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The Removal of Some Heavy Metals (Ni, Cu & Fe) from Palm Oil Mill Effluents Using Schiff Base from Sugarcane Bagasse

Eghe Amenze Oyedoh[a]*; Destiny Emmanuel Apakhade[a]

[a]Department of Chemical Engineering, Faculty of Engineering, University of Benin, Benin city, Nigeria.

*Email of the corresponding author; egheoyedoh@uniben.edu

Article Info	Abstract
	The disposal of palm oil mill effluent (POME) poses a significant environmental problem due to its high heavy metals content. Conventional methods (such as membrane filtration and ion exchange) for the removal of heavy metals from POME are often expensive and not environmentally friendly. This study investigated the use of Schiff base from sugarcane bagasse, a waste product of the sugar industry, as a low-cost adsorbent for the removal of heavy metals such as nickel (Ni), copper (Cu) and iron (Fe) from POME obtained from Nigerian Institute for Oilpalm Research at Ovia in Edo state, Nigeria. Schiff base, a type of organic ligand, was prepared from sugarcane bagasse through the condensation of the hydroxyl groups of sugarcane bagasse with NaOH and HCl then grafting it to a primary amine (L-lysine). The prepared Schiff base was then used as an adsorbent for the removal of heavy metals from POME. The batch adsorption process was studied under various conditions, such as pH, adsorbent dose and contact time to optimize the removal efficiency using Response Surface methodology (RSM). The results of this study shows that the prepared Schiff base was highly effective in removing heavy metals from POME, with up to 98.72% removal efficiency for Ni, 92.29% for Cu, and 71.81% for Fe. .

1.0. Introduction

Palm oil is a vegetable that comes from the mesocarp of the oil palm's fruit. The oil has a variety of applications, including food production, cosmetics production, and biofuel production. The refinery process produces a significant amount of agricultural run-off during the production of this oil. Palm Oil Mill Effluents (POME) contain toxic heavy metals which are non-biodegradable and bio-accumulate in living organisms. Direct disposal of these effluents would result in fast deoxygenation of water thereby necessitating treatment.

Several methods have been used for the removal of these heavy metals from aqueous solutions. These include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment and application of membrane technology. Adsorption can be an effective method for the removal of these heavy metals.

Adsorbents ranging from industrial products such as waste rubber tyres [1] to agricultural products such as wool, rice straws, coconut husks, peat moss, and orange peels have been employed in the past in the treatment of wastewater. Previous studies on the removal of heavy metals from aqueous

solutions have been reported in literature. Harripersadth et al reported the use of bagasse for the removal of heavy metals from aqueous solutions [2]. Ammara et al employed the use of sugarcane bagasse for the removal of copper ions from synthetic wastewater [3].Schiff bases (-RC=N-) can form extremely stable complexes with transition metal ions [4]. The interaction of unshared pairs of electrons and Π electrons with metal ions through electrostatic attraction between charged molecules and charged metal is attributed to Schiff bases' adsorptive effects. Schiff bases are formed through catalysis with acids or bases, or by using heat [4]. In this study, Schiff base synthesized from Sugarcane (*saccharum officinarum*) bagasse, an agricultural waste was used for the removal of some heavy metals. Sugarcane bagasse was used due to its cellulose content which permits new functions to be added to the bagasse making it more useful [5].

2. Materials and Methods
2.1 Materials

All chemical reagents used were of analytical grade. Distilled water was used as solvent in the preparation of dilute solutions. The POME was obtained from Nigeria Institute for Oilpalm Research (NIFOR) while the sugarcane bagasse was got from a waste dumpsite at Ikpoba-hill, Benin city Nigeria.

2.2 Schiff Base

The Schiff base synthesized from a sugarcane bagasse was used in this study [6]. The bagasse was thoroughly washed with water and allowed to dry for 48-72hrs under sunlight before subjecting to chemical treatment. The dried bagasse was blended to reduce the size of the particles. The blended bagasse was soaked in 2-3% NaOH solution for 6hrs at a temperature of 60^0C, this was done to remove the lignin and hemicellulose. The extracted cellulose (pulp) was filtered using a muslin cloth and washed with distilled water until all NaOH was removed and a neutral pH was achieved [4]. The pulp was obtained by filtration. The alkali treated pulp was then bleached by soaking in 10-15% solution of H_2O_2 and it was kept overnight to remove any residual lignin and hemicellulose. The bleached pulp was subsequently washed with distilled water and then allowed to dry at room temperature. Bleached pulp was then soaked in 10% HCl (1M) solution for another 4hrs [5]. The fibers were washed several times with distilled water until neutral pH was achieved and then dried. The fibers were again suspended in water and high sheared with a Blender, which resulted in defibrillation of agglomerates to finally form cellulose nanofibers (CNFs). The CNFs is oxidized in a basic chemical reactor using Sodium metaperiodate [4]. The mixture was reacted in an orbital shaker at room temperature for 72h under complete darkness. After the completion of the reaction, ethylene glycol was added to decompose the remaining periodate. The CNF was grafted to L-lysine at an adjusted pH of 7 and the Schiff base was formed [7]. The produced Schiff base was filtered and dried at room temperature

