

Competitive effects of Pb^{2+} and Cu^{2+} ions Removal from Binary System Using Apple Pomace

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Abstract—Water scarcity remains a global concern, driven by both quantity and quality challenges. One major contributor to water pollution is the discharge of heavy metal-laden wastewater into natural water bodies, often above acceptable limits, complicating treatment processes. Pb^{2+} and Cu^{2+} ions are amongst hazardous pollutants of major concern due to their toxicity, persistence and bioaccumulative nature. Therefore, this study investigates the potential of apple pomace as a biosorbent for the simultaneous removal of Cu^{2+} and Pb^{2+} ions from wastewater. The biosorbent was characterized before and after adsorption using Fourier Transform Infrared Spectroscopy (FT-IR) and Energy Dispersive X-ray (EDX). A Central Composite Design (CCD) within the framework of Response Surface Methodology (RSM) was employed to design the experiments with metal ion concentration ranging from 1-50 mg/L, adsorbent dosages from 0.1-1 g, particle sizes of 1-425 μm and a fixed pH of 5.5. Results revealed significant removal efficiency for both metal ions, with some Pb^{2+} and Cu^{2+} removal exceeding 90 %, at low initial concentrations. However, competitive interactions were observed, with Pb^{2+} ions exhibiting a significant suppressive effect on the adsorption of Cu^{2+} ions. The adsorption behaviour for both metal ions was best described by a quadratic model, with R^2 values above 0.9, indicating good model reliability. This study highlights the necessity of investigating multi-metal adsorption systems for realistic wastewater treatment applications.

Keywords—Wastewater, heavy metals, adsorption, apple pomace, competitive, Response Surface Methodology

I. INTRODUCTION

The rising global population has driven the expansion of industries and domestic activities, which has resulted in the generation of water polluted with various heavy metal [1-3]. Conventional treatment facilities were not fully designed to handle the excessive heavy metals being generated. Hence, as a result, some of the effluents are discharged, often exceeding the environmental thresholds set by responsible boards, which include the Environmental Protection Agency (EPA), World Health Organization (WHO) among others. Pb^{2+} and Cu^{2+} ions are amongst hazardous pollutants of major concern due to

their toxicity, persistence, and biocummulative nature [3-5]. The accumulation of Pb^{2+} and Cu^{2+} ions in the human body has a lot of negative impacts, which include affection of the reproductive system, damage to the central nervous system, and impairment of physical and mental functions, particularly in children, among other effects. [3, 5-9]. Most conventional treatment technologies such as chemical precipitation and membrane filtration, are often costly, energy-intensive, and generate large volumes of sludge [8, 10]. Consequently, attention has shifted toward biosorption as an environmentally friendly and cost-effective alternative for metal remediation. In water treatment, biosorption is a process whereby biomass adsorbents, e.g., agricultural wastes, are used for the remediation of wastewater [11]. Various adsorption studies have been conducted using various adsorbents; but however, most predominant studies focus on single solute metal solutions in isolation, while in practical situations, heavy metals coexist in varying concentrations and are not necessarily equimolar [12]. It is important to note that the individual behaviour of metals in a single solute is different from that in a multi-solute; this is because of the different affinities of the metal ions for the active site due to the differences in sizes of the atomic radius, among others [13]. When multiple species are present together in a system, they express competitive effects, where they compete for the same adsorption sites on the surface of an adsorbent [14]. This competition frequently results in reduction in adsorption rate for the competing molecule, a phenomenon known as the antagonistic effect. The molecule with more competitiveness or stronger attraction for the surface will preferentially adsorb [15]. These circumstances frequently lead to alterations and shifts in adsorption isotherms. Factors that determine the level of development of the antagonistic forces include the nature of adsorbates; when the adsorbates are chemically similar or have comparable physical properties, such as size, charge, or polarity. Also, if the adsorbent surface is heterogeneous, the antagonistic effects can be more complex. Coexistence can also result in synergetic effects, where one element promotes the adsorption of another on an adsorbent surface resulting in increased adsorption capacity. These can be achieved through the forming of hydrogen bonds, Van Der Waals forces, or electrostatic attractions between adsorbates. The novelty of this study lies in the application of apple pomace, an agrowaste that is underutilized, yet it is abundant and an

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environmental concern since it decomposes quickly, producing leachates that contaminate the soil and groundwater. In this process, methane, a greenhouse gas, is also released into the atmosphere, contributing to global warming. [5, 9, 16, 17]. It carries various functional groups; hence, it has enormous potential as a sustainable biosorbent for the removal of Pb^{2+} and Cu^{2+} ions from wastewater [8, 16, 18-20]. This work uniquely investigates the competitive and interactive effects among other process parameters, with particular emphasis on the competition between Cu^{2+} and Pb^{2+} ions, while also considering the influence of other operational variables. Beyond technical relevance, this work promotes sustainable wastewater treatment; it addresses SDG 6, clean water and sanitation. The study also captures SDG 12 of responsible consumption and production, as it seeks to valorise agricultural waste. Approximately 12 metric tons of apple pomace are produced annually worldwide [21].

II. MATERIALS AND METHODS

A. Preparation of biosorbent

Fresh apple pomace was sourced from Elgin Fruit Juices (Pty) Ltd in Cape Town, South Africa, and it oven-dried on-site at 110 °C for 24 h to minimize its high moisture content, temperature aligns with the mostly used range in literature [3]. The dried pomace was then transported to Durban, where it was re-dried at 60 °C to eliminate any residual moisture that might have accumulated during transportation. The dried material then underwent size reduction using a laboratory grinder followed by sieving into distinct particle size ranges. Next, the adsorbent was characterised before and after adsorption to determine its surface chemistry and the elements present.

B. Methodology

RSM was employed to investigate and model the interactive effects of critical process variables on the adsorption efficiency for the binary solute system of Pb^{2+} and Cu^{2+} ions. The response surface refers to the relationship between the response and one or more factors under investigation [22]. Design of experiments (DOE) was employed using design expert 13 software under the central composite face-centred design (CCFD) with four variables: Initial Concentration of Pb^{2+} (1 to 50 mg/L), initial concentration of Cu^{2+} (1 to 50 mg/L), adsorbent dosage (0.1 to 1 g), particle (1 to 425 μm) at 3 different levels namely -1, 0, and +1, and with 3 central points, yielding a total of 27 experimental runs for single solute systems. The matrix produced consisted of two response variables, Pb^{2+} and Cu^{2+} removal efficiencies, in percentage (%). CCFD guarantees reliable prediction of curvature effects and rotatability across the experimental design space [23]. To ensure both experimental feasibility and literature alignment, the independent variables and their associated values were established from early batch experiments and confined within ranges routinely reported for biosorption systems in literature. Model adequacy and statistical significance were rigorously evaluated using analysis of variance (ANOVA), together with the coefficients

of determination (R^2 , adjusted R^2 , and predicted R^2) to assess the goodness-of-fit, explanatory power, and predictive capability of the developed models. The investigation was conducted at a fixed pH of 5.5, which is within the ideal optimum range as shown by other studies in the literature, usually at high pH (≈ 6 or higher) the metals tend to precipitate into hydroxides [5, 6, 12, 17, 20, 24].

