Adsorption of Copper and Lead Ions in a Binary System: Optimization, Equilibrium, and Kinetic Study

Felicia. O Afolabi*[1], Paul. Musonge[1,2] and Babatunde. F. Bakare[3]

Abstract— An ever-increasing industrial effluent disposal to water bodies has made the quest for environmentally friendly treatment methods a priority. Agricultural waste materials have been proven to be efficient for heavy metal sequestration from wastewater. In this paper, the interactive effects of initial concentration, adsorbent dosage, and particle size on the removal of copper and lead ions in a binary system onto orange peels were investigated using a central composite design. The pHPZC of orange peels was determined to be 3.85. The Fourier transform infrared (FTIR) and Energy dispersive x-ray (EDX) revealed the functional groups and elemental composition present on the surface of the bio-sorbent respectively before and after adsorption. The ANOVA showed a good fit with a coefficient of determination (R^2) 0.973 and 0.993 for copper and lead ions respectively. The biosorption of copper and lead increased with increasing adsorbent dosage while the percentage removal of lead was consistently higher than copper. The kinetic and isotherm studies showed that pseudo-second order and Langmuir isotherm models fitted the experimental data suggesting chemisorption and monolayer adsorption respectively.

Keywords— Bio-sorption, Central composite design, Orange peels, Optimization, Wastewater.

I. INTRODUCTION

Copper and lead are toxic elements for plant, animal, human health and are major contaminants in drinking water. These metals are released into water bodies both naturally and via anthropogenic sources such as herbicides in agriculture, mining and industrial activities which are the major causes of surface and groundwater pollution [1]. The remediation of metal-contaminated wastewater generated from anthropological activities needs adequate management actions from designated authorities, however, mitigation technologies are required to control the natural sources of copper and lead. Lead is a carcinogen while copper is not, however, long-term exposure to copper can be very detrimental to life. These toxic metals can cause health problems in humans when ingested such as; skin diseases, nausea, vomiting, diarrhoea and abdominal disorder. Thus, the removal of these metal ions from wastewater is a serious concern for environmental sustainability and human health. The World Health Organization (WHO) and European Union (EU) have set the permissible limit for copper and lead in drinking water at 2 and 0.01 ppm, respectively [2]. In addition, the South African National Standard (SANS) has set the maximum limit for copper and lead in wastewater as 1 mg/L [3]-[4].

The conventional methods used for the removal of toxic metal ions from wastewater include ion exchange, coagulation, precipitation, electrochemical, membrane separation and so on. Among these techniques, adsorption has been proven to be more effective due to its ease of operation, low cost and simple design [5]. Recently, researchers have focused on the use of agricultural wastes as adsorbents for the removal of heavy metals from wastewater. These agricultural wastes also referred to as green adsorbents are readily available, cheap, and eco-friendly. These wastes include shells, hulls and peels from fruits and nuts, sawdust, corncob waste, sunflower stalks, and straw [6].

Citrus is the largest fruit in the world with an annual production of more than 124.3 million tons worldwide. After consumption, about 40 – 60 % of the fruit is discarded as unwanted waste. Yearly, 110 – 120 million tons of citrus waste are generated from citrus processing industries worldwide which create serious environmental challenges [7]. Presently, a huge amount of the wastes is not utilized nor processed but consumed by animals as feed or dumped on site. The citrus waste contains cellulose, hemicellulose with functional groups that enhance the adsorption of heavy metal ions from wastewater. Hence, the utilization of citrus waste as adsorbents will ensure environmental sustainability which is one of the millennium development goals. Citrus waste is, therefore, an inexpensive and sustainable resource biomaterial for laboratory and industrial research. This study is focused on the removal of copper and lead ions in the binary system from wastewater using orange peels by applying the central composite design (CCD) method.

Many physical and chemical factors affect the adsorption process of heavy metals from wastewater which are pH, initial metal ion concentration, temperature, adsorbent dosage, particle size etc. These factors control the overall performance of a bio-sorption process. Many studies have been reported on

Felicia. O Afolabi is with the Institute of Systems Science, Durban University of Technology, Durban, South Africa.

Paul. Musonge is with the Institute of Systems Science, Durban University of Technology, Durban, South Africa and the Faculty of Engineering, Mangosuthu University of Technology, Durban, South Africa.

Babatunde. F. Bakare is with the Department of Chemical Engineering, Mangosuthu University of Technology, Umlazi, Durban, South Africa.

the effect of different operating parameters on the biosorption of heavy metal ions, however, many of the studies have investigated one-factor-at-a-time (OFAT). This method wastes time and materials. In this study, the CCD was used to study the interactive effect of the operating parameters such as initial metal ion concentration, adsorbent dosage and particle size. In addition, many studies have focused on a single solute system, however, it is very rare for wastewater to contain a single metal ion. Even though many studies have been reported on the application of CCD in the field of environmental pollution, the interactive effect of different operating parameters in the binary solute system using CCD is an area of concern.

II. MATERIALS AND METHODS

A. Preparation of bio-sorbent and characterization

Ripened orange peels were collected from a local market in Durban, South Africa. The preparation processes were carried out as discussed by [8]. The Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, Frontier, USA) was used to determine the functional groups present on the surface of the bio-sorbent before and after adsorption. The elemental composition of the bio-sorbent before and after adsorption was determined using energy-dispersive x-ray spectroscopy (EDS) (Oxford X-Max detector and INCA software).