2.3 Preparation of Solution.
The mill effluents sample was collected locally from Nigerian Institute for Oilpalm Research (NIFOR). The POME was stored in a refrigerator to inhibit microbial growth. The POME was collected and filtered using a fine muslin cloth to remove tiny particles from the solution. The initial concentrations of heavy metals present in the solution was determined using atomic adsorption spectrophotometer (AAS). The solution was then adjusted to the required pH as suggested by design expert. The pH for the various solution varied from 3 – 9 as suggested by design expert using either 0.2mol/dm^3 of HCl/NaOH.

2.4 Batch Adsorption Studies

Batch adsorption studies were carried out in 250ml conical flasks containing 100 ml of POME and the suspensions were mixed in a jar test apparatus at room temperature in order to identify the effect of the following parameters as suggested by design expert:

Table 1: CCD experimental conditions for the percentage removal of heavy metals

Independent variables	Coding	levels		
		-1	0	+1
Contact time (mins)	A	50	145	240
pH	B	3	6	9
Adsorbent dosage (g)	C	0.1	0.3	0.5

Using standard recommendation methods for testing water and waste water, the final concentration of metallic ions (Ni^+, Cu^{2+}, Fe^{2+}) was evaluated with an atomic absorption spectrophotometer. The results shown are the averages of all assays performed. The following formulae were used to compute the percentage of metal removed from the POME and the amount of metal ions adsorbed by the Schiff base:

$$\text{Percentage removal} = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where C_i and C_e denotes the initial and equilibrium metal ion concentrations in solution, respectively.

3. Results and Discussion

3.1 Percentage Removal of Nickel, Iron and Copper

The Table **2** below shows the percentage removal of the metallic ions from POME and also the predicted value by Response Surface Methodology (RSM) against the actual/experimental. The percentage removal was highest in Nickel ion, followed by copper ion and Iron having the least percentage removal (This is due to the fact that iron ion has the highest concentration "128.59mg/L" in the POME). The concentration of the other 2 metals Copper and Iron was observed to be 21.32mg/L and 4.36mg/L respectively. Fig **1** shows the predicted vs the Actual plot for each metal. The percentage removal for nickel was within the range 93.00 – 98.72%, that for iron was within the range 38.21 – 73.30% and that for copper was within the range 83.55 – 93.48%.

Table 2: Experimental and predicted results for removal of metal ions (Ni, Fe, and Cu) from POME

