FACTORIAL DESIGN ANALYSIS OF PHOSPHATE REMOVAL FROM MODEL SOLUTION BY IRON-LOADED POMRGRANATE PEEL

Naoufal Bellahsen[1], Szabolcs Kertész[2], Cecilia Hodúr[2]

[1]*Materials and Solutions Structure Research Group, University of Szeged, H-6720 Szeged, Dóm tér 8, Hungary*
[2]*Department of Process Engineering, Faculty of Engineering, University of Szeged, Moszkvai krt. 9, 6725 Szeged, Hungary*
e-mail: naoufal.bel@hotmail.com

Abstract
This study investigated the removal of phosphate (PO_4^{3-}) from disodium hydrogen phosphate (Na_2HPO_4) solution using Iron-loaded pomegranate peel (IL-PP) as a bio-adsorbent. The full factorial design using Minitab19 software was applied to analyze the effects of influencing parameters and their interactions and derive the equation that adequately describe PO_4^{3-} removal by IL-PP. Effective PO_4^{3-} removal up to 90% was achieved within 60 min, at pH 9 and 25 °C temperature using a 150 mg dose of IL-PP.

Introduction
Excess release of phosphorus is the main culprit for the eutrophication of freshwater and marine ecosystems [1]. Furthermore, phosphorus which is a critical element for plant growth is threaten by exhaustion [2]. Therefore the recovery of phosphate from wastewater is highly required protect the ecosystem and sustain the environment. Biosorption process using agricultural and food waste (AFW) presents several advantages such as simplicity, cost-effectiveness, and wide availability of potential bio-adsorbents that can be further applied to soil as fertilizer after adsorption of phosphate.
Pomegranate peel (PP) is among the widely abundant AFW [3]. Valorization of PP as bio-adsorbent for heavy metals, dyes and other contaminants removal was investigated in several studies and it showed promising adsorptive characteristics in both raw and activated forms or even as active carbon [4–6]. The present study investigated the efficiency of IL-PP at PO_4^{3-} removal from Na_2HPO_4 model solution using factorial design methodology in order to prove the performance of IL-PP as an alternative to conventional phosphate adsorbents.

Experimental
PO_4^{3-} removal rate was calculated as follows:

$$\textbf{Removal}\ \% = \frac{C_i - C_f}{C_i} . 100$$

Where C_i (mg·L^{-1}) and C_f (mg·L^{-1}) are the initial and final PO_4-P concentrations, respectively.
2^3 full factorial design was used to evaluate the effect of pH, adsorbent dose, temperature and their interactions on PO_4^{3-} removal by IL-PP. Factorial design plots such as plots for the main effects and interactions, Pareto chart, and normal plot for the standardized effects describe how the effect of one factor varies with the level of the other factors. This technique investigates all possible combinations and verifies the accuracy of the obtained mathematical model through the analysis of variance (ANOVA) to achieve optimum removal of PO_4^{3-}. Parameters such as initial PO_4-P concentration (40 mg.L^{-1}), contact time (60 min) and stirring speed (150 rpm) were kept constant and the three factors pH, adsorbent dose, and temperature of solution were varied at two levels as given in (Table 1). A centre point was duplicated and added to matrix in order to verify the curvature of the studied model.

Table 1. Factors and levels used in the factorial design for PO_4^{3-} removal by IL-PP

Factor	Symbol	Low level (-1)	High level (+1)	Centre point (0, 0, 0)
pH	A	3	9	6
Adsorbent dose	B	100	150	125
Temperature	C	25	45	35

Results and discussion

The mean of the experimental results for the respective high and low levels of pH, adsorbent dose and temperature are shown in Figure 1.

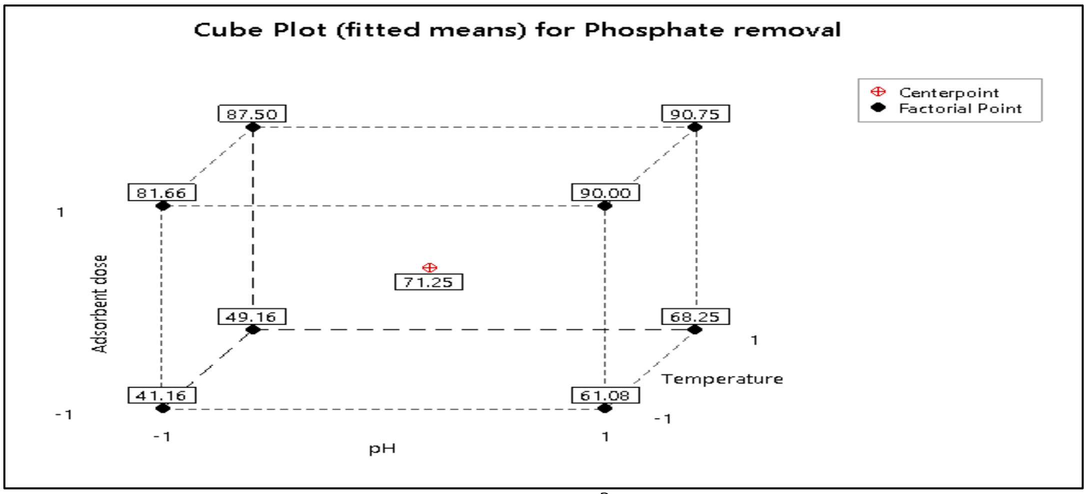

Figure 1. Cube plots for PO_4^{3-} removal by IL-PP

Table 2 presents the main effects and interactions, model coefficients, standard deviation of each coefficient, standard errors, Fisher test value (F-value), and probability value (P-value).