B. Preparation of the synthetic solution

A 1000 mg/L solution containing a mixture of copper and lead was prepared in a volumetric flask by dissolving 3.8 g of $Cu(NO_3)_2.3H_2O$ and 1.6 g $PbNO_3$ in distilled water. The chemicals were of analytical grade purchased from Laboratory Analytical Supplies Limited, South Africa. The desired concentration needed for each experimental run was obtained from the prepared stock solution by dilution. A digital pH meter (edge pH HI 2002, USA) was used to determine the pH value of the solution while 0.1M H_2SO_4 or 0.1M $NaOH$ was added in drops to obtain the desired pH value.

C. Batch adsorption studies

The batch experiments were conducted at room temperature. All experiments were carried out using 250 mL conical flasks containing a 100 mL mixed solution of copper and lead nitrate ions with varying initial concentrations (10-100 mg/L). The adsorbent dosage and the particle size were also varied from $0.1 - 1$ g and 75 - 455 μm respectively. The pH of the solution was maintained at 5 which is the optimum pH obtained for the single solution systems [8]. The solution mixing was achieved using a linear shaker (Orbital shaker 262) with an agitation speed of 180 rpm and contact time of 120 min. After adsorption, the supernatant portion of the solution was filtered using Whatman paper and syringe filters of 0.45 μm. Thereafter, the samples were analyzed using a micro-plasma atomic emission spectrophotometer (MP-AES, MY 18379001, Agilent, USA). The percentage removal of the metal ions in the solution and the quantities of metal ions adsorbed onto orange peels were calculated using equations (1) and (2) respectively.

$$\% \, Removal = \frac{(C_0 - C_e)}{C_0} * 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_e)}{m}V \quad (2)$$

Where, C_0 and C_e are the initial and final concertation (mg/L) respectively, q_t is the amount of metal ion adsorbed (mg/g), M and V are the mass of the adsorbent (g) and the volume of the solution (mL) respectively.

D. Bio-sorption equilibrium

An adsorption isotherm study is one of the methods of comparing the amount of metal ion adsorbed during the adsorption process. Langmuir and Freundlich isotherm models are suitable for predicting the experimental equilibrium parameters of a bio-sorption process and these models are mostly used by researchers [9].
The Langmuir isotherm model assumes that the surface of the bio-sorbent is homogenous, and bio-sorption occurs in a single surface layer. The bio-sorption process is uniform, and the active sites are equal [10]. The model equation is expressed in Equation (3).

$$q_e = \frac{q_{max}bC_e}{1 + bC_e} \quad (3)$$

Where, q_{max} is the bio-sorption capacity (mg/g) and b is the Langmuir isotherm constant (L/mg). the dimensionless factor R_L expression is presented in Equation (4). The value of R_L is used to determine whether the bio-sorption process is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), or irreversible ($R_L = 0$) [11].

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

The Freundlich isotherm assumes the surface of the bio-sorbent is heterogeneous and the surface-active site energy of the bio-sorbent is different [12]. The Freundlich isotherm is presented in Equation (5).

$$q_e = K_f C_e^{1/n} \quad (5)$$

Where, K_f (mg/g) and n are the Freundlich constants. The value of n suggests the bio-sorption condition. The values n<1, the bio-sorption process is insignificant, n>1 bio-sorption process is significant and n=1 indicates the bio-sorption process is linear [13].

The adsorption kinetic study explains the adsorption reaction with time at the solid-solution interface. The two most popular adsorption kinetic models; pseudo-first order and pseudo-second order models are used in this study. The pseudo-first order model expression is given below:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (6)$$

The pseudo-second order model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

Where q_e and q_t (mg/g) are the quantity of metal ions adsorbed at equilibrium and at any time t. K_1 and K_2 are the pseudo-first order (min^{-1}) and pseudo-second order (g mg^{-1} min^{-1}) rate constant respectively and t is the contact time (min).

E. Central composite design (CCD)

The design expert software (11.1.0.1) was used to generate the statistical design of the experimental runs. The experimental design was done using face centred CCD adapted from the RSM using three factors at three levels (-1, 0, +1) and six centre points or replicate runs for the operating parameters. The three operating parameters selected for the biosorption of copper and lead ions ions in binary solute system onto orange peels are; initial metal ion concentration, adsorbent dosage and particle size at specified factor levels (Table 1). The CCD generated a total of 20 experimental runs with six replicates using face centred design. In the optimization study, the second-order polynomial equation was used to explain the interactive effects of the independent variables. The quadratic model used to optimize the process variables is shown below.

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j + \varepsilon \qquad (8)$$

where Y is the predicted response, X_i and X_j are the independent variables, β_0, β_i, β_{ii}, and β_{ij} are the regression coefficient and ε is the residual error. The interpretation of the experimental results and the significant variables are explained using mathematical functions called the analysis of variance (ANOVA).

TABLE 1
OPERATING PARAMETERS, RANGES, AND LEVELS.

Parameters	Factor	Range and level		
		-1	0	+1
Initial concentration	X_1	10	55	100
Adsorbent dosage	X_2	0.1	0.55	1
Particle size	X_3	75	265	455