Equation (1) presents the formula for computing the removal (%) of the heavy metals.

$$\text{Percentage removal (\%)} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

Where C_i represents initial adsorbate concentration (mg/L), C_f denotes the final adsorbate concentration (mg/L)

III. RESULTS AND DISCUSSION

A. FT-IR analysis

FT-IR spectroscopy was employed to identify the surface functional groups of the apple pomace adsorbent and to evaluate their potential alterations after adsorption. The spectra were acquired using a Cary 630 FT-IR spectrometer (Agilent Technologies, USA) fitted with an attenuated total reflectance (ATR) accessory. The analytical process involved positioning approximately 15 mg of each sample directly onto the ATR crystal and secured using a pressure clamp to guarantee optimal spectrum acquisition. Spectra were obtained throughout the wavenumber range of 4000-500 cm^{-1} at a spectral resolution of 4 cm^{-1} , averaging 32 scans to enhance the signal-to-noise ratio. The FT-IR spectrums (**Figure 1**) prior to adsorption exhibited multiple significant peaks, indicating the presence of active functional groups on the biosorbent surface. The peaks observed in the range of 3000 to 3600 cm^{-1} and around 1000 cm^{-1} correspond to -OH stretching vibrations. A peak between 2800 and 3000 cm^{-1} signifies C-H stretching in aliphatic chains, while the region between 1400 and 1700 cm^{-1} was associated with -C=O, -NH, and -C=C groups. Post-adsorption, significant shifts and alterations in transmittance intensity were detected in these locations, signifying interactions between metal ions and surface functional groups. Upward shifts in peak positions and spectral changes suggested that the identified functional groups actively participated in the binding of Pb^{2+} and Cu^{2+} ions. The existence of negatively charged functional groups like the hydroxyl and carboxylic groups points to the conclusion that the adsorption of both Pb^{2+} and Cu^{2+} ions in both systems occurred primarily through ion exchange, whereby Pb^{2+} ions substitute other native cations (Ca^{2+} , K^{+} , or H^{+}) present on the surface of the adsorbent. This will be verified through EDX analysis in the subsequent section. Additionally, hydrogen bonding and Van der Waals forces have potential to contribute to the Pb^{2+} and Cu^{2+} retention through the involvement of oxygen and hydrogen containing groups.

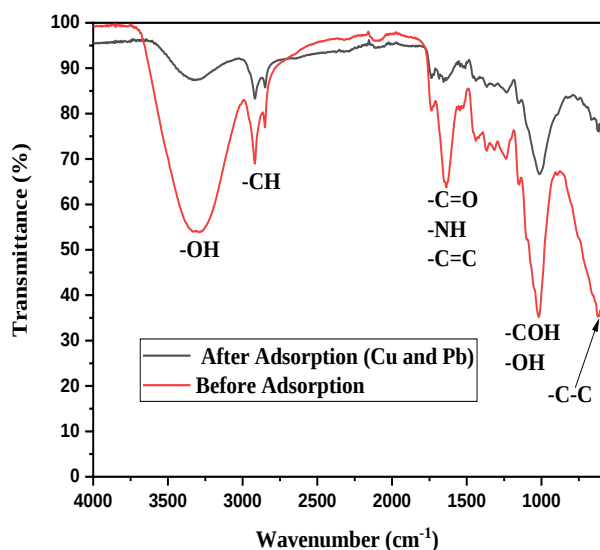


Fig. 1: FT-IR spectrum: apple pomace (before and after adsorption)

B. EDX analysis results

Formal quantitative evidence of the dominating adsorption process and qualitative confirmation of the uptake of Pb^{2+} and Cu^{2+} ions, together with the elemental composition assessment of the biosorbent was comprehensively conducted using Oxford X-Max EDX detector (UK) before and after adsorption. The EDX spectrum of the Apple Pomace before adsorption confirms that the adsorbent is predominantly organic, with the highest wt.% attributed to Carbon (C) at 63.89 wt. % and Oxygen (O) at 35.73 wt. %. These elements confirm the lignocellulosic nature of the biomass. The native exchangeable ions, native inorganic species, namely Potassium (K) and Calcium (Ca) were identified to present at 0.30 wt. % and 0.07 wt. % respectively. The potential of an adsorption process through ion exchange is strongly suggested by the presence of these mobile ions, which can be involved in the exchange with the heavy metal ions.

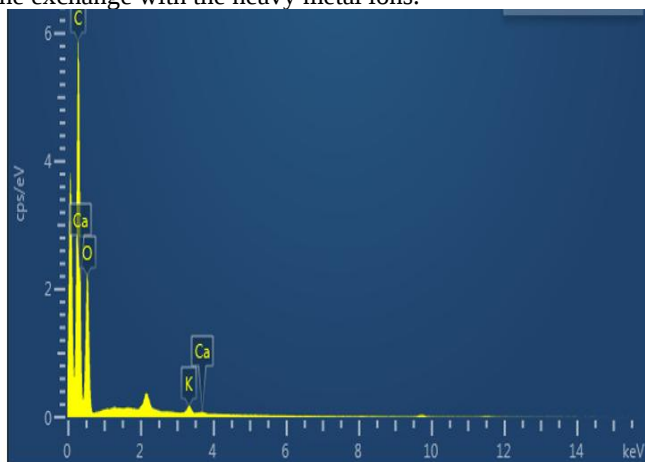


Fig. 2: FT-IR spectrum: apple pomace before adsorption

The analysis following the adsorption process indicates that Pb^{2+} and Cu^{2+} ions were successfully adsorbed onto the biosorbent surface, with loadings of 1.74 wt.% and 1.34 wt.% respectively. This adsorption resulted in a noticeable shift in the elemental composition presented in **Table 1**. The reduction in carbon content (62.65 wt.%) and the increase in oxygen content (34.28 wt.%) further demonstrate that apple pomace interacted with Pb^{2+} and Cu^{2+} ions through its carboxylic and hydroxyl groups. In conclusion, it can be reported that the biosorbent surface exhibited signs of ion exchange, evidenced by the absence of potassium and calcium after adsorption, which coincided with the appearance of Pb^{2+} and Cu^{2+} ions, suggesting an ion exchange adsorption mechanism. Figure 2 and 3 illustrates the EDX spectra recorded before and after adsorption.

