10.51975/25400104.som
Journal of the Nigerian Society of Chemical Engineers, 40(1), 2025

OPTIMIZING LEAD IONS REMOVAL EFFICIENCY OF MELON HUSK BIO-ADSORBENT USING RESPONSE SURFACE METHODOLOGY AND PYOMO

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ABSTRACT
This study aims to optimize the removal efficiency of melon husk as a bio-adsorbent for lead ions in water. Response Surface Methodology (RSM) and Pyomo were employed to analyze experimental data from literature and identify optimal operating conditions. The independent variables used were dosage of melon husk and contact time. It was observed that time had a more positive influence on removal efficiency than dosage. Using the Stat-Ease 360 software, a quadratic model, exhibiting an excellent fit with an adjusted R-squared of 0.6862, was developed to describe the relationship between dosage and contact time on lead removal efficiency. RSM identified an optimal melon husk dosage of 0.64 g and a contact time of 49 minutes. However, Pyomo optimization revealed a slightly more efficient configuration with an optimal dosage of 0.63 g and a contact time of 44.8 minutes. This suggests that Pyomo may be a more effective tool for predicting the optimal conditions in this particular application.
Keywords: Melon husk; Water Treatment; Response Surface Methodology, Pyomo Optimization; Process Modelling.

1. INTRODUCTION

Water is a vital resource needed for various human activities, including domestic and industrial purposes. Despite natural replenishment through rainfall, increasing pressure on water resources is evident due to growing demand and pollution has become a major concern (Debnath & Saha, 2020). Over the years, industrialization has significantly contributed to the pressure on and contamination of water bodies through agricultural runoffs and improper discharge of effluent water, chemical spills, etc. Take the recent incident at Walsall, where cyanide spilled into a canal, killing numerous fishes and endangering the health and lives of those that use the water for domestic purposes (Jessica, 2024). Many similar cases of chemical and oil spills have been reported in communities in Nigeria, accompanied by deaths and illnesses in those who live in the area of spillage (Chiamaka, 2024). The presence of heavy metals in concentrations above the WHO limits can pose harm to aquatic organisms and humans. One of such metals often seen in household domestic water is lead (Pb) ions. Lead ions contamination typically stems from the corrosion of lead-based plumbing systems, pipes, and fixtures, industrial discharges, mining runoff, and certain agricultural activities. Lead ions exposure can result in developmental delays, learning disabilities, and neurological problems in children, while adults may experience cardiovascular and kidney issues (Igwe, 2007). According to WHO (2006), the maximum acceptable level of lead ions in drinking water is 0.05 mg/L. Several methods have been used to treat water contaminated with heavy metals like lead, including ion exchange, reverse osmosis, chemical precipitation, adsorption, electro-dialysis, membrane filtration, etc. (Camilo *et al*., 2021; Mesut, 2021; Bhaumik & Hiren, 2022, Mohamed *et al*., 2024). Most of these methods heavily rely on chemicals like chlorine, coagulants, flocculants, which can create toxic sludge and byproducts after the treatment process (Seragadam *et al*., 2024). Among these conventional methods, adsorption is a relatively simple and inexpensive method for removing heavy metals from water. Materials used as adsorbents include carbon-based adsorbents like activated carbon and graphene, chitosan-based adsorbents, mineral adsorbents like zeolites and clay, bio-adsorbents, etc. Following the drive for more environmentally friendly solutions, there has been a growing interest in using agricultural waste materials, such as melon husk, rice husk, shea butter husk, orange peels, watermelon rind, groundnut husk, etc. as bio-adsorbents for heavy metals removal from aqueous solutions (Bernard *et al*., 2018; Kebru *et al*., 2022; Naik *et al*., 2022; Hadid *et al*., 2023). These bio-adsorbents are cheaper and readily available than the chemical alternatives. They are biodegradable and non-toxic and thus safe for use in removal of heavy metals in household water. They can also be regenerated and reused, making the whole treatment process low-cost. The removal of heavy metals like Lead from water using bio-adsorbents like melon husk has been proposed to be a physisorption process (Mustapha *et al*., 2016). Bernard & Jimoh (2021) investigated the use of melon seed husk-derived activated carbon for Cr (VI) ion removal from electroplating wastewater. The activated carbon effectively adsorbed Cr (VI) ions, with ultrasound assistance significantly enhancing the adsorption rate. The Langmuir model best described the adsorption isotherm, and the pseudo-second-order model accurately represented the adsorption kinetics. Nwankwo & Mogbo (2014) demonstrated the effectiveness of urea-activated melon husk as a low-cost adsorbent for removing Cd (II) ions from industrial effluents. The adsorption process followed pseudo-second order kinetics, and both Langmuir and Freundlich isotherm models accurately described the adsorption behaviour. Ayantola *et al*.