III. RESULTS AND DISCUSSION

A. Point of zero charge of orange peels (pHPZC)

The point of zero charges (pHPZC) is a surface property usually investigated to determine the potential of a bio-sorbent for the removal of metal ions from an aqueous solution. The point of zero charges of an adsorbent is the point at which the surface of the adsorbent has zero net charges [14]. The pHPZC of an adsorbent gives insight into the ionization potential and the interactive effect between the adsorbent surface and the adsorbate. When the pHPZC is less than the solution pH, adsorption of cations is favoured and when the pHPZC is greater than the solution pH, the adsorption of anions is favoured. In Figure 1, the pHPZC of natural orange peels gave 3.85. This means that the surfaces of orange peels are acidic and therefore favour the adsorption of cations.
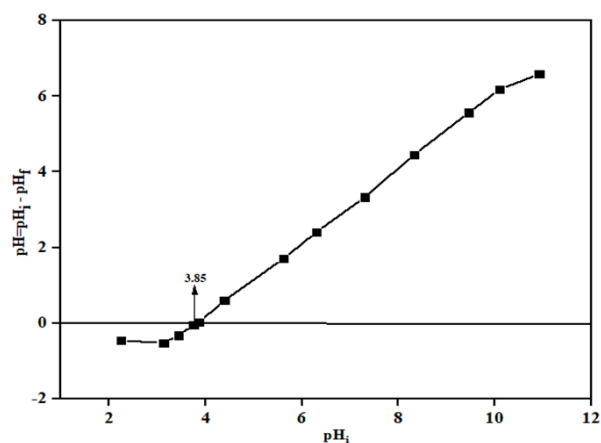

Fig. 1 Point of zero charges (pHPZC) of orange peels.

B. FTIR spectroscopy analysis

The FTIR spectrum is used to identify the functional groups present on the surface of an adsorbent. Adsorption is a physical phenomenon that involves the interaction between the functional groups on the surface of a bio-sorbent and the metal ions in an aqueous solution. These functional groups provide active sites for the adsorption of the metal ions on the surface of the adsorbent. The FTIR spectra represented in Figure 2 shows the functional groups present on the surface of orange peels before adsorption. The FTIR of natural orange peels were obtained within the range of 500 to 4000 cm-1 wavenumber.

The spectra of orange peels before and after adsorption show the presence of a broad peak at 3382.62 cm-1, which indicates the presence of an intermolecular bonded O-H group consisting of alcohols and phenols. The peaks at 2918.92 cm-1, 2850.97 cm-1, 1441.94cm-1, 1374.74 cm-1 and 887.26 cm-1 indicate the presence of a saturated C-H substitution bond which can be likened to alkanes that are available in the pulp. The peaks at 1734.38 cm-1 and 1607.04 cm-1 reveal the presence of the carboxylic C=O bond and the unsaturated C=C bond respectively which are attributed to aldehydes and ketones. The existence of a high quantity of hydroxyl and carboxyl groups on the surface of the bio-sorbent suggest the

tendency of orange peels to adsorb positively charged metal ions. The presence of these functional groups plays an important role in the bio-sorption of heavy metals through ion exchange which occurs as a result of the affinity of metal ions to the functional groups.

A comparison of FTIR spectra of orange peels before and after adsorption is represented in Figure 2. All four patterns look similar which suggest that the same functional groups are present on the surface of the bio-sorbent before and after adsorption. However, there are significant shifts in the peaks and intensities of the spectrum. These shifts are attributed to the interaction between the functional groups present on the surface of the bio-sorbent and the copper and lead ions in the solution. The significant shift occurred after adsorption in the peaks representing the O-H and C-O-H stretching which are peculiar to the adsorption of both copper and lead. This shows that hydroxyl and carboxyl groups played a major role in the adsorption of copper and lead.
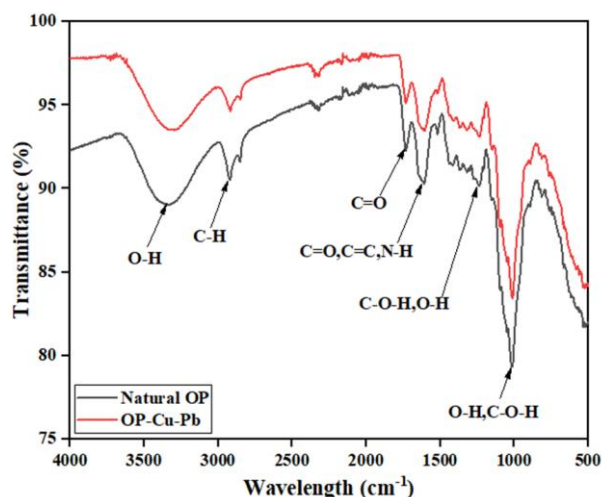

Fig. 2 FTIR spectroscopy of natural orange peels before and after adsorption.

C. Energy dispersive x-ray

The EDX analysis of orange peels bio-sorbent before and after adsorption is shown in Figures 3a and b respectively. Figure 3a reveals the chemical composition of orange peel bio-sorbent, the surface indicated the presence of carbon, oxygen, magnesium, sulphur, potassium, and calcium. The EDX spectra of orange peels after adsorption of copper and lead

ions in a binary system is shown in Figures 3b. The EDX spectra of orange peel loaded with copper and lead ions in a binary system indicates the presence of only carbon and hydrogen with Cu and Pb peaks. It is apparent that all other elements except carbon and hydrogen disappeared and were replaced with Cu and Pb. The percentage composition of Pb adsorbed on the surface of orange peel is more than Cu which suggests that orange peel bio-sorbent has more affinity for copper and lead ions.
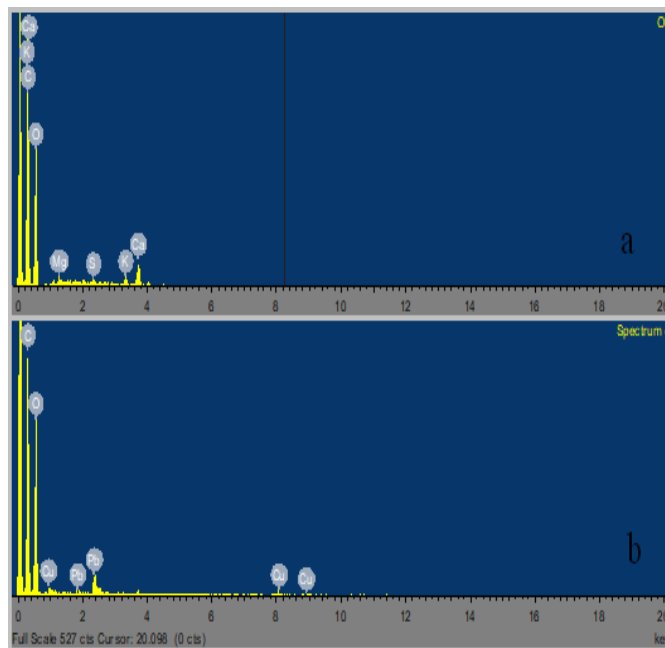