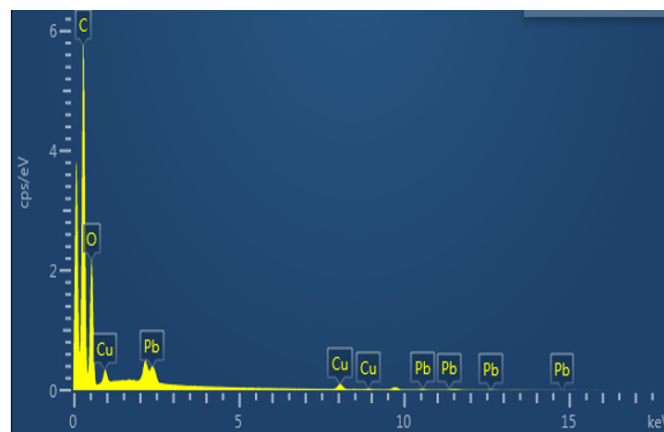


Fig. 3: FT-IR spectrum: apple pomace after adsorption

TABLE 1: APPLE POMACE ELEMENTALLY COMPOSITION BEFORE AND AFTER ADSORPTION

Element	Wt% Before Adsorption	Wt% After Adsorption
C	66.63	62.65
O	32.25	34.28
K	1.12	0
Cu	0	1.34
Pb	0	1.74
Total	100	100

IV. RESPONSE SURFACE METHODOLOGY RESULTS

This section outlines the results derived from the Response Surface Methodology (RSM) applied to the binary mixture of Cu^{2+} and Pb^{2+} ions, with the matrix encompassing all variables and responses displayed in Table 2 below. Analysis of variance (ANOVA) confirmed that the quadratic models developed for Cu^{2+} and Pb^{2+} removal were statistically significant, with Model F-values of 30.34 and 47.96, respectively ($p < 0.0001$).

TABLE II: CCFD EXPERIMENTAL MATRIX FOR BINARY MIXTURE OF Cu^{2+} AND Pb^{2+} IONS AND RESPONSES

		A:	B:	C:	D:	Pb²⁺	Pb²⁺	Cu²⁺	Cu²⁺
	Std	Run	Initial	Initial	Adsorbent	Particle	Removal	Removal	Removal
			Cu²⁺	Pb²⁺	Dosage	size	Exp	Predicted	Exp
			Conc	Conc					Pred
			mg/L	mg/L	g	mg/L	%	%	%
	19	1	25,5	1	0,55	250	86,98	85,80	78,9
	3	2	1	50	0,1	75	53,09	51,83	41,9
	22	3	25,5	25,5	1	250	79	76,58	69
	13	4	1	1	1	425	92,5	91,99	90,23
	7	5	1	50	1	75	84,9	83,72	77,06
	24	6	25,5	25,5	0,55	425	70,61	68,04	65,1
	8	7	50	50	1	75	66,98	67,97	56
	27	8	25,5	25,5	0,55	250	75,26	74,35	66,9
	23	9	25,5	25,5	0,55	75	74,01	77,06	70,04
	15	10	1	50	1	425	78,12	76,20	77,06
	21	11	25,5	25,5	0,1	250	39,40	42,30	28,08
	20	12	25,5	50	0,55	250	69,10	70,76	61,47
	5	13	1	1	1	75	95,24	99,90	90,31
	9	14	1	1	0,1	425	55,99	56,19	47,90
	26	15	25,5	25,5	0,55	250	72,26	74,35	75,58
	11	16	1	50	0,1	425	36,21	39,57	31,25
	16	17	50	50	1	425	59,98	62,58	51,14
	6	18	50	1	1	75	86,10	81,43	83,14
	17	19	1	25,5	0,55	250	83,27	83,82	76,09
	14	20	50	1	1	425	73,19	75,64	75,58
	10	21	50	1	0,1	425	39,10	38,97	28,04
	2	22	50	1	0,1	75	46,40	49,50	37,28
	18	23	50	25,5	0,55	250	67,40	67,33	56,22
	4	24	50	50	0,1	75	36,01	35,21	29,52
	1	25	1	1	0,1	75	72,75	68,84	64,18
	25	26	25,5	25,5	0,55	250	76,98	74,35	68,16
	12	27	50	50	0,1	425	28,55	25,08	22,28
									17,36

The linear effects of initial Cu^{2+} concentration (A), initial Pb^{2+} concentration (B), adsorbent dosage (C), particle size (D), and the quadratic term of adsorbent dosage (C^2) were significant ($p < 0.05$), indicating that these parameters exerted the most substantial influence on metal removal efficiency. In contrast, the interaction and remaining quadratic terms were

insignificant, suggesting minimal synergistic effects among factors. The non-significant Lack of Fit F-values (1.14 for Cu^{2+} and 2.60 for Pb^{2+}) demonstrated that the models adequately represented the experimental data without large systematic deviation. The ANOVA results for both Pb^{2+} and Cu^{2+} ions are shown in Table 3 and 4 respectively

TABLE III: ANOVA FOR THE QUADRATIC MODEL (Cu²⁺ IONS)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8949,87	14	639,28	47,96	< 0,0001	Significant
A-Initial Cu Concentration	1222,72	1	1222,72	91,73	< 0,0001	
B-Initial Pb Concentration	1017,32	1	1017,32	76,32	< 0,0001	
C-Adsorbent Dosage	5287,48	1	5287,48	396,68	< 0,0001	
D-Particle size	366,51	1	366,51	27,50	0,0002	
AB	7,42	1	7,42	0,5566	0,4700	
AC	0,7578	1	0,7578	0,0569	0,8156	
AD	4,51	1	4,51	0,3382	0,5716	
BC	0,6995	1	0,6995	0,0525	0,8227	
BD	0,1560	1	0,1560	0,0117	0,9156	
CD	22,48	1	22,48	1,69	0,2185	
A ²	3,84	1	3,84	0,2881	0,6013	
B ²	39,70	1	39,70	2,98	0,1100	
C ²	571,72	1	571,72	42,89	< 0,0001	
D ²	8,36	1	8,36	0,6271	0,4438	
Residual	159,95	12	13,33			
Lack of Fit	148,53	10	14,85	2,60	0,3095	not significant
Pure Error	11,42	2	5,71			
Cor Total	9109,82	26				

The high determination coefficients ($R^2 = 0.9824$ for Pb²⁺ and $R^2 = 0.9725$ for Cu²⁺) confirm the model's robustness and predictive accuracy, demonstrating that the quadratic model effectively encapsulates the experimental data, **Table 5**. The quadratic regression models developed for the removal of Pb²⁺ (**Y_{Pb}**) and Cu²⁺ (**Y_{Cu}**) ions are presented in Equations (2) and (3), respectively.