| Std	Run	Factor 1 A: Time (mins)	Factor 2 B: pH -	Factor 3 C: Adsorbent dosage (g)	Percentage removal of Nickel %		Percentage removal of Iron %		Percentage removal of Copper %	
					Actual Value (%)	Predicted Value (%)	Actual Value (%)	Predicted Value (%)	Actual Value (%)	Predicted Value (%)
12	1	145.00	9.00	0.30	93.00	93.03	38.21	38.24	84.02	84.31
2	2	201.49	4.22	0.18	98.25	98.10	53.92	53.78	89.22	89.11
10	3	240.00	6.00	0.30	97.69	97.87	43.71	42.56	84.55	84.64
13	4	145.00	6.00	0.10	97.97	98.02	47.48	48.30	86.67	87.00
16	5	145.00	6.00	0.30	98.10	98.02	44.47	45.74	85.45	85.15
20	6	145.00	6.00	0.30	98.13	98.02	46.61	45.74	85.33	85.15
14	7	145.00	6.00	0.50	97.98	98.15	46.20	46.78	89.12	89.26
8	8	201.49	7.78	0.42	96.03	95.89	40.79	41.30	86.25	86.18
18	9	145.00	6.00	0.30	97.93	98.02	46.08	45.74	85.01	85.15
5	10	88.51	4.22	0.42	98.65	98.50	71.86	70.27	92.44	92.29
9	11	50.00	6.00	0.30	98.32	98.37	55.44	57.98	86.14	86.52
17	12	145.00	6.00	0.30	97.92	98.02	41.73	45.74	85.04	85.15
19	13	145.00	6.00	0.30	98.01	98.02	46.98	45.74	85.11	85.15
1	14	88.51	4.22	0.18	98.72	98.70	73.30	71.81	91.77	91.51
4	15	201.49	7.78	0.18	95.56	95.55	40.96	41.57	84.45	84.27
3	16	88.51	7.78	0.18	95.87	95.84	41.38	40.24	83.55	83.27
11	17	145.00	3.00	0.30	97.19	97.38	71.24	72.59	93.48	93.66
7	18	88.51	7.78	0.42	95.89	95.88	42.47	41.62	86.22	86.00
6	19	201.49	4.22	0.42	98.33	98.20	50.43	50.59	89.11	89.06
15	20	145.00	6.00	0.30	98.09	98.02	48.80	45.74	85.06	85.15
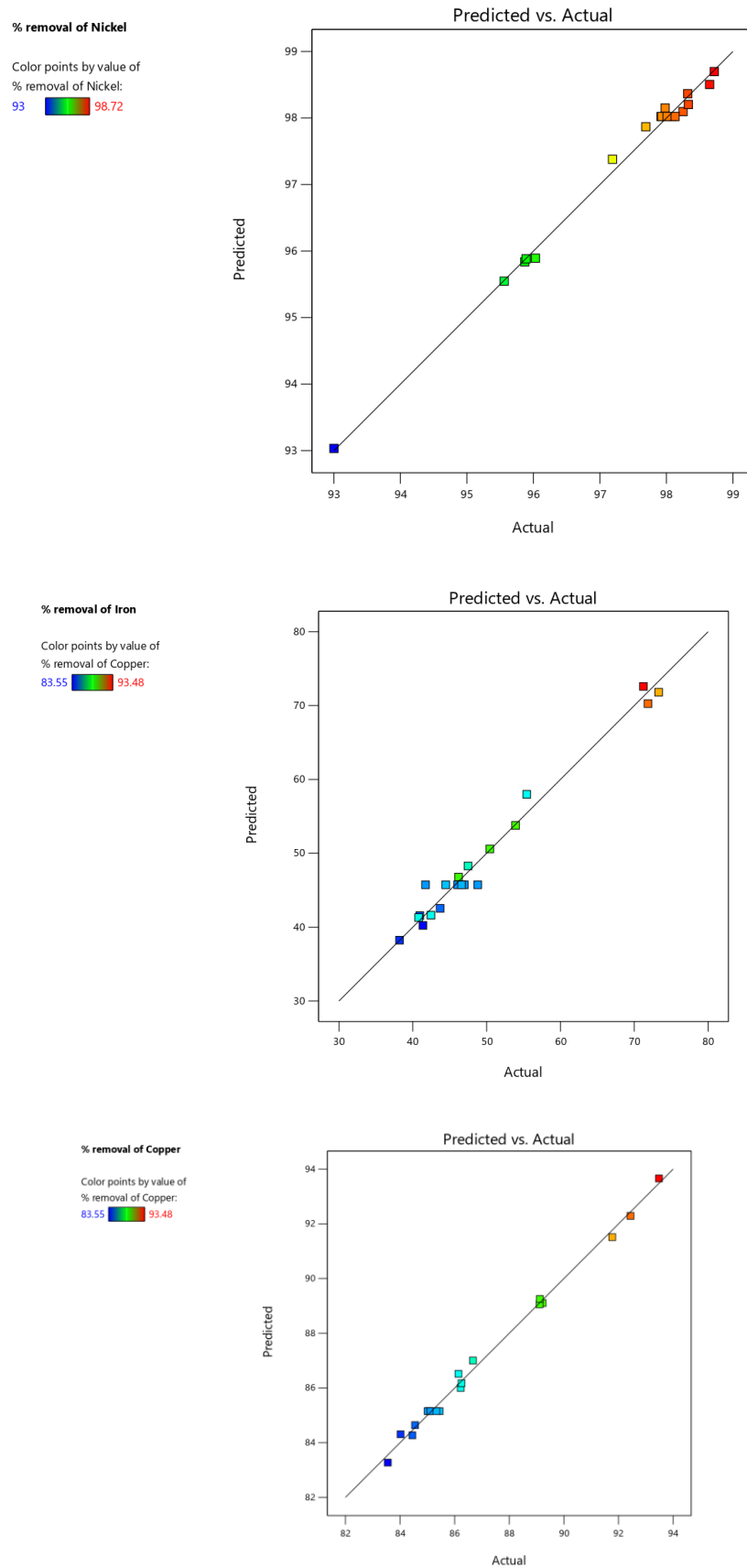
Figure 1: Predicted vs Actual plot (a) %removal of Nickel (b) %removal of iron (c) %removal of copper

The plots in Figure 1 shows the relevance of the model. The points are close to the line which shows the accuracy of the experiment.

3.2 Analysis of Percentage Removal of Metallic ions in POME.

The results of all 20 runs carried out to remove heavy metals from POME are shown in Table **2**. The RSM model developed for the experiment generated a quadratic model for the results gotten from the experiment. The experimental data were fitted into the generated quadratic model through multiple regression analysis. The resulting equation is shown in equation 2, 3 and 4 for Ni, Fe and Cu ion respectively.

