chemical oxidation and reduction, dilution, air stripping, solvent extraction, electrodialysis, cementation, steam stripping, and adsorption have drawbacks [4]. One of the major challenges of these methods is the sludge generated during the treatment process which contains solid residue hence a license is required from the environmental management body for the disposal of the produced sludge. Among these methods adsorption has emerged to be more efficient because of its simplicity and cost-effectiveness [5].

In the past decades, researchers have proven the efficiency and sustainability of the adsorption process in the removal of heavy metals from wastewater. Biosorption involves the use of biomaterial/biowaste as an adsorbent which is derived from agricultural and industrial wastes. These biowastes are locally available, cheap, and environmentally eco-friendly and are composed of lignin, cellulose, hemicellulose, and high molecular carbohydrates which make them potential and efficient adsorbents [6]. Some of these wastes used for biosorption studies include rice husk [7], pine sawdust [8], Java plum and amaltash seed [9], banana peel [10], acorn shell [11], sugarcane bagasse [12], eggshell [13], pine bark [14], seaweed [15] etc. Natural Pinus halepensis sawdust was explored as an alternative biosorbent for the removal of

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copper and lead from aqueous solution[8]. The authors reported that the adsorption capacity of the metal ions increased with an increase in initial concentration. The fixed bed column modeling of lead and cadmium ions biosorption on sugarcane bagasse was investigated [12]. The percentage removal of lead and cadmium was 91 % and 90 % respectively. Orange peel residue carbon nanoparticles was used as an adsorbent for the removal of copper ions from an aqueous solution [16]. The numerical optimization showed that the optimum removal of 94 % was obtained.

Oranges are the biggest citrus type in South Africa and account for 60 % of the citrus fruits produced from approximately 45,000 hectares of cultivated land. South Africa produces an average of 1.5 million mega tons of oranges annually, some of which are exported and used to produce fruit juice [17]. Unwanted peels of orange generate a huge quantity of waste from households, markets, and restaurants, which is disposed of on dumping sites. These peels could become a nuisance to the environment if not properly disposed of. These wastes can be used as low-cost, readily available, and eco-friendly adsorbents for the removal of copper and lead from wastewater thereby reducing environmental pollution. The concept of using agricultural wastes for water remediation is an ideal approach which will foster the realization of the Sustainable Development Goal (SDG:6) which buttresses on clean water and sanitation. The usage of biowaste is also a waste management strategy that should be encouraged in wastewater treatment. Adsorption studies can be carried out in the laboratory using either batch or dynamic studies and the combination of both. Most adsorption studies reported in literature have focused on batch studies, however, these do not provide sufficient information to enable the practical industrial application of the adsorbents. Therefore, this present study explored the potential of orange peels for the removal of Cu^{2+} and Pb^{2+} in column studies. The column studies investigated the performance of the adsorbent in a typical industrial treatment plant using a laboratory-scale fixed bed column. In addition, the effect of the operating parameters such as initial metal concentration, bed height and flow rate were examined.

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 showed the highest performance towards the adsorption of Cu^{2+} and Pb^{2+} among the fruit peels (orange and banana peels) investigated in the batch mode [18]. The preparation and processing of the raw adsorbent were carried out as discussed by [19], after which the powdered orange peel was sieved using an 800-mesh screen and preserved in an airtight container for further use.

B. Preparation of the metal solution

The stock solution of copper and lead was prepared from 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. The chemical reagents used for the experimental study were of analytical reagent (AR) grade purchased from Sigma. All the adsorption experiments were conducted at a constant pH of 5, an optimum pH for the adsorption of Cu^{2+} and Pb^{2+} using orange peels confirmed by investigating batch study operating parameters [18].