Fig. 3 EDX spectra of orange peels (a) before adsorption (b) after adsorption of Cu ad Pb.

D. Experimental design

The experimental design matrix for the biosorption of copper and lead ions onto orange peels is presented in Table 2 with the predicted and experimental responses. The second-order polynomial Equation 6 with multiple regression analysis was used to generate the responses (percentage removal of copper and lead ions) using the three design factors.

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TABLE II
CCD EXPERIMENTAL MATRIX AD RESPONSES OF LEADAND COPPER IONS REMOVAL ONTO ORANGE PEELS.

Std	Run	Initial Conc. (mg/L)	Adsorbent dosage (g)	Particle size (µm)	Responses			
					Lead % removal		Copper % removal	
					Exp	Pred	Exp	Pred
15	1	55	0.55	265	83.75	83.93	72.89	71.48
5	2	10	0.1	455	80.34	80.56	59.1	59.06
2	3	100	0.1	75	62.07	61.95	79.5	78.69
17	4	55	0.55	265	82.86	83.93	70.17	71.48
12	5	55	1	265	90.47	91.18	85.06	86.65
4	6	100	1	75	88.12	88.04	84.72	84.77
6	7	100	0.1	455	70.86	71.13	59.95	60.57
20	8	55	0.55	265	84.15	83.93	73.72	71.48
9	9	10	0.55	265	90.12	88.88	72.82	70.86
3	10	10	1	75	98.85	98.71	86.2	85.60
16	11	55	0.55	265	84.45	83.93	72.1	71.48
1	12	10	0.1	75	77.97	78.86	68.98	70.76
19	13	55	0.55	265	83.21	83.93	69.65	71.48
8	14	100	1	455	84.78	84.03	82.65	80.89
18	15	55	0.55	265	84.05	83.93	70.25	71.48
10	16	100	0.55	265	78.15	78.83	69.29	71.19
14	17	55	0.55	455	81.75	81.75	65.98	66.34
13	18	55	0.55	75	83.45	82.90	74.55	74.13
11	19	55	0.1	265	76.06	74.80	70.53	68.98
7	20	10	1	455	86.95	87.21	87.32	88.14

The quadratic regression model showing the model parameters generated for the responses; percentage removal of lead (Y_1) and percentage removal of copper (Y_2) written for coded factors as a function of initial concentration (A), adsorbent dosage (B) and the particle size (C) are represented in Equations 9 and 10 respectively.

$$Y_1(Pb) = 83.93 - 5.03A + 8.19B - 0.578C + 1.56AB + 1.87AC - 3.3BC - 0.0709A^2 - 0.9409B^2$$
$$- 1.61C^2 \qquad (9)$$

$$Y_2(Cu) = 71.48 + 0.169A + 8.79B - 3.89C - 2.19AB - 1.61AC + 3.56BC - 0.4577A^2$$
$$+ 6.28B^2 - 1.25C^2 \qquad (10)$$

Model equations 7 and 8 comprise three main effects (A, B, C), three interactive effects (AB, AC, BC) and three quadratic effects (A^2, B^2, C^2). The order of the interactive factors to increase the percentage removal of lead is AC > AB > BC while for percentage removal of copper is BC > AC > AB.

E. Analysis of variance (ANOVA) for the models

The regression models were evaluated using ANOVA to determine the significant factors that fitted well with the models as presented in Tables 3 and 4. The ANOVA helps to identify the factors that had no significant influence on the model and the adsorption process. The models gave a 95 % confidence level, 5 % significance level and a degree of freedom of 9. All the model features; the sum of squares, F-values (Fisher variation ratio), P-values, adequate precision and the lack of fit values were acceptable and show the significance of the models. The P-values of less than 0.05 shows that the regression model terms are highly significant.

The P-values of the regression models representing percentage removal of lead and copper ions gave <0.0001 which implies that the regression model equation fitted well with the experimental data. The lack of fit value greater than 0.05 signifies that the models have one or more terms that have no significant influence on the regression models because of pure error or noise. However, such terms were included in the model to justify the parent terms and the interactive behaviour. In the case of percentage removal of lead, the significant model parameters are initial concertation A, adsorbent dosage B, interactive terms (AB, AC, BC) and quadratic term C^2 while particle size C, quadratic terms (A^2 and B^2) are not significant. The significant model parameters for the percentage removal of copper are adsorbent dosage B and particle size C which have a first-order main effect, interactive terms (AB, AC, BC), and quadratic term B^2 while initial concentration A and quadratic terms (A^2, and C^2) are not significant.