$R1_{(coded\ response\ 1)} = 98.0229 + -0.147877A - 1.29215B + 0.0378431C + 0.0775AB + 0.075AC + 0.06BC + 0.0332689A^2 - 0.995571B^2 + 0.0226623C^2$ *Equation 2a*

$R1_{(actual\ response\ 1)} = 93.4171 - 0.0136058A + 2.83378B - 3.95922C + 0.000769134AB + 0.0111648AC + 0.282843BC + 1.04264e\text{-}05A^2 - 0.312878B^2 + 1.60247C^2$ *(2b)*

$R2_{(coded\ response\ 2)} = 45.739 - 4.58747A - 10.2134B - 0.450597C + 4.83875AB - 0.41175AC + 0.73125BC + 1.60182A^2 + 3.42156B^2 + 0.635206C^2$ *(3a)*

$R2_{(actual\ response\ 2)} = 191.63 - 0.496534A - 26.6263B - 42.5337C + 0.0480212AB - 0.061295AC + 3.44715BC + 0.000502009A^2 + 1.07529B^2 + 44.9159C^2$ *(3b)*

$R3_{(coded\ response\ 3)} = 85.1533 - 0.558258A - 2.781B + 0.670022C + 0.85125AB - 0.20625AC + 0.48875BC + 0.15063A^2 + 1.35448B^2 + 1.05219C^2$ *(4a)*

$R3_{(actual\ response\ 3)} = 127.424 - 0.0650504A - 8.58325B - 48.3785C + 0.00844807AB - 0.0307033AC + 2.30399BC + 4.72073e\text{-}05A^2 + 0.425672B^2 + 74.4011C^2$ *(4b)*

The statistical significance of equations 2 – 4 was assessed using analysis of variance (ANOVA) with results shown in Table **2**. The model was significant (p<0.0001) for Nickel, Iron and Copper ion while lack of fit was not significant (p = 0.0606) for Nickel ion, (p = 0.6964) for Iron ion and (p = 0.0739) for copper ion.

The regression coefficients for the removal of the Nickel, Iron and Copper from the adsorbate at the end of the adsorption process are illustrated in Table 3 – 5. The independent factors A and B has a significant effect and achieved very high confidence level (p < 0.05) for all 3 metals. pH and contact time enhanced the adsorption of Ni, Fe and Cu significantly (p < 0.05) while the adsorbent dosage was not significant for the adsorption except in copper where it was significant. According to Table **3**, model A, B, and B^2 are significant model terms (p < 0.05), however, model terms C, AB, AC, BC, A^2 and C^2 are not significant (p > 0.05). According to Table **4**, model terms A, B, AB, A^2 and B^2 are significant model terms (p < 0.05), however, model terms C, AC, BC, C^2 are not significant (p > 0.05). According to Table **5**, model terms A, B, C, AB, BC, B^2, C^2 are significant model terms (p < 0.05), however, model terms AC and C^2 are not significant (p > 0.05).

Table 3: ANOVA response for the removal of nickel

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	37.96	9	4.22	187.41	< 0.0001	significant
A-Time	0.2986	1	0.2986	13.27	0.0045	
B-pH	22.80	1	22.80	1013.26	< 0.0001	
C-Adsorbent dosage	0.0196	1	0.0196	0.8691	0.3732	
AB	0.0480	1	0.0480	2.14	0.1747	

AC	0.0450	1	0.0450	2.00	0.1877	
BC	0.0288	1	0.0288	1.28	0.2843	
A²	0.0160	1	0.0160	0.7088	0.4195	
B²	14.28	1	14.28	634.73	< 0.0001	
C²	0.0074	1	0.0074	0.3289	0.5790	
Residual	0.2250	10	0.0225			
Lack of Fit	0.1846	5	0.0369	4.56	0.0606	not significant
Pure Error	0.0405	5	0.0081			
Cor Total	38.18	19				

Table 4: ANOVA response for the removal of iron.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2100.09	9	233.34	49.02	< 0.0001	significant
A-Time	287.41	1	287.41	60.38	< 0.0001	
B-pH	1424.59	1	1424.59	299.29	< 0.0001	
C-Adsorbent dosage	2.77	1	2.77	0.5825	0.4629	
AB	187.31	1	187.31	39.35	< 0.0001	
AC	1.36	1	1.36	0.2849	0.6051	
BC	4.28	1	4.28	0.8987	0.3655	
A²	36.98	1	36.98	7.77	0.0192	
B²	168.71	1	168.71	35.44	0.0001	
C²	5.81	1	5.81	1.22	0.2949	
Residual	47.60	10	4.76			
Lack of Fit	18.13	5	3.63	0.6155	0.6964	not significant
Pure Error	29.46	5	5.89			
Cor Total	2147.69	19				