C. Fixed bed column study

The batch adsorption studies do not give complete information on the industrial application of wastewater treatment. Therefore, batch equilibrium and kinetic studies are always supported by continuous studies to determine the contact time, bio-sorbent efficiency, exhaustion time, mass transfer zone, and most importantly scale-up for industrial treatment plants. These parameters are characteristics of the breakthrough adsorption curve. 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 as shown in **Figure 1**. The column was designed mainly for this study, it has a spout that allows passage of the effluent. The experiments were performed in a downward flow mode which provides maximum contact between the bio-sorbent and the adsorbates in the inlet stream. A peristaltic pump was used to achieve the desired flow rate. The column was packed with glass beads of 50 mm to a height of 2 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 loss. To get rid of air trapped in the bed, distilled water was passed through the column for 3 h before starting the experiments. This ensured that the adsorbent bed was fully wetted and void of air.

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. The flow rate was adjusted using a calibrated peristaltic pump (Flexflo A1N11E-4T). The adsorbent dosage variation was used to achieve different bed height values. 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. Samples were collected at intervals until the outlet concentration reached the inlet 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). All the experiments were carried out at room temperature of 25 ^{0}C ± 2 ^{0}C. All experiments were carried out duplicate, and the average values were used for further calculations. 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.

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

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

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).

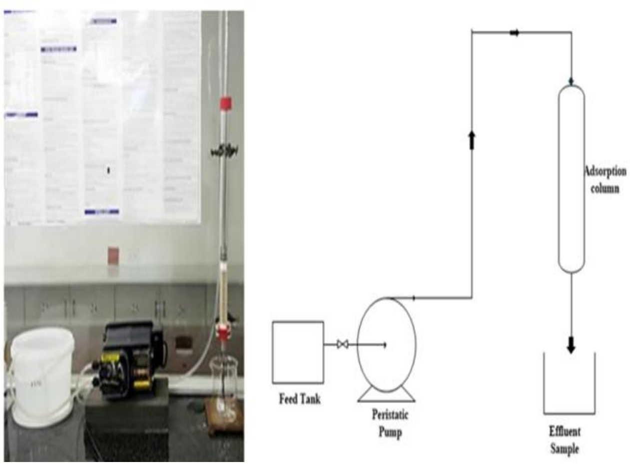

Fig. 1. Set-up for the column experiment

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E. Author Contributions

Conceptualization, J.O.A., S.K.O.N., B.S.C., J.W.L. and V.I.O.; writing—original draft preparation, J.O.A.; writing—review and initial editing, J.O.A., S.K.O.N., B.S.C., J.W.L. and V.I.O.; supervision, S.K.O.N., B.S.C., J.W.L. and V.I.O.; project administration, S.K.O.N. and V.I.O.; funding acquisition, S.K.O.N. and V.I.O. All authors have read and agreed to the published version of the manuscript.

III. Results And Discussion

The batch studies are not viable economically and cannot be used for the design and the practice of industrial adsorption columns [20]. The data obtained in the batch studies are not relatively applicable in the continuous adsorption system where the contact time between the adsorbate and adsorbent is not sufficient for equilibrium to be reached [2]. Hence, it is important to study the performance of adsorbents to remove heavy metals in a continuous process to ascertain their applicability on an industrial scale. In addition, the study of continuous adsorption processes via the fixed-bed column allows more proper utilization of the adsorption efficiency than the batch studies and can explore the major influencing operating parameters such as bed height, flow rate and the initial metal ion concentration, etc., that is paramount to the design of a fixed-bed adsorber.

A. Effect of flowrate

This is the rate at which the metal solution traverses the fixed bed. The inlet flow rate of the metal solution is an essential operating parameter that must be investigated in the performance and efficiency of an adsorption column in a fixed bed [21]. The effect of flow rate on the adsorbent efficiency was conducted by considering the flow rate 1 mL/min and 3 mL/min, while initial metal concentration (50 mg/L) and bed height (3 cm) were kept constant. The breakthrough curves obtained from the experimental results of Cu2+ and Pb2+ sorption at the flow rates are represented in Figure 2.