(2020) studied the removal of Fe (II) and Pb (IV) ions from industrial wastewater using melon husk activated carbon. They found that adsorbent dosage significantly influenced Fe (II) ions removal, with an optimal dosage point. Pb (IV) removal was less dependent on dosage, except for H_2SO_4 activated carbon. Adesola *et al*. (2014) investigated the biosorption of Ni (II), Cr (III), and Co (II) ions by melon seed husk. The study found that various factors, including pH, contact time, biosorbent dose, initial metal ion concentration, and temperature, influenced biosorption efficiency. Pseudo-second-order kinetics best described the biosorption process. Melon husk dosage significantly affected metal ion removal. The Freundlich isotherm model best fit the experimental data, suggesting a multilayer adsorption mechanism. The order of spontaneity for metal ion removal was Ni (II) ion > Co (II) ion > Cr (III) ion. Adelagun *et al*. (2014) modified melon seed husk with NaOH and studied its Pb (II) ion removal efficiency. The Freundlich isotherm model best described the adsorption process, indicating heterogeneous adsorption. The pseudo-second-order kinetic model suggested chemisorption as the dominant mechanism with an optimal dosage of 0.6 g. Kabir & Samson (2022) investigated the use of H_2SO_4 modified melon husk activated carbon for removing lead ions from electroplating wastewater. The adsorption process followed pseudo-second-order kinetics, indicating chemisorption. The Langmuir and Freundlich isotherms fit the data well, with R^2 values between 0.888 and 1.000. Melon husk activated carbon was more effective in adsorbing Pb^{2+} than Fe^{2+} from the wastewater.

While these studies have demonstrated the potential of melon husk as a low-cost, readily available bio-adsorbent for lead ion removal from water, there remains a lack of comprehensive investigations into the optimal operating conditions for maximizing removal efficiency. This study aims to evaluate the influence of key parameters (e.g., melon husk dosage and contact time) on lead ion removal from waste water using melon husk. By employing optimization methods like Response Surface Methodology and Pyomo, the optimal values of these parameters to achieve the highest possible removal efficiency is determined.

2. MATERIALS AND METHODS

This study employs Response Surface Methodology (RSM) and the Pyomo Python package to optimize the removal of lead ions from water using melon husk and identify the influence of key parameters (dosage and time) that maximize removal efficiency of melon husk.

2.1 Response Surface Methodology

Response Surface Methodology (RSM) is a statistical technique used to explore and optimize the relationship between a response variable like removal efficiency and multiple input variables (e.g., dosage and time). Typically, RSM involves designing an experiment (DoE), however due to the challenges associated with performing different runs at different conditions, it has been shown that RSM can be used on existing data, especially in this age of big data (Mochammad *et al*., 2022)**.** Stat-Ease 360 was utilized for modelling and analysis of the data in Table 1 adapted from an already conducted experiment by Adelagun *et al*., (2014).

The problem consisted of two (2) factors: Dosage (A) and Time (B); and one response variable: Removal efficiency. Table 1 shows the response surface design matrix (actual) of the existing data. Tables 2 and 3 show the minimum and maximum levels of the factors and response.

Table 1. Response Surface Methodology (RSM) Design Matrix (Actual)

Run	Factor 1 A: Dosage of melon husk (g)	Factor 2 B: Time (mins)	Response Removal efficiency (%)
1	1	0	0
2	0.6	60	0.965
3	1	120	0.989
4	0.2	120	0.944
5	0.6	0	0
6	1	10	0.671
7	0.6	10	0.656
8	0.2	60	0.934
9	0.2	40	0.913
10	0.2	0	0
11	0.6	20	0.934
12	0.2	20	0.212
13	0.6	60	0.965
14	0.2	10	0.48
15	0.6	40	0.952
16	0.6	120	0.983
17	1	20	0.983
18	1	40	0.985
19	1	60	0.987

Table 2. Independent Variables used in the RSM Design

Factor	Name	Units	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	Dosage	g	0.2000	1.0000	-1 ↔ 0.20	+1 ↔ 1.00	0.6000	0.3266
B	Time	mins	0.0000	120.00	-1 ↔ 0.00	+1 ↔ 120.00	42.63	40.39

Table 3. Dependent Variable used in the Response Surface Methodology (RSM) Design

Response	Name	Unit	Observations	Minimum	Maximum	Mean	Std. Dev.
R1	Removal efficiency	%	55.00	0	0.989	0.7133	0.3787