TABLE V: FIT STATISTICS FOR Pb²⁺ AND Cu²⁺ IONS ADSORPTION

R ²	Adjusted R ²	Predicted R ²	Std. Dev.	Mean	C.V. %	Adeq Precision
0.9824	0.9620	0.8758	3.65	66.64	5.48	27.49
0.9725	0.9405	0.822	4.95	59.94	8.26	21.21

$$Y_{Pb} = 74.35 - 8.24A - 7.52B + 17.14C - 4.51D - 14.91C^2 \quad (2)$$

$$Y_{Cu} = 67.33 - 8.71A - 8.22B + 18.84C - 3.38D - 17.34C^2 \quad (3)$$

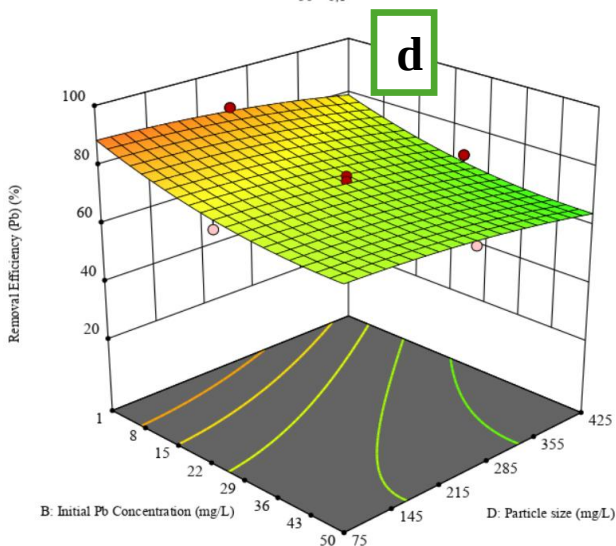
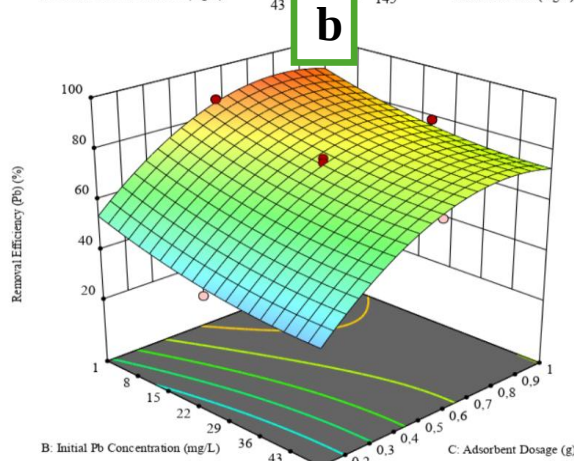
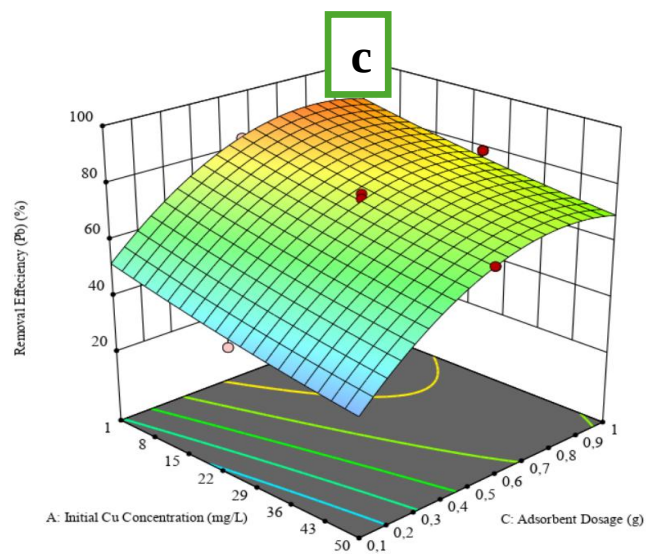
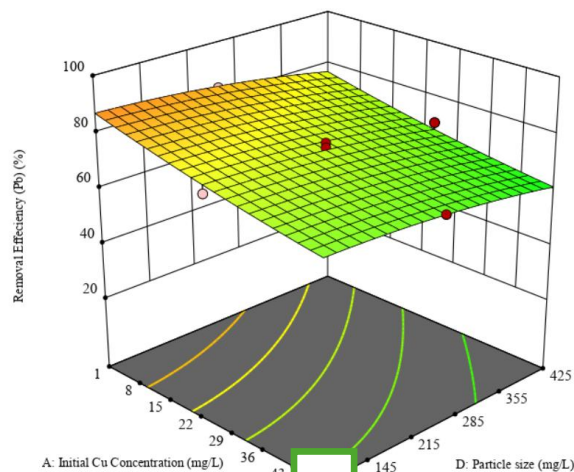
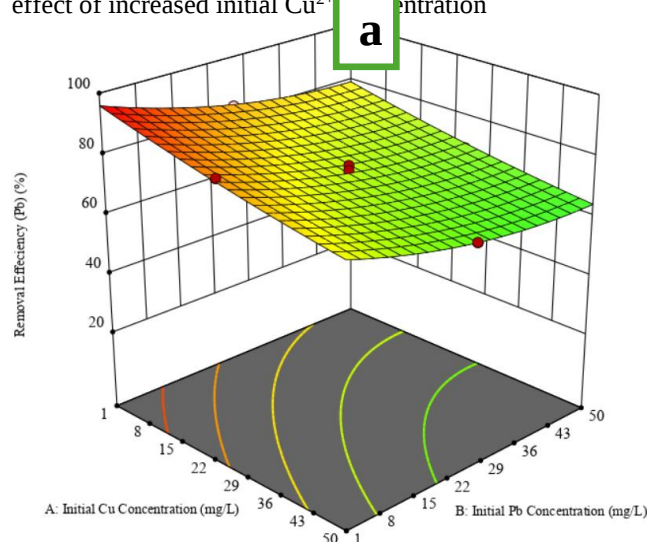
TABLE IV: ANOVA FOR THE QUADRATIC MODEL Pb²⁺ IONS