Table 5: ANOVA response for the removal of copper

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	162.82	9	18.09	218.92	< 0.0001	Significant
A-Time	4.26	1	4.26	51.50	< 0.0001	
B-pH	105.62	1	105.62	1278.13	< 0.0001	
C-Adsorbent dosage	6.13	1	6.13	74.19	< 0.0001	
AB	5.80	1	5.80	70.15	< 0.0001	
AC	0.3403	1	0.3403	4.12	0.0699	
BC	1.91	1	1.91	23.13	0.0007	
A²	0.3270	1	0.3270	3.96	0.0747	
B²	26.44	1	26.44	319.94	< 0.0001	
C²	15.95	1	15.95	193.07	< 0.0001	
Residual	0.8264	10	0.0826			
Lack of Fit	0.6642	5	0.1328	4.10	0.0739	not significant
Pure Error	0.1621	5	0.0324			
Cor Total	163.65	19				

3.3 Interactive Effect of Variables and Three-Dimensional (3D) Response Surface Plots & Contour Plots.

Three-dimensional response surface plots were constructed to determine the individual and interactive effects of variables, i.e., pH, adsorbent dose, and contact time. In this session, the

simultaneous effect of parameters on the rate of simultaneous adsorption of Ni, Fe and Cu ions was investigated by the Schiff base (Figure 2 – 4).
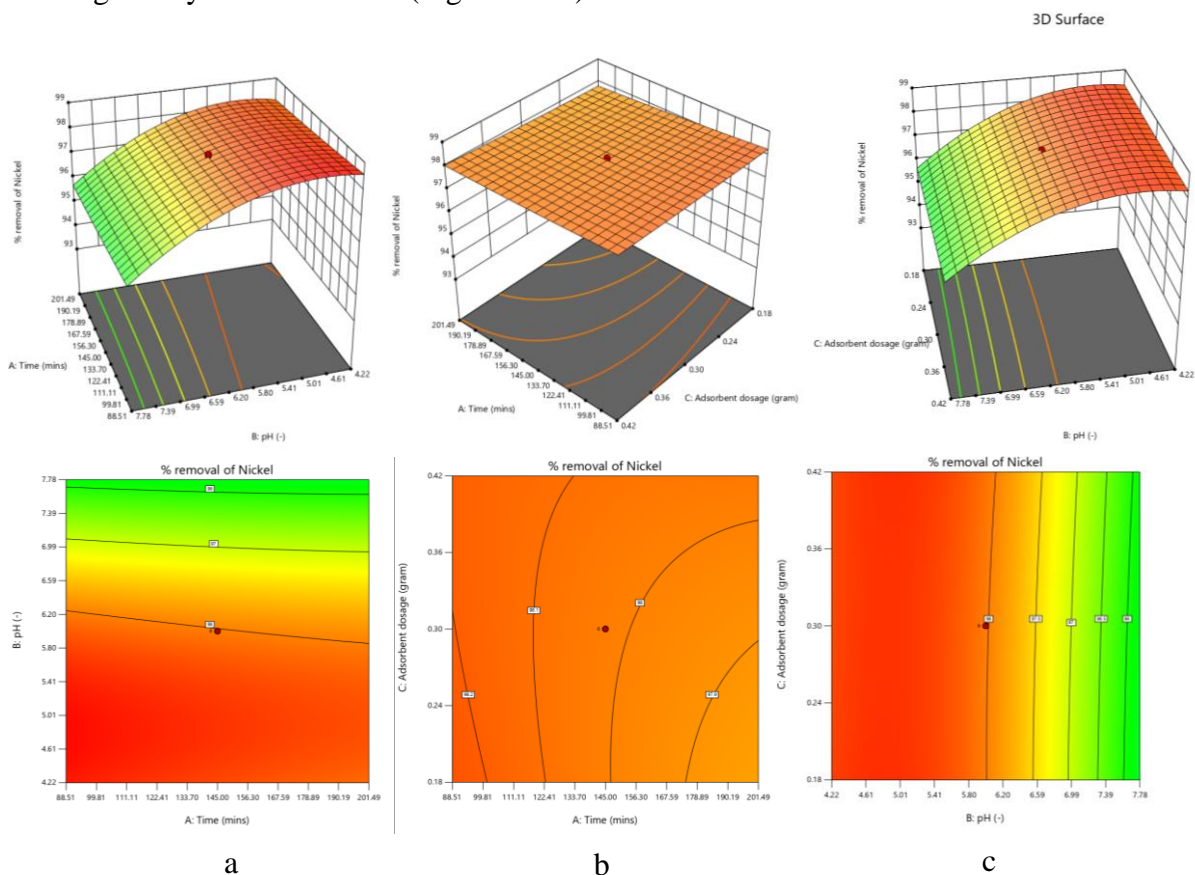