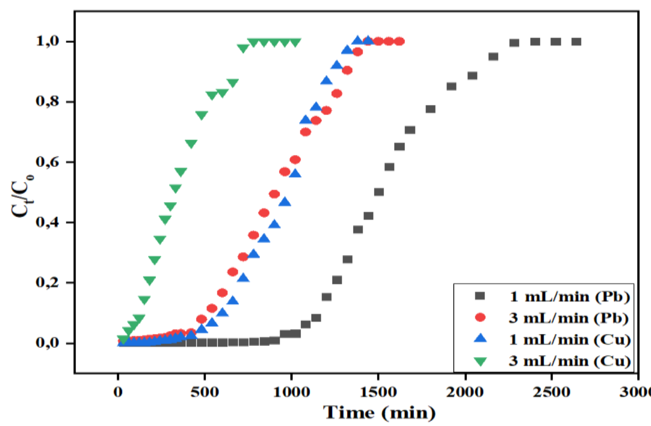

Fig. 2. Effect of flow rate on the breakthrough curve of Cu^{2+} and Pb^{2+} biosorption at different flow rates.

The summary of the breakthrough curve parameters such as; breakthrough adsorption capacity (Q_b), breakthrough exhaustion time (t_e), breakthrough time (t_b), the volume of aqueous solution treated at breakthrough (V_b) and exhaustion time (V_e) were determined and represented in **Table 1** for Cu^{2+} and Pb^{2+} bio-sorption. In this study, the breakthrough time for Cu^{2+} and Pb^{2+} was obtained when the effluent concentration reached 1 mg/L, which is according to the World Health Organization (WHO) and the South African National Standards (SANS) [22].

From **Table 1**, a low flow rate resulted in more processing time to reach the breakthrough and exhaustion points. Therefore, the volume of aqueous solution processed at breakthrough decreased as the flow rate increased while the volume treated at exhaustion increased with the increased flow rate. This trend was observed for Cu^{2+} and Pb^{2+} breakthrough curves. Notably, the breakthrough time for Pb^{2+} at 1 mL/min and 3 mL/min are 928 min and 277 min respectively. This shows a decrease in the breakthrough time

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as the flow rate increases. The breakthrough time for Cu^{2+} however decreased from 360 min to 36 min at flow rates 1 mL/min and 3 mL/min respectively. This is because, at a high flow rate, the residence time reduces which shortens the adsorbate-adsorbent contact time. The volume of the aqueous solution treated at breakthrough decreased for both Cu^{2+} and Pb^{2+} from 0.36 L to 0.108 L for copper and 0.928 L to 0.831 L for the Pb^{2+} at 1 mL/min and 3 mL/min respectively. The bed performance/efficiency decreased with increased flow rate, which can be a result of shortened adsorbent-adsorbate contact time at a high flow rate. The increase in flow rate also gave steeper breakthrough curves, the breakthrough curve shifted closer to the origin. This also shortens the mass transfer zone thus reducing the residence time in the column.

As a result of the reduction in mass transfer zone, the adsorption capacity at the breakthrough point decreased from 7.73 to 6.93 mg/g for Pb^{2+} bio-sorption and 3.00 to 1.90 mg/g for Cu^{2+} bio-sorption at 1 mL/min and 3 mL/min respectively. These results are reasonable and agree with the findings reported in similar studies [21, 23, 24]. Yahya, Abubakar [23] reported that the breakthrough curve formed a steep gradient at a higher flow rate for Cr^{3+} and Cu^{2+}.

TABLE I: SUMMARY OF THE FIXED BED PARAMETERS AT BREAKTHROUGH AND EXHAUSTION POINTS FOR CU^{2+} AND PB^{2+} SORPTION AT DIFFERENT FLOW RATES.

Sorbate	Flow rate (mL/min)	Q_b (mg/g)	Breakthrough time t_b (min)	Volume processed at t_b (L)	Exhaustion Time t_e (min)	Volume processed at t_e (L)
Pb	1	7.73	928	0.928	2160	2.16
	3	6.93	277	0.831	1365	4.10
Cu	1	3.00	360	0.360	1297	1.30
	3	1.90	36	0.108	704	2.11

B. Effect of Bed Height

The effect of bed height is an important operating parameter in the continuous operation of fixed-bed columns. It is highly essential for column design and scale-up. The effect of the bed height investigating the adsorbent performance was conducted at bed heights of 1 cm and 3 cm at an initial concentration of 50 mg/L and flow rate of 3 mL/min. When the bed height is varied in an adsorption process, it means the active sites on the adsorbent and the contact time between the adsorbate and the adsorbent are varied [2]. The breakthrough curve of Cu2+ and Pb2+ bio-sorption at different bed heights is depicted in Figure 3.