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	10416,81	14	744,06	30,34	< 0,0001	Significant
A-Initial Cu Concentration	1365,81	1	1365,81	55,70	< 0,0001	
B-Initial Pb Concentration	1214,94	1	1214,94	49,54	< 0,0001	
C-Adsorbent Dosage	6387,58	1	6387,58	260,48	< 0,0001	
D-Particle size	205,69	1	205,69	8,39	0,0134	
AB	0,0040	1	0,0040	0,0002	0,9901	
AC	0,0298	1	0,0298	0,0012	0,9727	
AD	0,2237	1	0,2237	0,0091	0,9255	
BC	40,83	1	40,83	1,66	0,2213	
BD	6,77	1	6,77	0,2762	0,6088	
CD	59,67	1	59,67	2,43	0,1448	
A ²	0,1920	1	0,1920	0,0078	0,9310	
B ²	47,62	1	47,62	1,94	0,1887	
C ²	773,39	1	773,39	31,54	0,0001	
D ²	7,33	1	7,33	0,2989	0,5946	
Residual	294,26	12	24,52			
Lack of Fit	250,18	10	25,02	1,14	0,5558	not significant
Pure Error	44,08	2	22,04			
Cor Total	10711,08	26				

V. INTERACTIVE EFFECTS OF PARAMETERS

The 3D response surface plots, generated through RSM, illustrate the complex interplay between different operational parameters on the binary adsorption efficiency of Cu²⁺ and Pb²⁺ ions using apple pomace. Each response (Cu²⁺ or Pb²⁺ removal) has six 3D surface plots which demonstrate the simultaneous variation of two independent parameters while other two parameters are held constant at their centre-point values. Firstly, the effect of parameters on the Cu²⁺ removal was assessed. **Figure 4a** on the effect of initial Cu²⁺ Concentration versus initial Pb²⁺ concentration proves that increasing the initial Cu²⁺ concentration generally decreases Cu²⁺ removal due to the saturation of available binding sites on the apple pomace. Crucially, an increase in the initial Pb²⁺ concentration also leads to a reduction in Cu²⁺ removal. This is a direct manifestation of the competitive adsorption effect. Pb²⁺ ions compete with Cu²⁺ ions for the same active sites. Given the typically higher affinity of biomaterials for Pb²⁺ compared to Cu²⁺ (often due to smaller ionic radius/higher electronegativity difference leading to stronger complexation), this competition is significant. The steepest decline in Cu²⁺

removal at high Pb^{2+} suggests that Pb^{2+} preferentially occupies the binding sites. In **Figure 4b**, assessing effect of initial Cu^{2+} concentration against adsorbent dosage, as expected, increasing the adsorbent dosage (apple pomace) significantly enhances Cu^{2+} removal. A higher dosage provides a greater number of available binding sites, overcoming the negative effect of increased initial Cu^{2+} concentration



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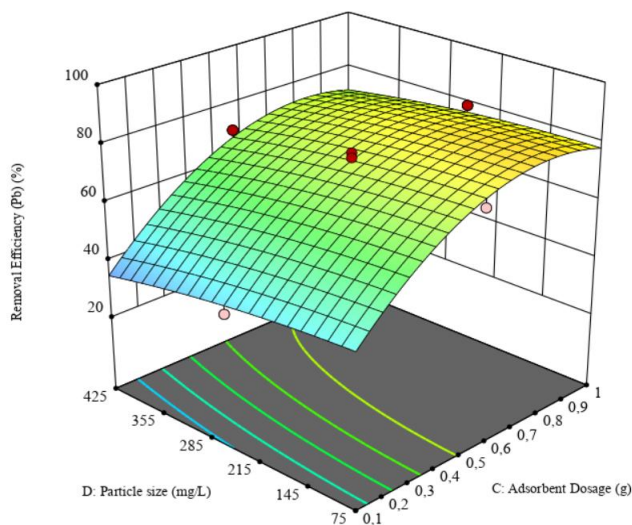
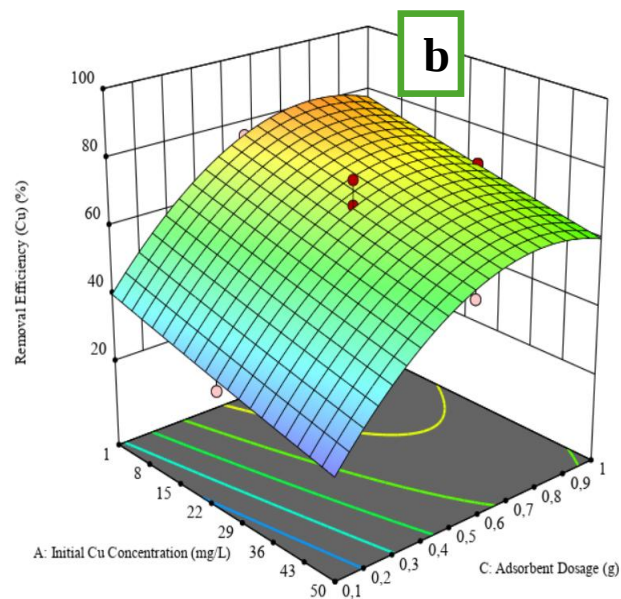
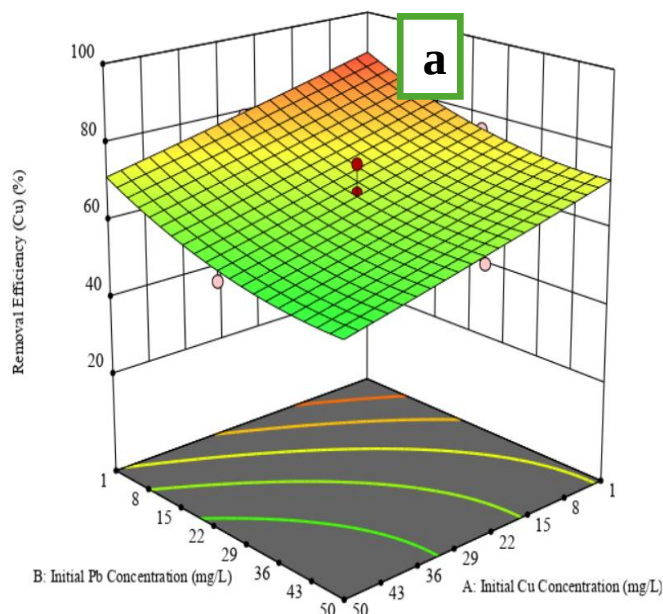