The overall performance of the models was evaluated based on the regression coefficient of determination R^2, the adjusted R^2 and the predicted R^2. The R^2 helps to ascertain the closeness of the experimental values to the predicted values which range from 0 to 1, where 0 denotes no correlation between the data. The R^2 obtained for the regression models were found to be close to 1, which implies a good fit between the experimental and the predicted data as represented in Figure 4. The predicted R^2 and the adjusted R^2 for the regression models of lead and copper ions are in reasonable agreement with a difference of less than 0.2, which validates the significance of the models. The R^2 values for the models were found to be 0.9927 and 0.9725 for percentage lead removal and percentage copper ions removal respectively. The adequate precision of the models, which is a measure of the signal to noise ratio, was desirable for a ratio greater than 4.

TABLE III
ANOVA FOR % PB REMOVAL USING ORANGE PEELS

Source	Sum of squares	df	Mean square	F-value	P-value Prob>F	Comments
Pb Model	1088.25	9	120.92	151.21	< 0.0001	Significant
A-Initial concentration	252.51	1	252.51	315.76	< 0.0001	
B-Adsorbent dosage	670.27	1	670.27	838.17	< 0.0001	
C-Particle size	3.34	1	3.34	4.18	0.0682	
AB	19.47	1	19.47	24.35	0.0006	
AC	28.05	1	28.05	35.08	0.0001	
BC	87.12	1	87.12	108.94	< 0.0001	
A²	0.0138	1	0.0138	0.0173	0.8980	
B²	2.43	1	2.43	3.04	0.1116	
C²	7.09	1	7.09	8.87	0.0139	
Residual	8.00	10	0.7997			
Lack of Fit	6.17	5	1.23	3.39	0.1034	not significant
Pure Error	1.82	5	0.3647			
Cor Total	1096.25	19				
Std. Dev. 0.8942	**R² 0.9927**	**Adjusted R² 0.9861**	**Predicted R² 0.9483**	**Adeq. Precision 58.15**	**Mean 82.62**	**C. V. % 1.08**

TABLE IV
ANOVA FOR % CU REMOVAL USING ORANGE PEELS.

| Source	Sum of squares	df	Mean square	F-value	P-value Prob>F	Comments
Cu Model	1230.20	9	136.69	39.32	< 0.0001	significant
A-Initial concentration	0.2856	1	0.2856	0.0822	0.7802	
B-Adsorbent dosage	772.47	1	772.47	222.22	< 0.0001	
C-Particle size	151.71	1	151.71	43.64	< 0.0001	
AB	38.37	1	38.37	11.04	0.0077	
AC	20.67	1	20.67	5.95	0.0349	
BC	101.39	1	101.39	29.17	0.0003	
A²	0.5762	1	0.5762	0.1658	0.6925	
B²	108.53	1	108.53	31.22	0.0002	
C²	4.28	1	4.28	1.23	0.2931	
Residual	34.76	10	3.48			
Lack of Fit	20.79	5	4.16	1.49	0.3365	not significant
Pure Error	13.97	5	2.79			
Cor Total	1264.96	19				
Std. Dev. 1.86	**R² 0.9725**	**Adjusted R² 0.9478**	**Predicted R² 0.7934**	**Adeq. Precision 22.06**	**Mean 73.77**	**C. V. % 2.53**
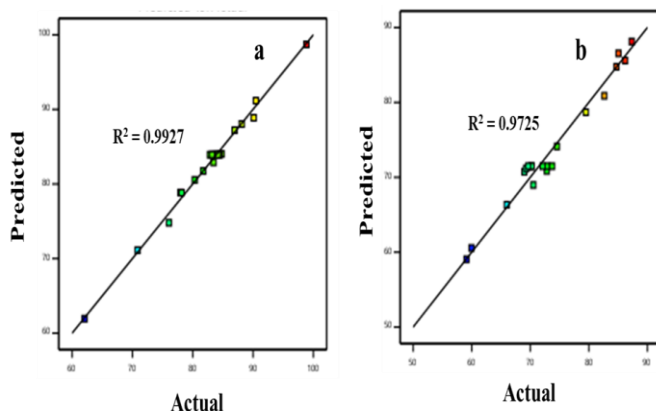
Fig. 4 Graph showing actual (%) vs predicted (%) removal percentages for (a) Pb ad (b) Cu

F. 3D representation of the interactive effects on the responses

The graphical representation of the interactive effects of the model parameters on each of the responses is shown in 3D plots depicted in Figure 5a-c. The surface plots were generated by writing code using MATLAB (MATLAB R2019a). Figure 5a shows the interaction between initial concentration and adsorbent dosage with the percentage removal of lead and copper ions. The bio-sorption capacity of lead increased with increasing adsorbent dosage while an increase in the initial concentration had no significant changes on the adsorption capacity. This suggests that the surface of the bio-sorbent has reached the saturation point. In the case of the percentage removal of copper, the initial concentration and the adsorbent dosage increased with increasing percentage removal. The percentage removal of lead and copper increased with the increasing dosage of orange peels. This result is reasonable because a little amount of bio-sorbent relates to a small active site, since the surface of the bio-sorbent is acidic more active sites must be occupied for proton metal ion competition.

Figure 5b shows the interactive effect of initial concentration and particle size on the percentage removal of lead and copper. The highest bio-sorption capacity of lead was obtained at the initial concentration of 10 mg/L, while the particle size had no significant changes in the adsorption process. On the contrary, the percentage removal of copper increased with increasing initial concentration and particle size.