Figure 2: Reduction of Ni ion in POME by Schiff base as a response of the interaction between independent factors (a) Interaction between pH and contact time. (b) Interaction between adsorbent dosage and contact time. (c) Interaction between adsorbent dosage and pH

In Figure 2a, the result indicates that at a lower contact time and a decrease in the pH will increase the amount of nickel ion removal and adsorption (keeping the adsorbent dosage constant). In Figure 2b, the result indicates that there is a minimal difference in the percentage removal of Nickel ion when varying adsorbent dosage and contact time (keeping pH constant). In Figure 2c, the result shows that reducing the pH will increase the removal efficiency of the nickel ion in the solution. The maximum nickel ion removal was obtained at a PH of 4.2 and an adsorbent (Schiff base) dosage of 0.30g.

In Figure 3a, the result indicates that at a lower contact time and a decrease in the pH will increase the amount of Iron ion removal and adsorption (keeping the adsorbent dosage constant) and at a higher contact time and an increase in pH, the amount of iron removal will decrease. This decrease in the percentage removal can be attributed to desorption taking place. In Figure 3b, the result indicates that there is a minimal difference in the percentage removal of iron ion when varying adsorbent dosage but an increase in contact time results in a decrease in percentage removal, this is as a result of desorption taking place after the optimum removal has been met (keeping pH constant). In Figure 3c, the result shows that reducing the pH will increase the removal efficiency of the Iron ion in the solution and increasing the adsorbent dosage will slightly reduce the percentage removal of the iron ion. Figure **3** shows that the maximum iron ion removal was obtained at a PH of 3 and an adsorbent (Schiff base) dosage of 0.10g and contact time at 50mins.
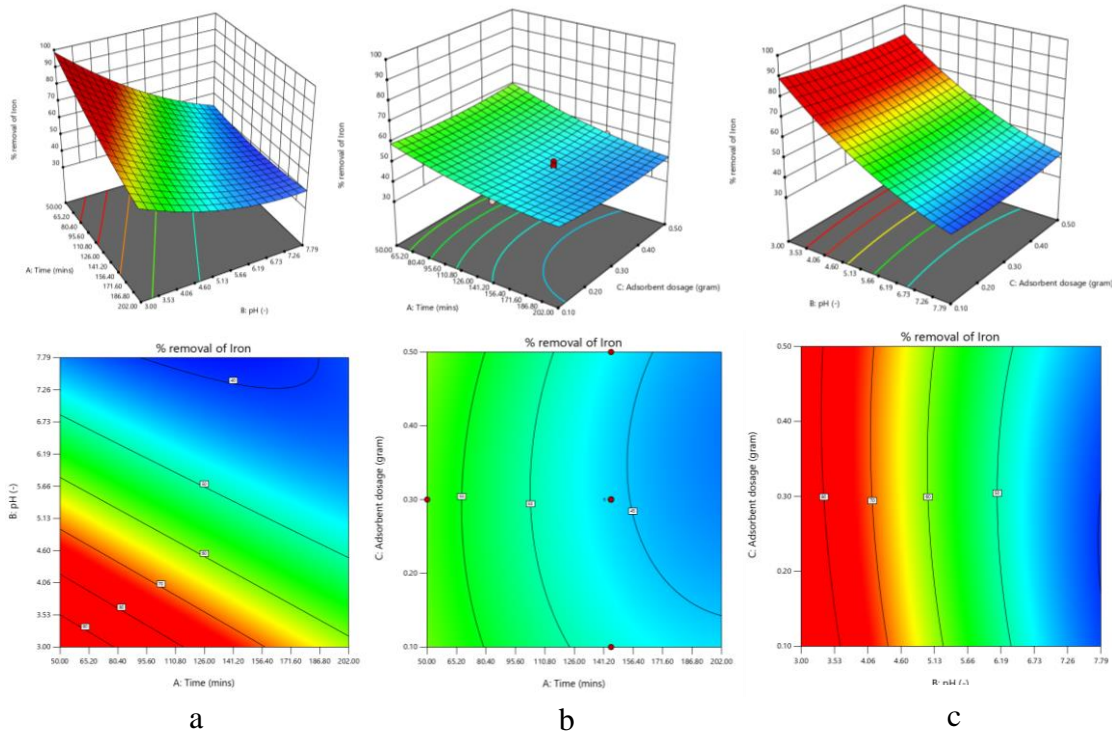
Figure 3: Reduction of Fe ion in POME by Schiff base as a response of the interaction between independent factors (a) Interaction between pH and contact time. (b) Interaction between adsorbent dosage and contact time. (c) Interaction between adsorbent dosage and pH
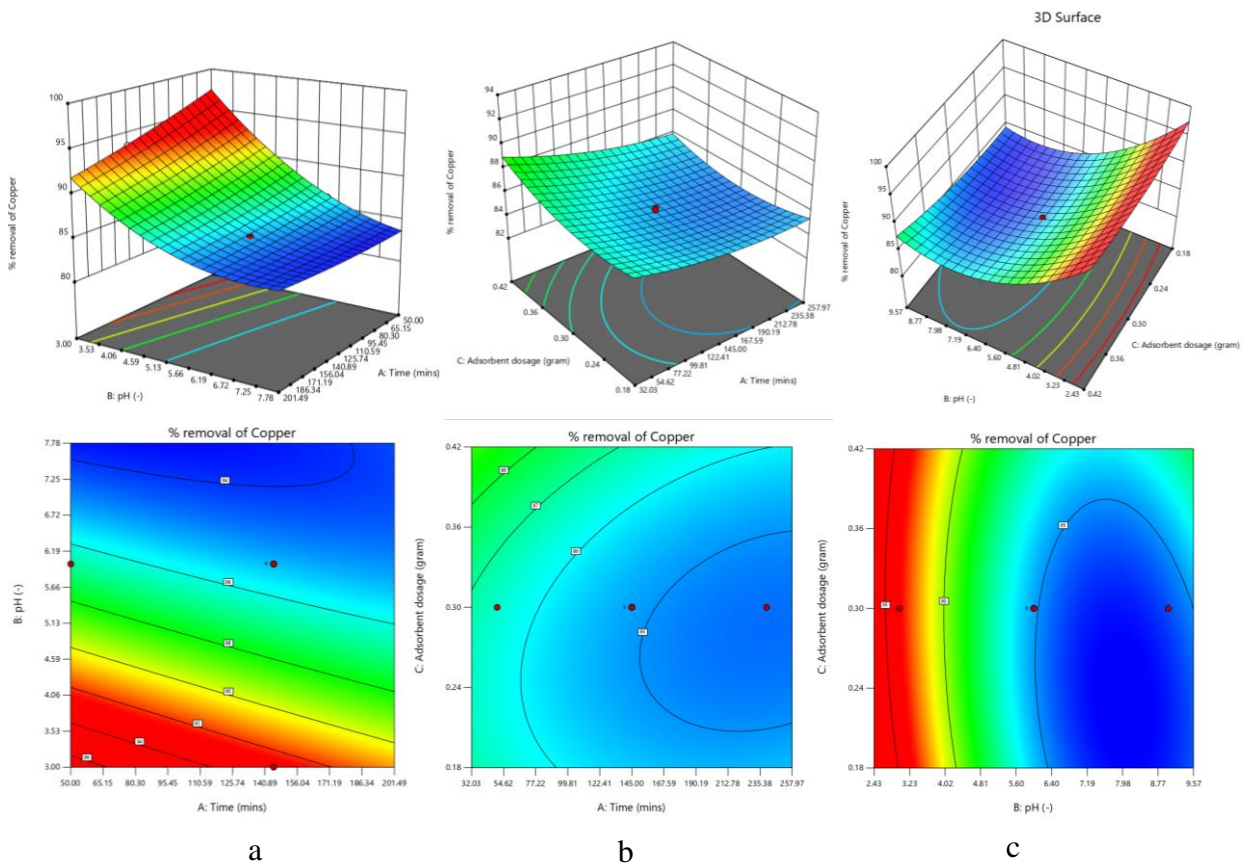