Fig. 4: Interactive effect on Pb^{2+} ions adsorption

The optimal Cu^{2+} removal is achieved at a low initial Cu^{2+} concentration and a high adsorbent dosage, where the concentration gradient is minimized, and the binding sites are in large excess relative to the metal ions. The red peak in the surface plot clearly delineates this optimal region. On analysis the effect of adsorbent dosage against initial Pb^{2+} concentration on Cu^{2+} removal efficiency (**Figure 4d**). This plot provides the clearest visual evidence of the binary system interaction. Cu^{2+} is maximized at high adsorbent dosage (due to site availability) and low initial Pb^{2+} concentration (to minimize competitive hindrance). The surface shows a saddle-like shape or a gradient that slopes steeply downwards as Pb^{2+} concentration increases, even at high adsorbent dosage. This suggests that while increasing the adsorbent dosage mitigates the total adsorption capacity constraint, it is less effective at high Pb^{2+} concentrations because the highly competitive Pb^{2+} ions occupy the newly introduced sites, still suppressing Cu^{2+} uptake, this is consistent with reported literature [25]. The elimination of Cu^{2+} was significantly influenced by particle size and its initial concentration. Adsorption efficiency improves with smaller particle size and lower initial Cu^{2+} concentrations, as smaller particles provide more surface area for adsorption. Furthermore, at lower concentrations, competition for the restricted active sites is decreased, hence increasing removal efficiency (**Figure 4e**). **Figure 4f** depicts the influence of adsorbent dose on the removal of Cu^{2+} ions. Removal efficiency is constrained at low doses due to an inadequate number of accessible active sites. Increase in adsorbent dose, the increases availability of adsorption sites which results in an increase in Cu^{2+} ions removal. However, beyond an optimal dosage, a further increase can lead to a decline or plateau in removal efficiency, likely due to particle agglomeration, which reduces the effective surface area and hinders mass transfer [26, 27]. Furthermore, the removal of Cu^{2+} is marginally impacted by particle size, with smaller particles often showing marginally greater removal efficiencies because of their larger specific surface area.



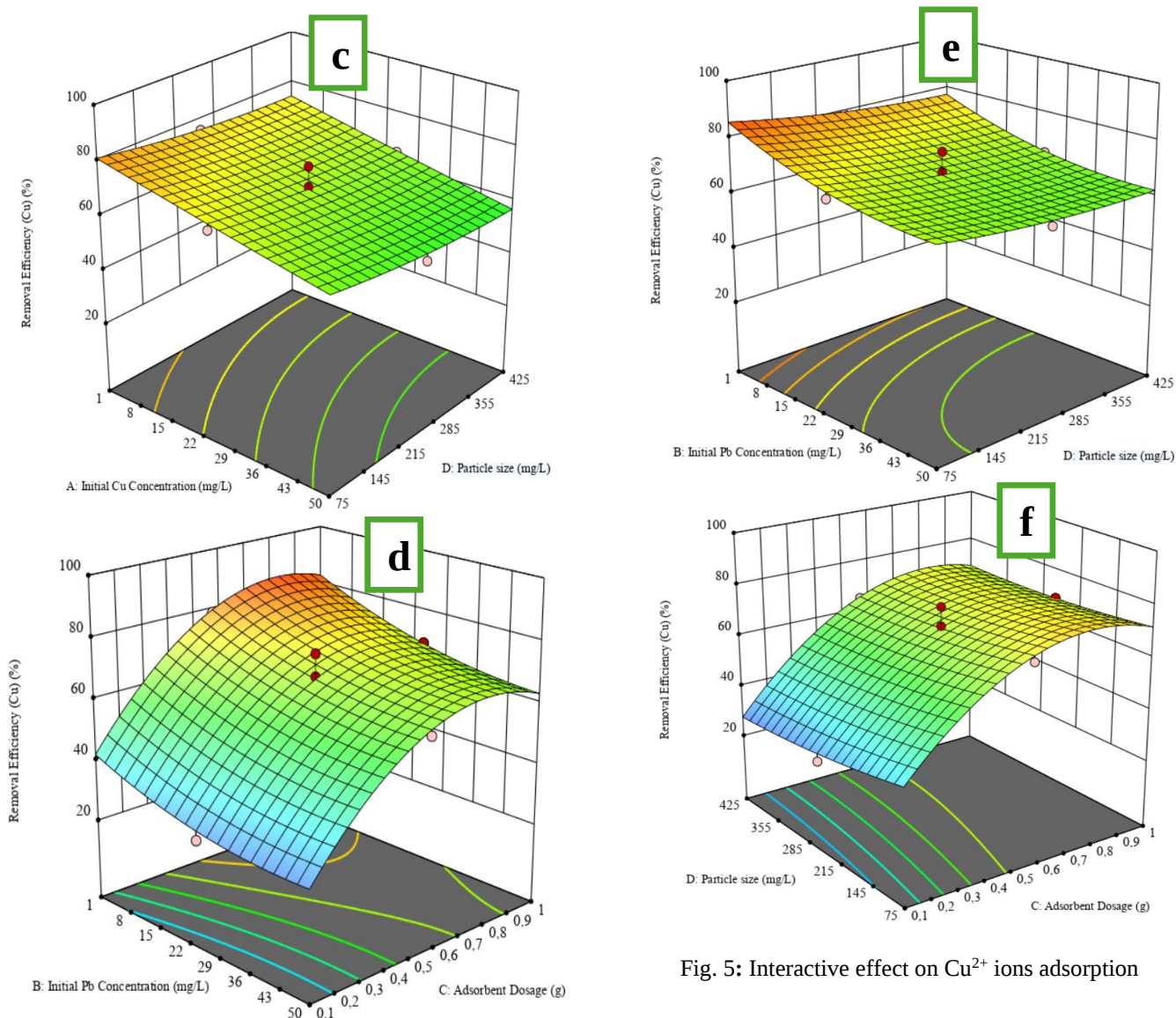
Fig. 5: Interactive effect on Cu^{2+} ions adsorption