2.2 Pyomo Optimization

Pyomo is a Python-based modelling library specifically designed for optimization problems. It provides a flexible and powerful framework for solving mathematical optimization problems. It also employs various solvers like Interior Point Optimizer (IPOPT), Couenne, and Solving Constraint Integer Problems (SCIP) to find the optimal values of the decision variables. The model developed from Stat-Ease 360 was implemented in Pyomo as a Concrete Model. This means that all the variables, parameters, constraints, and objective function have been defined with specific values and expressions as seen in Figure 1.

```
m.T = pyo.Var(within = NonNegativeReals, bounds=(0,m.Tmax))
m.D = pyo.Var(within = NonNegativeReals, bounds=(0.2,m.Dmax))

a = -0.072368478054635
b = 0.70774472999147
c = 0.024205467565955
d = -0.0023722030981067
e = -0.31089133408641
f = -0.00013881719522709


m.obj = pyo.Objective(expr=a + b*(m.D) + c*(m.T) + d*(m.D)*(m.T) + e*(m.D)**2 + f*(m.T)**2, sense=pyo.maximize)


solver = SolverFactory('couenne')
results = solver.solve(m)
```

Figure 1: Pyomo Concrete Model

The Couenne solver was used to solve this optimization problem. Couenne is a powerful open-source solver for mixed-integer nonlinear programming (MINLP) problems such as the one in this study. Couenne employs global optimization techniques to ensure that it finds the globally optimal solution, rather than just a local optimum.

3. RESULTS AND DISCUSSION

3.1 Response Surface Methodology

The factors shown in Table 2 were used as independent variables and the response shown in Table 3 was used as the dependent variable to be maximized. A quadratic model was found to best fit the data. Table 4 shows the evaluation of the model terms. From the low R^2 values, it can be seen that there is no correlation between the terms as this would render the model a poor one. VIFs of 1.0 and close to 1.0 show that there is no multicollinearity in the design.

10.51975/25400104.som
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Table 4: Model Terms Evaluation

Term	Standard Error	VIF	R_i^2	Power
A	0.3173	1.2	0.1724	82.9 %
B	0.3504	1.0	0.0014	75.1 %
AB	0.4311	1.2	0.1724	57.4 %
A^2	0.4779	1.0	0.0098	97.1 %
B^2	0.5730	1.0	0.0090	89.7 %

The quadratic model developed to describe the process is shown below:

i. Final equation in terms of coded factors:

Removal efficiency = 1.107544319277 + 0.0769371772805[illegible]A + 0.3[illegible]B - 0.056932874354561AB + 0.049742613453826A² - 0.4997[illegible]B² --- *1*

ii. Final equation in terms of actual factors:

Removal efficiency = -0.072368478054635+ 0.70774472999147A + 0.024205467565955B - 0.0023722030981067AB - 0.31089133408641A² - 0.00013881719522709B² ---- *2*

where A = Dosage, B = Time

3.2 Fit Summary

Table 5 shows the fit summary of the RSM design. It can be seen that the quadratic model best maximises the adjusted R^2 (0.6862) which is also very close to the Predicted R^2 (0.5576) indicating that the model is a good fit to the data provided.

Table 5. Model Fit Summary Statistics for the Response Surface Methodology Design

Source	Sequential p-value	Adjusted R²	Predicted R²	
Linear	0.0074	0.3908	0.2130	
2FI	0.6696	0.3583	-0.0764	
Quadratic	**0.0038**	**0.6862**	**0.5576**	**Suggested**
Cubic	0.0920	0.7797	0.5046	**Aliased**

3.3 Analysis of Variance (ANOVA)

The analysis of variance (ANOVA) for statistical significance of the quadratic model is computed on Table 6.

Table 6. ANOVA Analysis of the Quadratic Model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.00	5	0.3993	8.87	0.0008	significant
A-Dosage	0.0588	1	0.0588	1.31	0.2737	
B-Time	1.10	1	1.10	24.44	0.0003	
AB	0.0174	1	0.0174	0.3874	0.5444	
A²	0.0108	1	0.0108	0.2407	0.6319	
B²	0.7606	1	0.7606	16.90	0.0012	
Residual	0.5851	13	0.0450			
Lack of Fit	0.5851	12	0.0488			
Pure Error	0.0000	1	0.0000			
Cor Total	2.58	18				

The F-value of 8.87 implies the model is significant and the subsequent values for the parameters show their degree of effects on the response variable, Removal Efficiency. High F-values and P-values less than 0.05 indicate model terms are significant. In this case, the Time terms (**B** and **B²**) are the most significant model terms.