The breakthrough capacity (Q_b), breakthrough time (t_b), the exhaustion time (t_e), the volume of aqueous solution treated at breakthrough (V_b), and exhaustion (V_e) times for the bio-sorption of Cu^{2+} and Pb^{2+} in a single solute solution as determined from the breakthrough curves are summarized in **Table 2**. The breakthrough time for both Cu^{2+} and Pb^{2+} increased with an increase in bed height resulting in a similar breakthrough profile. This shows that at a high bed height, there are more active sites available on the surface of the adsorbent, hence resulting in a longer breakthrough time and higher volumes of the aqueous solution being treated at the breakthrough point. The breakthrough time for Pb^{2+} bio-sorption increased from 53 min to 1003 min while it increased from 36 min to 341 min for Cu^{2+} bio-sorption for 1 cm and 3 cm bed height respectively. This is reasonable because a smaller bed height suggests a smaller quantity of adsorbent. An increase in the bed height means the metal ion has additional time to interact with the adsorbent leading to greater uptake of Cu^{2+} and Pb^{2+} in the column.

The adsorption capacity of Cu^{2+} and Pb^{2+} at the breakthrough point increased with an increase of bed height from 2.65 to 16.67 mg/g for Pb^{2+} and 0.75 to 5.68 mg/g for Cu^{2+} at 1 cm and 3 cm bed height respectively. An increase in bed height broadens the mass transfer zone which results in the availability of more sorption sites on the surface of the adsorbent [24]. In addition, when the bed height is increased, the diffusion mass transfer predominates in comparison with the axial dispersion phenomenon. Therefore, a great increase in the breakthrough time was observed. Abdolali, Ngo [21] revealed that a high bed height is more desirable for more active binding sites to be provided and for better performance of a fixed-bed column.

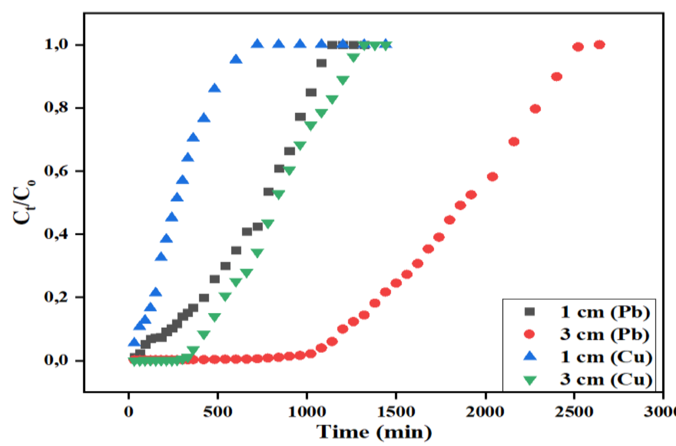

Fig. 3. Effect of bed height on the breakthrough curve of Cu^{2+} and Pb^{2+} adsorption.

TABLE II. SUMMARY OF THE FIXED BED PARAMETERS AT BREAKTHROUGH AND EXHAUSTION POINTS FOR CU^{2+} AND PB^{2+} SORPTION AT DIFFERENT BED HEIGHTS.