Figure 5 also displays the 3D surface plots for analysing the interactive effects of parameters, for Pb^{2+} ions removal. This section shows the effect of the same operational parameters on the Pb^{2+} removal efficiency. Effect of initial Pb^{2+} concentration against the initial Cu^{2+} ions concentration (**Figure 5a**) shows that increasing the initial Pb^{2+} concentration likely decreases Pb^{2+} removal due to site saturation. The effect of the Cu^{2+} concentration on Pb^{2+} removal is less pronounced than the reverse, consistent with research indicating that Pb^{2+} ions preferentially adsorb [13]. This observation is a hallmark of selective adsorption. If the binding affinity of apple pomace for Pb^{2+} is significantly higher than for Cu^{2+} , the presence of Cu^{2+} only moderately reduces Pb^{2+} . The surface slope is gentler along the Cu^{2+} concentration axis compared to the Pb^{2+} concentration axis. This selective behaviour confirms that Pb^{2+} is the preferred adsorbate. The investigation of the effect of adsorbent dosage and initial Cu^{2+} concentration (**Figure 5d**) on Pb^{2+} removal shows that removal is further maximized at high adsorbent dosage and low Pb^{2+} concentration (same as discussed for Cu^{2+} removal). Crucially, this plot helps quantify the impact of the less competitive ion (Cu^{2+}) on the more competitive ion

(Pb²⁺). The relatively high Pb²⁺ removal (**Figure 5a**) maintained even at high Cu²⁺ concentrations (for a given optimal dosage) further strengthen the conclusion that apple pomace has a strong selectivity for Pb²⁺ over Cu²⁺ ions. The rest of the factors have effects that are like those seen with Cu²⁺ removal, as shown in **Figures 5e** and **5f**. Overall, the interactive surface plots unequivocally demonstrate that the binary adsorption of Pb²⁺ and Cu²⁺ onto apple pomace is governed by a noticeable competitive inhibition, primarily driven by the superior affinity and selectivity of the biosorbent for Pb²⁺ ions.

VI. CONCLUSIONS AND RECOMMENDATIONS

First key finding is on the selectivity that exists between the two heavy metals, the removal efficiency of Cu²⁺ is far more sensitive to an increase in the initial Pb²⁺ concentration than the Pb²⁺ removal efficiency is to an increase in the initial Cu²⁺ concentration. This empirical evidence validates a Pb²⁺ >> Cu²⁺ selectivity order, likely attributed to the hard/soft acid/base (HSAB) principle or the superior complexation ability of Pb²⁺ with the carboxylic and hydroxyl groups prevalent in the pectin and cellulose of apple pomace. Another key finding is that achieving maximum simultaneous removal requires a compromise: a high adsorbent dosage to minimize site competition and low initial concentrations of the respective competitive ion (Pb²⁺ for Cu²⁺ removal, and to a lesser extent, Cu²⁺ for Pb²⁺ removal). The high determination coefficients ($R^2 = 0.9824$ for Pb²⁺ and $R^2 = 0.9725$ for Cu²⁺) confirm the model's robustness and predictive accuracy, demonstrating that the quadratic model effectively encapsulates the experimental data. Under optimized conditions, both systems achieved removal efficiencies exceeding 90% at low initial metal ion concentrations, with Pb²⁺ exhibiting a marginally higher removal than Cu²⁺. Pragmatic wastewater applications require understanding the competing and synergistic impacts of various metal concentrations, as a rapid increase in specific heavy metal ion levels in wastewater systems may substantially influence the adsorption process. Future research should examine the kinetics and isotherms in competitive systems to ascertain whether competition influences the reaction rate and to elucidate the related adsorption mechanisms. For practical application, column studies under dynamic flow should be performed to validate process performance, alongside regeneration assessments to determine reusability. Advanced modelling and optimization techniques are also recommended to refine process predictability and scalability. Future research should also incorporate a technoeconomic evaluation of utilizing apple pomace as an adsorbent for wastewater cleanup, alongside a comparative analysis with alternative adsorbents. Overall, apple pomace demonstrates significant potential as a sustainable biosorbent for heavy metal remediation, offering both environmental and economic benefit.

ACKNOWLEDGMENT

The authors express their gratitude to Durban University of Technology (DUT) for offering the resources necessary for this research. We also acknowledge Elgin Pvt Ltd for supplying apple pomace, which served as the adsorbent. Finally, we express our gratitude to the Lord God Almighty for His direction and wisdom during this research period.