Figure 5c depicts the interaction between the adsorbent dosage and the particle size on the percentage removal of lead and copper. The bio-sorption capacity of lead and copper ions increased with increasing adsorbent dosage while the particle size had little effect on the adsorption efficiency of the metal ions. The intersection of the two graphs shows that the maximum percentage removal of lead and copper ions in the binary system was reached with a particle size of 75 μm. This result is significant because smaller particle sizes have a larger surface area and enhance adsorption capacity than bigger particle sizes. Furthermore, Figure 5a-c showed that the percentage removal of lead was higher than copper with all the interactions which are because of reactivity of lead than copper

[15]. Hence, lead ions were more adsorbed in the binary system than copper ions, as represented in Table 2. In conclusion, adsorbent dosage had the highest influence on the percentage removal of lead and copper ions in the binary system followed by the initial concentration while particle size had little or no significant effect.
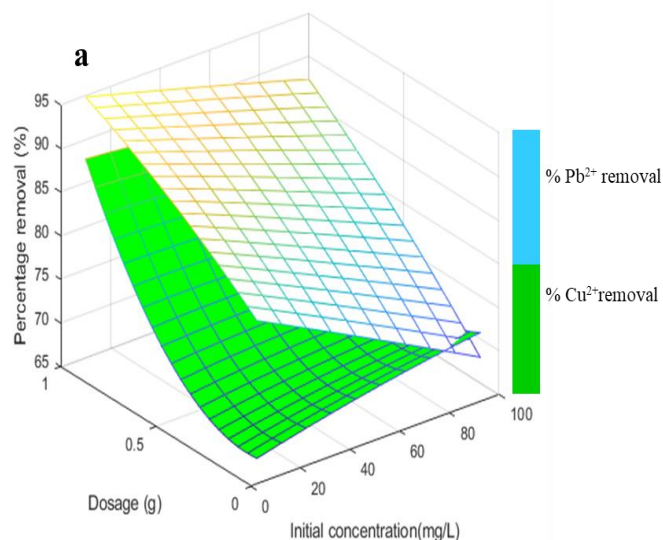

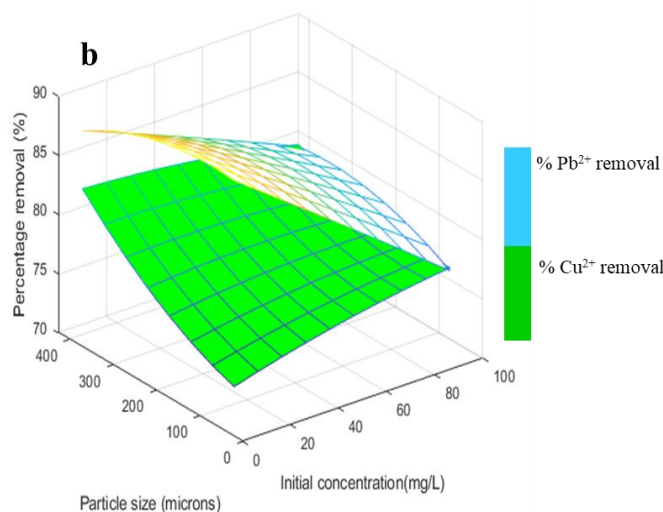Fig. 5a 3D surface plot of %Cu and %Pb with interactive effect of initial concentration and dosage.

Fig. 5b 3D surface plot of %Cu and %Pb with interactive effect of initial concentration and particle size.
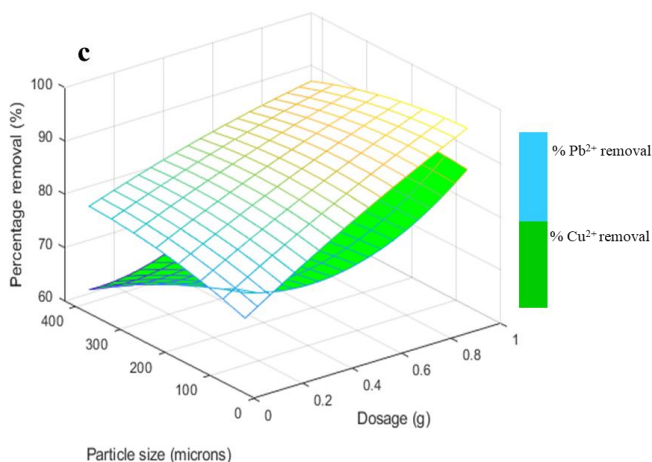
Fig. 5c 3D surface plot of %Cu and %Pb with the interactive effect of dosage and particle size.

The goal of optimization is to obtain the optimal values for the operating parameters involved in a process. The purpose is to maximize the percentage removal of the metal ions to achieve the highest removal. The desirability of the solution is used to evaluate the suitability of the optimum condition obtained. The optimization also helps to determine the performance and capacity of the adsorbent in the binary solute system. The optimized variable condition for the biosorption of copper and lead ions in the binary system using orange peels gave 92.039 % and 86.77 % removal for lead and copper ions respectively, with an initial concentration of 100 mg/L, an adsorbent dosage of 1 g and particle size of 75 µm. The desirability of the solution gave 0.895 which signifies that the optimum condition is reasonably acceptable.

G.Mechanism of adsorption of copper and lead ions

The biosorption uptake of copper and lead ions onto orange peels were achieved by the combination of the operating parameters. The functional groups identified on the surface of orange peels played a significant role in the biosorption process. The major shifts in the peaks representing -COOH and -OH after adsorption of copper and lead confirmed ion exchange as the adsorption mechanism. These functional groups become deprotonated at a solution pH higher than the pHPZC of the bio-sorbent which favours adsorption uptake of cations. In addition, the displacement of the metals present on the surface of orange peels after adsorption (Fig. 3), also revealed ion exchange as the adsorption mechanism responsible for the biosorption of copper and lead ions in a binary system using orange peels.