Figure 4: Reduction of Cu ion in POME by Schiff base as a response of the interaction between independent factors (a) Interaction between pH and contact time. (b) Interaction between adsorbent dosage and contact time. (c) Interaction between adsorbent dosage and pH.

In Figure 4a, the result indicates that at a lower contact time and a decrease in the pH will increase the amount of copper ion removal and adsorption (keeping the adsorbent dosage constant) and at a higher contact time and an increase in pH, the amount of iron removal will decrease. This decrease in the percentage removal can be attributed to desorption taking place. In Figure 4b, the result indicates that there is a minimal difference in the percentage removal of copper ion when varying adsorbent dosage although, a notable decline in the percentage when adsorbent dosage is decreased was observed but an increase in contact time results in a decrease in percentage removal, this is as a result of desorption taking place after the optimum removal has been met (keeping pH constant). In Figure 4c, the result shows that reducing the pH will increase the removal efficiency of the copper ion in the solution and increasing the adsorbent dosage will slightly reduce the percentage removal of the Iron ion. Figure **4** shows that the maximum copper ion removal was obtained at a PH of 3 and an adsorbent (Schiff base) dosage of 0.10g and contact time at 50mins.

3.4 Optimization of the Adsorption Process by Schiff Base

The optimal parameters for the adsorption of heavy metals from the POME using the Schiff base exhibited strong interactions ($p < 0.05$) and was achieved at pH 4.86, 88.708 mins contact time and an adsorbent dosage of 0.234g and a percentage removal of 98.72% for nickel ion. pH 4.216, 88.516 mins contact time and an adsorbent dosage of 0.419g which result in a percentage removal of 92.289% for copper ion. pH 4.216, 88.513 mins contact time and an adsorbent dosage of 0.181g which results in a percentage removal of 71.807%. These results can be found in Table **6.**

Table 6: Optimum parameters for each metal.

Metals	Time	pH	Adsorbent Dosage	%Removal	Desirability
Nickel	88.708	4.86	0.234	98.728	1
Iron	88.516	4.216	0.181	71.807	0.957
Copper	88.513	4.216	0.419	92.289	0.880

4. Conclusion

The high percentage removal of 93.00 – 98.72% for nickel, 38.21 – 73.30% for iron, and 83.55 – 93.48% for copper showed that Schiff base synthesized from sugarcane was effective in the removal of these metal ions from POME. This therefore helps in creating more use for waste rather than being dumped, thereby reducing pollution of the environment by bagasse. The treatment of the POME also prevents the environment from being contaminated by these heavy metals. It can be concluded that response surface methodology proved very efficient in the analysis of the effect of various parameters on the adsorption of the Ni, Fe and Cu from POME.

References

[1] W. R. Knocke and L. H. ll, "Mercury(Ii) Sorption By Waste Rubber," 1981.

[2] C. Harripersadth, P. Musonge, Y. Makarfi Isa, M. G. Morales, and A. Sayago, "The application of eggshells and sugarcane bagasse as potential biomaterials in the removal of heavy metals from aqueous solutions," *S Afr J Chem Eng*, vol. 34, pp. 142–150, Oct. 2020, doi: 10.1016/j.sajce.2020.08.002.

[3] Ammara Waheed, Rabia Sabir, Awais Salahuddin, "Comparative study on raw and modified forms of sugarcane bagasse for biosorption of Cu^{+2} from wastewater" International Journal of Scientific & Engineering Research Volume 11, Issue 1, January-2020

[4] A. Xavier and N. Srividhya, "'Synthesis and Study of Schiff base Ligands,'" IOSR Journal of Applied Chemistry 2014. www.iosrjournals.org

[5] M. Bansal, G. S. Chauhan, A. Kaushik, and A. Sharma, "Extraction and functionalization of bagasse cellulose nanofibres to Schiff-base based antimicrobial membranes," *Int J Biol Macromol*, vol. 91, pp. 887–894, Oct. 2016, doi: 10.1016/j.ijbiomac.2016.06.045.

[6]   E.A Oyedoh and N.O. Sale "Preparation of Schiff Base from Sugarcane Bagasse for the removal of heavy metals from Palm Oil Mill Effluents" The Journal of the Nigerian Institution of Production Engineers, Vol. 27, pp272-290, March 2023

[7]   S. Kumari and G. S. Chauhan, "New cellulose-lysine Schiff-base-based sensor-adsorbent for mercury ions," *ACS Appl Mater Interfaces*, vol. 6, no. 8, pp. 5908–5917, Apr. 2014, doi: 10.1021/am500820n.

[8]   H. Y. Zhu *et al.*, "Adsorption removal of congo red onto magnetic cellulose/Fe3O4/activated carbon composite: Equilibrium, kinetic and thermodynamic studies," *Chemical Engineering Journal*, vol. 173, no. 2, pp. 494–502, Sep. 2011, doi: 10.1016/j.cej.2011.08.020.

[9]   H. Gu *et al.*, "Calcium oxide modification of activated sludge as a low-cost adsorbent: Preparation and application in Cd(II) removal," *Ecotoxicol Environ Saf*, vol. 209, Feb. 2021, doi: 10.1016/j.ecoenv.2020.111760.

[10]   K. Sun, J. Tang, Y. Gong, and H. Zhang, "Characterization of potassium hydroxide (KOH) modified hydrochars from different feedstocks for enhanced removal of heavy metals from water," *Environmental Science and Pollution Research*, vol. 22, no. 21, pp. 16640–16651, Jun. 2015, doi: 10.1007/s11356-015-4849-0.

[11]   M. A. Betiha, Y. M. Moustafa, M. F. El-Shahat, and E. Rafik, "Polyvinylpyrrolidone-Aminopropyl-SBA-15 schiff Base hybrid for efficient removal of divalent heavy metal cations from wastewater," *J Hazard Mater*, vol. 397, Oct. 2020, doi: 10.1016/j.jhazmat.2020.122675.