REFERENCES

- [1] Z. A. Gadooa and M. N. Abbas, "Review: Mathematical Modelling of Heavy Metals Removal from Petroleum Refinery Wastewater," *Journal of Engineering and Sustainable Development*, vol. 25, no. Special, pp. 3-31-3-42, 2021, doi: 10.31272/jeasd.conf.2.3.3.
- [2] M. A. B. Abdullah et al., "Review on Adsorption of Heavy Metal in Wastewater by Using Geopolymer," *MATEC Web of Conferences*, vol. 97, 2017, doi: 10.1051/mateconf/20179701023.
- [3] Y. Gomravi, A. Karimi, and H. Azimi, "Adsorption of heavy metal ions via apple waste low-cost adsorbent: Characterization and performance," *Korean Journal of Chemical Engineering*, vol. 38, no. 9, pp. 1843-1858, 2021, doi: 10.1007/s11814-021-0802-8.
- [4] A. K. M. K. M. S. J. S. and N. S., "Removal of heavy metal ions from industrial wastewater using magnetic nanoparticles," *Journal of Engineering Research*, 2021, doi: 10.36909/jer.6924.
- [5] K. Gryko, M. Kalinowska, and G. Świdorski, "The Use of Apple Pomace in Removing Heavy Metals from Water and Sewage," presented at the *Innovations-Sustainability-Modernity-Openness Conference (ISMO'21)*, 2021.
- [6] E. Heraldly, W. W. Lestari, D. Permatasari, and D. D. Arimurti, "Biosorbent from tomato waste and apple juice residue for lead removal," *Journal of Environmental Chemical Engineering*, vol. 6, no. 1, pp. 1201-1208, 2018, doi: 10.1016/j.jece.2017.12.026.
- [7] S. Xie, "Biosorption of heavy metal ions from contaminated wastewater: an eco-friendly approach," *Green Chemistry Letters and Reviews*, vol. 17, no. 1, 2024, doi: 10.1080/17518253.2024.2357213.
- [8] P. Chand and Y. B. Pakade, "Synthesis and characterization of hydroxyapatite nanoparticles impregnated on apple pomace to enhanced adsorption of Pb(II), Cd(II), and Ni(II) ions from aqueous solution," *Environ Sci Pollut Res Int*, vol. 22, no. 14, pp. 10919-29, Jul 2015, doi: 10.1007/s11356-015-4276-2.
- [9] L. Li et al., "Adsorption of Pb(II) and Cu(II) by succinic anhydride-modified apple pomace," *Biochemical Engineering Journal*, vol. 201, 2024, doi: 10.1016/j.bej.2023.109136.
- [10] Jumina, Y. Priastomo, H. R. Setiawan, Mutmainah, Y. S. Kurniawan, and K. Ohto, "Simultaneous removal of lead(II), chromium(III), and copper(II) heavy metal ions through an adsorption process using C-phenylcalix[4]pyrogallolarene material," *Journal of Environmental Chemical Engineering*, vol. 8, no. 4, 2020, doi: 10.1016/j.jece.2020.103971.
- [11] A. Demirbas, "Heavy metal adsorption onto agro-based waste materials: a review," *J Hazard Mater*, vol. 157, no. 2-3, pp. 220-9, Sep 15 2008, doi: 10.1016/j.jhazmat.2008.01.024.
- [12] J. Bayuo, M. J. Rwiza, M. Sillanpaa, and K. M. Mtei, "Removal of heavy metals from binary and multicomponent adsorption systems using various adsorbents - a systematic review," *RSC Adv*, vol. 13, no. 19, pp. 13052-13093, Apr 24 2023, doi: 10.1039/d3ra01660a.
- [13] F. O. Afolabi, P. Musonge, B. F. Bakare, and H. Arellano-Garcia, "Bio-sorption of copper and lead ions in single and binary systems onto banana peels," *Cogent Engineering*, vol. 8, no. 1, 2021, doi: 10.1080/23311916.2021.1886730.
- [14] B. Tekin and U. AÇikel, "Adsorption Isotherms for Removal of Heavy Metal Ions (Copper and Nickel) from Aqueous Solutions in Single and Binary Adsorption Processes," *Gazi University Journal of Science*, vol. 36, no. 2, pp. 495-509, 2023, doi: 10.35378/gujs.1066137.
- [15] X. Zhang, Y. Hao, X. Wang, Z. Chen, and C. Li, "Competitive Adsorption of Cadmium(II) and Mercury(II) Ions from Aqueous Solutions by Activated Carbon from *Xanthoceras sorbifolia* Bunge Hull," *Journal of Chemistry*, vol. 2016, pp. 1-10, 2016, doi: 10.1155/2016/4326351.

- [16] K. Bindon, S. Qi, S. Kassara, L. Nicolotti, A. Jouin, and M. Beer, "Apple Pomace Compositional Data Highlighting the Proportional Contribution of Polymeric Procyanidins," *Molecules*, vol. 28, no. 14, Jul 18 2023, doi: 10.3390/molecules28145494.
- [17] G. Ungureanu, I. M. Enache, I. G. Cara, I. Motrescu, and A. Patras, "Insights into the environmental benefits of using apple pomace for biosorption of lead from contaminated water," *Heliyon*, vol. 10, no. 17, p. e36811, Sep 15 2024, doi: 10.1016/j.heliyon.2024.e36811.
- [18] L.-Y. Wu et al., "Application of NaOH-HCl-Modified Apple Pomace to Binding Epigallocatechin Gallate," *Food and Bioprocess Technology*, vol. 9, no. 6, pp. 917-923, 2016, doi: 10.1007/s11947-016-1683-4.
- [19] L. R. Bonetto, J. S. Crespo, R. Guégan, V. I. Esteves, and M. Giovanela, "Removal of methylene blue from aqueous solutions using a solid residue of the apple juice industry: Full factorial design, equilibrium, thermodynamics and kinetics aspects," *Journal of Molecular Structure*, vol. 1224, 2021, doi: 10.1016/j.molstruc.2020.129296.
- [20] P. Chand and Y. B. Pakade, "Removal of Pb from Water by Adsorption on Apple Pomace: Equilibrium, Kinetics, and Thermodynamics Studies," *Journal of Chemistry*, vol. 2013, pp. 1-8, 2013, doi: 10.1155/2013/164575.
- [21] P. Hobbi et al., "Chemical Composition, Antioxidant Activity and Cytocompatibility of Polyphenolic Compounds Extracted from Food Industry Apple Waste: Potential in Biomedical Application," *Molecules*, vol. 28, no. 2, Jan 9 2023, doi: 10.3390/molecules28020675.
- [22] X. Zhao, L. Baharinikoo, M. D. Farahani, B. Mahdizadeh, and A. A. K. Farizhandi, "Experimental modelling studies on the removal of dyes and heavy metal ions using ZnFe(2)O(4) nanoparticles," *Sci Rep*, vol. 12, no. 1, p. 5987, Apr 9 2022, doi: 10.1038/s41598-022-10036-y.
- [23] M. A. Bezerra, R. E. Santelli, E. P. Oliveira, L. S. Villar, and L. A. Escalera, "Response surface methodology (RSM) as a tool for optimization in analytical chemistry," *Talanta*, vol. 76, no. 5, pp. 965-77, Sep 15 2008, doi: 10.1016/j.talanta.2008.05.019.
- [24] Y. Liu, Z. Xu, X. Hu, N. Zhang, T. Chen, and Z. Ding, "Sorption of Pb(II) and Cu(II) on the colloid of black soil, red soil and fine powder kaolinite: effects of pH, ionic strength and organic matter," *Environmental Pollutants and Bioavailability*, vol. 31, no. 1, pp. 85-93, 2019, doi: 10.1080/26395940.2019.1578186.
- [25] A. Sdiri and T. Higashi, "Simultaneous removal of heavy metals from aqueous solution by natural limestones," *Applied Water Science*, vol. 3, no. 1, pp. 29-39, 2012, doi: 10.1007/s13201-012-0054-1.
- [26] G. James, D. A. Sabatini, C. T. Chiou, D. Rutherford, A. C. Scott, and H. K. Karapanagioti, "Evaluating phenanthrene sorption on various wood chars," *Water Res*, vol. 39, no. 4, pp. 549-58, Feb 2005, doi: 10.1016/j.watres.2004.10.015.
- [27] K. Y. Foo and B. H. Hameed, "Insights into the modeling of adsorption isotherm systems," *Chemical Engineering Journal*, vol. 156, no. 1, pp. 2-10, 2010, doi: 10.1016/j.cej.2009.09.013.