3.4 Response Surface Design

The interaction effect of dosage and time is shown in Figures 2 and 3. It can be confirmed that time has more influence on removal efficiency than dosage. Time appears to have a positive effect on the removal efficiency until it gets to a maximum at about 81 mins when a decline starts to occur.

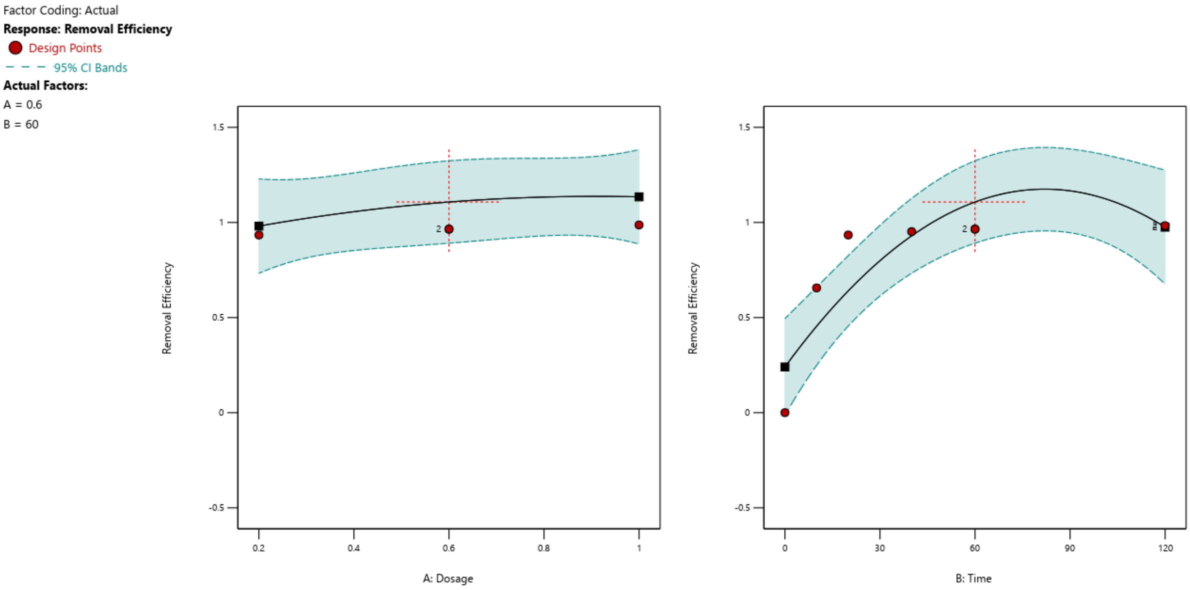

Figure 2: Interaction effect of dosage and time on Removal Efficiency

3.5 Numerical Optimization from RSM

Optimization using the Response Surface Methodology approach yielded the following optimal values for a maximum Removal Efficiency as seen in Figure 4.

Optimum Dosage = 0.64 g, Optimum Time = 49 mins

The optimal dosage obtained in this study is close to 0.6 g reported by Adelagun *et al*., (2014).

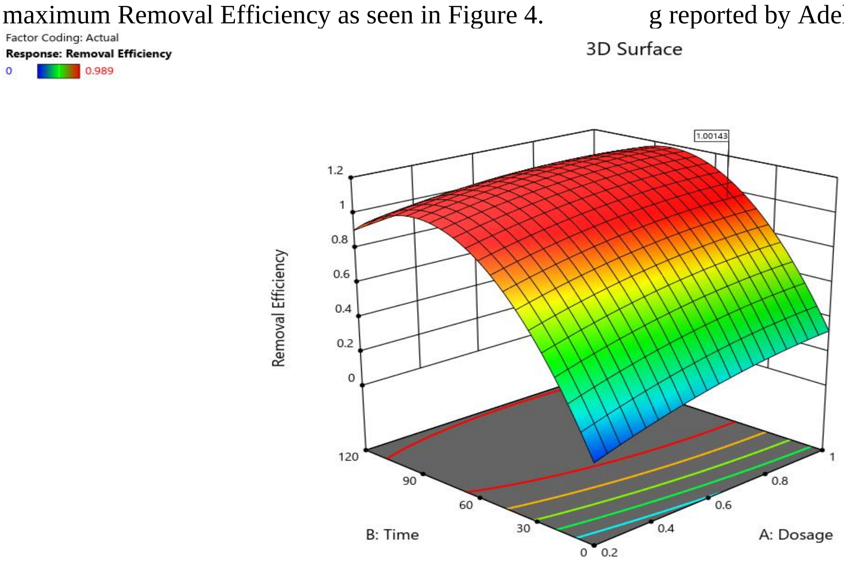

Figure 3: 3-dimensional response surface plots showing the effects of dosage and time on Removal Efficiency