IV. EQUILIBRIUM STUDY

The adsorption process experimental data of copper and lead onto orange peels were fitted with Langmuir and Freundlich isotherm models. A very important guide to determining the best isotherm is to fit the experimental data with different isotherm models for estimation and then compare the correlation coefficient (R^2) values obtained [16].
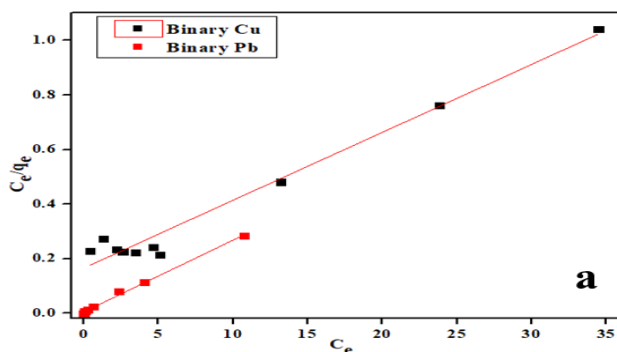

Fig. 6a Langmuir isotherm of copper and lead onto orange peels in the binary system at pH 5. The symbols are the experimental results while the solid lines are the linear fittings.
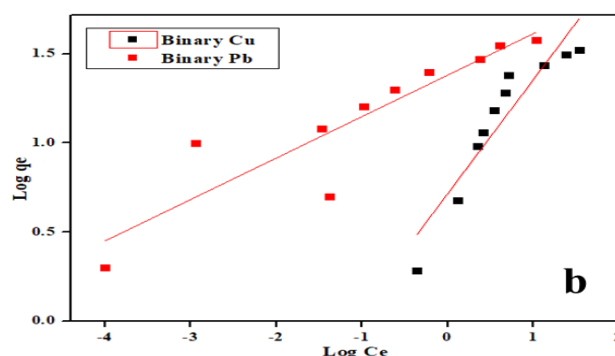

Fig. 6b Freundlich isotherm of copper and lead onto orange peels in the binary system at pH 5. The symbols are the experimental results while the solid lines are the linear fittings.

The Langmuir isotherm model is a semi-empirical model that explains the adsorption mechanism based on the assumption that the surface of the bio-sorbent is energetically homogenous and adsorption energy is uniform for all sites [17]. The isotherm studies were performed with a fixed amount of bio-sorbent but varying initial concentrations. The quantity adsorbed for the binary adsorption system of lead and copper ions using orange peels is presented in Table 5.

TABLE V
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS

Ion	System	Langmuir				Freundlich		
		b (L/mg)	q_m (mg/g)	R^2	R_L	K_f	n	R^2
Cu^{2+}	Binary	0.15	38.18	0.98 8	0.4	5.19	1.5 6	0.93 4
Pb^{2+}	Binary	0.77	40.05	0.99 8	0.0 2	24.0 6	4.2 9	0.89 8

Figure 6a shows the experimental data for the adsorption isotherm of copper and lead ions in the binary system as well as the linear fits for the Langmuir isotherm model. The adsorption of copper and lead increased with increasing initial metal ion concentrations. The Langmuir isotherm constant "b" is higher for lead (0.77 L/mg) than copper (0.15 L/mg), which

buttress the fact that lead was more adsorbed than copper. In addition, the quantity adsorbed of lead was higher than copper. Therefore, lead has a higher affinity for the active sites on the surface of orange peels. Comparing the correlation coefficient R^2 value for Langmuir and Freundlich isotherm models (Table 5), it is obvious that Langmuir isotherm fitted the experimental data well for both copper and lead with values of R^2 very close to 1. Another important characteristic of the Langmuir isotherm model can be represented by a dimensionless factor R_L, also known as the separation factor. This is used to determine the adsorption behaviour of the bio-sorbent as presented in Table 5. The separation factor, R_L for the adsorption of lead and copper in binary system onto orange peels fall within the range of $0<R_L<1$, which implies that the adsorption process is favourable within the concentration range studied. Hence, the orange peel is efficient for the adsorption of lead and copper ions from aqueous solutions.

The Freundlich isotherm assumes the surface of an adsorbent is heterogeneous and adsorption energy is exponentially distributed [18]. Figure 6b represents the plot of the experimental data and the Freundlich isotherm linear fit of lead and copper. The parameters K_f and n are the Freundlich isotherm constants describing the adsorption capacity and intensity, respectively. The measure of the exponent 'n' explains the adsorbent – sorbent phenomenon capacity and favorability [19]. Table 5 shows the values of n and the interpretation. The Freundlich isotherm constant "n" which evaluates the adsorption intensity of the metal ions was determined to be greater than 1 and in the range $1 < n < 10$ for lead and copper in the binary system. This shows that the adsorption process is favourable and highly chemisorption. This implies there exist great bonds between the adsorbent and the adsorbate because of the chemisorption reactions.

V. KINETIC STUDY

The kinetic study of lead and copper onto orange peels in binary systems with the effect of time at different initial concentrations (10, 55 and 100 mg/L) were investigated using the linearized pseudo-first and pseudo-second order model. The calculated constant parameters obtained from the pseudo-first order and pseudo-second order linear models using orange peels are presented in Table 6. The effect of time on different initial concentrations was studied in the binary system containing copper and lead. Figure 7a represents the plot of $\log(q_e - q_t)$ against t for the binary system of copper and lead using orange peels. The correlation coefficient (R^2) for the binary solute copper and lead pseudo-first order model was in the range 0.762 to 0.958. The pseudo-second order model showed that the quantity of lead adsorbed is higher than copper for all the initial concentrations. The pseudo-second order constant K_2 value for lead was higher than copper signifying adsorption of copper is negatively affected in the coexistence of lead. The correlation coefficient for the pseudo-second order was observed to be very close to 1 for copper

and lead at the different initial concentrations, which suggests that the adsorption rate is chemically controlled. Figure 7b shows the graph representing the linear form of the pseudo-second order model of copper and lead in a binary system using orange peels. It can be observed that the graph started from the origin, indicating the good fit of the model.