Sorbate	Bed height (cm)	Q_b (mg/g)	Breakthrough time t_b (min)	Volume processed at t_b (L)	Exhaustion Time t_e (min)	Volume processed at t_e (L)
Pb	1	2.65	53	0.106	1088	2.18
	3	16.67	1003	2.0	2465	4.93
Cu	1	0.75	15	0.03	600	1.2
	3	5.68	341	0.682	1250	2.5

C. Effect of initial concentration

The effect of initial concentration is an essential operating parameter in a fixed-bed column adsorption study. It helps to determine the adsorption capacity of an adsorbent. The effect of varying initial concentrations of Cu2+ and Pb2+ ions was studied in the range of 10 to 100 mg/L at a constant bed height of 3 cm and flow rate of 3 mL/min. The breakthrough curves are depicted in Figure 4. The breakthrough capacity (Qb), breakthrough time (tb), exhaustion time (te), the volume of aqueous solution treated at breakthrough (Vb), and exhaustion (Ve) times for the bio-sorption of Cu2+ and Pb2+ on the effect of initial concentration as determined from the breakthrough curves are summarized in Table 3.

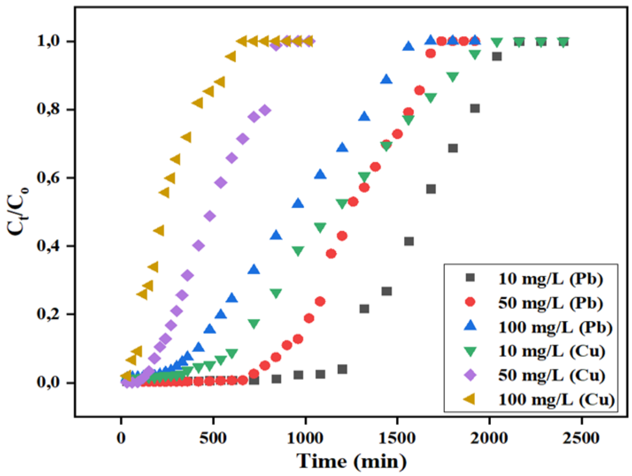

Fig. 4. Effect of initial concentration on the breakthrough curve of Cu^{2+} and Pb^{2+} adsorption.

Observation of Figure 4 shows that orange peels were spent faster at higher inlet concentrations for both Cu^{2+} and Pb^{2+} ions. A preliminary breakthrough point was observed at high concentrations. The breakpoint time of Pb^{2+} was obtained after 1241, 700, and 15 min while it was observed at 616, 129, and 15 min for Cu^{2+} at 10, 50, and 100 mg/L respectively. A decrease in the inlet concentration resulted in a prolonged breakthrough curve, suggesting that a high volume of the aqueous solution is treated. This means a low concentration gradient leads to a lengthened journey through the column due to a reduction in the mass transfer coefficient as indicated by [23]. Specifically, from **Table 3**, the adsorption capacity of copper and lead increased with increasing inlet concentration. For copper, at inlet concentrations of 10, 50, and 100 mg/L the adsorption capacity gave 4.13, 11.67, and 15.83 mg/g while for lead adsorption capacity gave 2.05, 2.15, and 3.83 mg/g respectively. The increase in adsorption capacity at high inlet concentration occurred because of an increase in the solid-liquid phase, a driving force for column adsorption. This will enhance the scale-up when the column is operating at an optimum condition.

TABLE III. SUMMARY OF THE FIXED BED PARAMETERS AT BREAKTHROUGH AND EXHAUSTION POINTS FOR CU^{2+} AND PB^{2+} SORPTION IN SINGLE SOLUTE AT DIFFERENT INITIAL CONCENTRATIONS.

Sorbate	Initial concentration (mg/L)	Q_b (mg/g)	Breakthrough time t_b (min)	Volume processed at t_b (L)	Exhaustion Time t_e (min)	Volume processed at t_e (L)
Pb	10	4.13	1241	2.48	2035	4.07
	50	11.67	700	1.4	1672	3.34
	100	15.83	15	0.95	1520	3.04
Cu	10	2.05	616	1.23	1894	3.79
	50	2.15	129	0.258	828	1.656
	100	3.83	15	0.23	596	1.19

IV. CONCLUSIONS

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 experimental results showed that the performance of the bed was improved with an increase in the 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. Therefore, bio sorbent derived from orange peels is capable of sequestering metal ions (Cu^{2+} and Pb^{2+}) from wastewater.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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