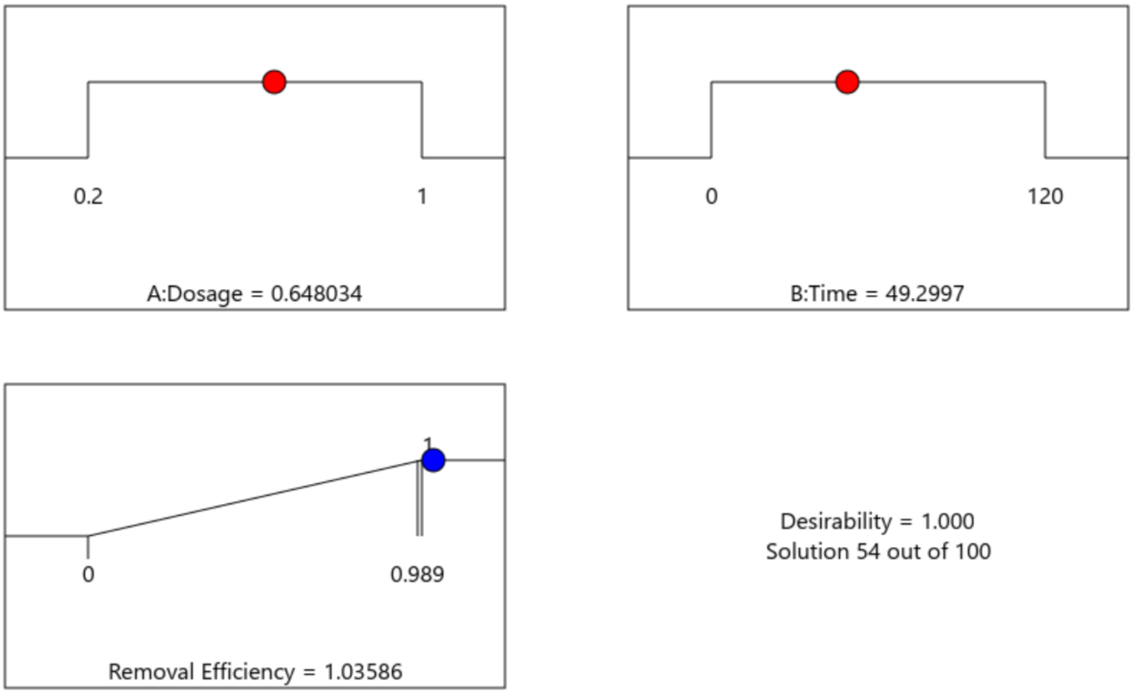

Figure 4: Optimization Solution from Response Surface Methodology Design.

3.6 Optimal Values from Pyomo

The model generated from Stat-Ease shown in equation 2 was used as the Objective Function for the Pyomo optimization problem. Optimization using the Couenne solver yielded optimal values for a maximum Removal Efficiency of 99 % as seen in Figure 5.

Optimum Dosage = 0.63 g, Optimum Time = 44.8 mins

This is very close to the optimum gotten from Response Surface Methodology.

```
[ ]  value(m.obj)
     0.9900000105944394

[ ]  m.T.extract_values()
     {None: 44.81097574261496}

[ ]  m.D.extract_values()
     {None: 0.6344597500315144}

     results.solver.termination_condition
     <TerminationCondition.optimal: 'optimal'>
```

Figure 5. Pyomo Optimization Results

4. CONCLUSIONS

This study successfully optimized the removal efficiency of melon husk for lead ions using Response Surface Methodology (RSM) and Pyomo. A quadratic equation was determined to be the most suitable model, with an adjusted R^2 of 0.6862 and a predicted R^2 of 0.5576 indicating a good fit to the experimental data. Pyomo optimization identified an optimal dosage of 0.63 g and RSM yielded an optimal dosage of 0.64 g, both of which are close to the experimental value of 0.6 g (Adelagun *et al*., 2014). Pyomo yielded a slightly lesser optimal time for maximized removal efficiency, suggesting its potential superiority over RSM in this case. While both methods yielded similar results, Pyomo's slightly more accurate dosage prediction and reduced computational time make it a promising tool for future optimization studies. The study also found that contact time positively affects removal efficiency, while dosage has a less pronounced impact. Future research could explore the influence of other factors, such as pH, temperature, and particle size, to further optimize the removal process.

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