TABLE VI
PSEUDO-FIRST-ORDER MODEL PARAMETERS FOR THE ADSORPTION OF COPPER AND LEAD USING ORANGE PEELS.

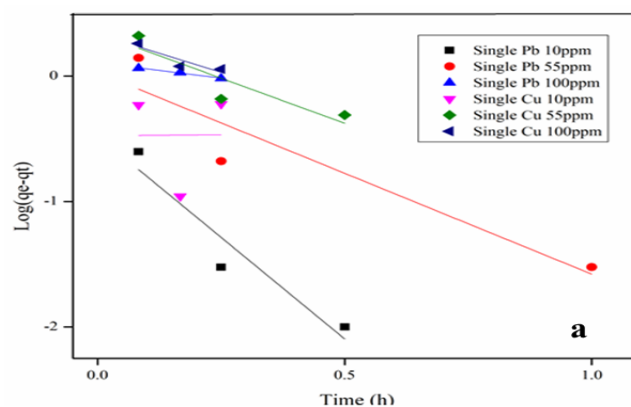| Metal ion concentration		Cu			Pb		
		10 mg/L	55 mg/L	100 mg/L	10 mg/L	55 mg/L	100 mg/L
Pseudo-first order	Binary						
q_e		6.83E6	465.27	2087.37	0.05	14.72	2.18
K_1		48.96	6.96	10.59	8.83	11.06	0.33
R^2		0.958	0.762	0.897	0.970	0.891	0.924
Pseudo-second order	Binary						
q_e		42.48	9.49	13.39	3.82	15.96	17.09
K_2		0.02	0.44	0.04	10.71	0.55	0.30
R^2		0.999	0.999	0.999	1.000	0.999	0.999

Fig. 7a Pseudo-first-order model graph of binary copper and lead at different initial concentrations.
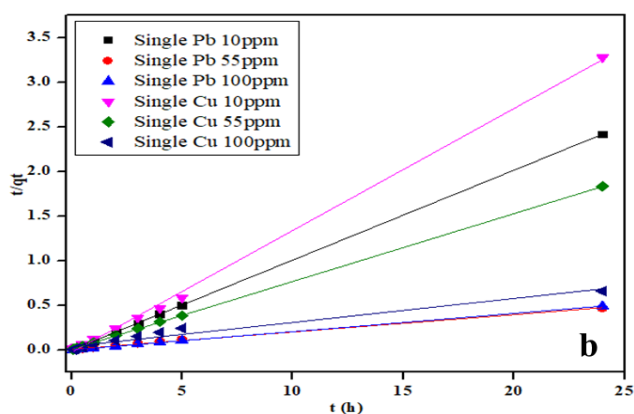
Fig. 7b Pseudo-second-order model graph of binary copper and lead at different initial concentrations.

VI. COMPARISON OF COPPER AND LEAD IONS ADSORPTION CAPACITY USING ORANGE PEELS WITH OTHER BIO-SORBENTS

The maximum uptake of copper and lead ions in binary solution is 38.18 mg/g and 40.05 mg/g respectively. The adsorption uptake of lead was higher than copper which implies that orange peels have a higher affinity for lead than copper. The maximum uptake of the metal ions obtained in this study is compared with other results reported using bio-sorbents as presented in Table 7.

TABLE VII
COMPARISON OF CU2+ AND PB2+ IONS UPTAKE CAPACITY WITH OTHER BIO-SORBENTS.

Bio-sorbent	Cu^{2+} uptake (mg/g)	Pb^{2+} uptake (mg/g)	Reference
Orange peels	38.18	40.05	This study
Mango plant	22.51	24.4	[20]
Banana peels	28	7.97	[21]
Fumaria Indica	6.62	9.15	[22]
Banana peels	29.26	39.32	[23]
Cabbage waste	12.96	61.27	[18]
Orange peels	33.99		[24]
Orange peels	16.64		[25]
Orange peels	31.79		[26]

VII. CONCLUSION

The adsorption of copper and lead in a binary system from an aqueous solution using orange peels as a low-cost bio-sorbent was experimentally investigated in a batch mode. The interactive effect of the operating parameters such as initial metal concertation, adsorbent dosage and particle size was examined using CCD. The adsorption capacity of lead was consistently higher than copper in all the experimental runs. The percentage removal increased with an increasing adsorbent dosage which is attributed to the increase in the active sites available on the surface of the bio-sorbent. The adsorption of copper and lead occurred at a pH higher than the pHPZC of orange peels which is 3.85. This reveals that the adsorption of cation is favoured at pH > pHPZC of the

adsorbent. The EDX analysis also showed that potassium, magnesium, and calcium disappeared on the surface of the bio-sorbent after adsorption. Hence, ion exchange is confirmed as the adsorption mechanism for the biosorption of copper and lead.

The equilibrium and kinetic experimental results fitted well with Langmuir and pseudo-second order models respectively. This suggests that adsorption occurred on monolayer and the adsorption process is highly chemisorption. Overall, this study suggests that orange peels is an efficient and inexpensive adsorbent suitable for the removal of copper and lead from wastewater in a bi-solute system.

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