Table 2. Estimated effects and coefficients for PO_4^{3-} removal by IL-PP

Term	Effect	Coef	SE coef	t-value	p-value	VIF
Constant		71.195	0.125	569.56	0.001	
pH (A)	12.650	6.325	0.125	50.60	0.013	1.00
Adsorbent dose (B)	32.565	16.282	0.125	130.26	0.005	1.00
Temperature (C)	5.440	2.720	0.125	21.76	0.029	1.00
A*B	−6.855	−3.428	0.125	−27.42	0.023	1.00
A*C	−1.480	−0.740	0.125	−5.92	0.107	1.00
B*C	−2.145	−1.072	0.125	−8.58	0.074	1.00
A*B*C	−1.065	−0.533	0.125	−4.26	0.147	1.00
Ct Pt		0.055	0.280	0.2	0.876	1.00
S	0.135015					
R^2	100.00%					
R^2 (Adj)	99.96%					

The effects of pH (A), adsorbent dose (B), temperature (C), and the interaction (A*B) were significant at a 5% probability level ($P < 0.05$). However the effects of interactions (A*C), (B *C) and (A*B *C) were not significant ($P > 0.05$). Furthermore, the adjusted square correlation coefficient R^2 (adj) had a value of 99.96%, which indicates that the presented model perfectly fit the statistical model [7].

In this way, PO_4^{3-} removal by IL-PP could be expressed using Eq. (1).

$$\text{Phosphate removal\%} = 71.195 + 6.325\,A + 16.282\,B + 2.720\,C - 3.428\,A\cdot B + 0.740\,A\cdot C - 1.072\,B\cdot C - 0.533\,A\cdot B\cdot C + 0.055\,Ct\,Pt \quad (1)$$

where: A (pH), B (adsorbent dose), C (temperature), AB, AC and BC (their 2- way interaction) and ABC (their 3-way interaction). (3< pH <9, 100 mg< Adsorbent dose < 150 mg, 25 °C < temperature < 45°C).

ANOVA was performed to investigate the significance of parameters affecting PO_4^{3-} removal to ensure the accuracy of the model. Table 3 presents the sum of the squares used to estimate the effect of factors, the F-ratio (i.e., the ratio of individual mean square effects to the mean square error) and the P-value (i.e., the level of significance leading to the rejection of the null hypothesis). The results showed are in accordance with the estimated effects shown in Table 2 and thus confirm the accuracy of the factorial design model.

Table 3. ANOVA for PO_4^{3-} removal by IL-PP

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	2610.03	1118,32	2610.03	0.015
Linear	3	2500.19	2499.60	6667.18	0.009
pH (A)	1	320.05	959.50	2560.36	0.013
Adsorbent dose (B)	1	2120.96	6361.90	16967.67	0.005
Temperature (C)	1	59.19	177.40	473.50	0.029
2-Way Interactions	3	107.56	107.54	286.84	0.043
A*B	1	93.98	281.88	751.86	0.023
A*C	1	4.38	13.13	35.05	0.107
B*C	1	9.20	27.63	73.62	0.074
3-Way Interactions	1	2.27	6.77	18.15	0.147
A*B*C	1	2.27	6.77	18.15	0.147
Curvature	1	0.00	0.00	0.04	0.876
Error	1	0.13	0.02		
Total	9	2610.15			

Figure 2 shows the main effects of each parameter on PO_4^{3-} removal by IL-PP and thus helps to identify which parameters affect the response variable the most. A larger deviation is synonymous with a large effect [8]. Accordingly, adsorbent dose appears to have the greater effect on PO_4^{3-} removal by IL-PP, followed by pH and then temperature that has a negligible effect.

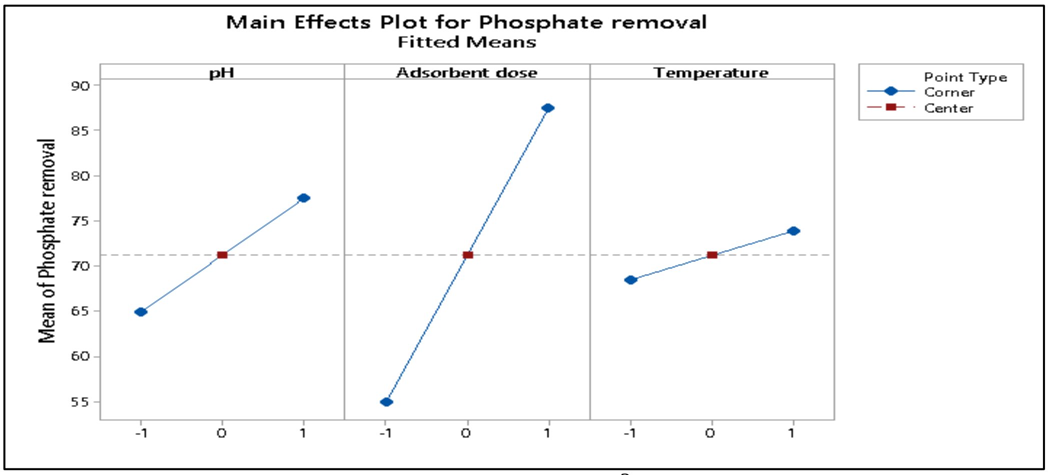

Figure 2. Main effects plot for PO_4^{3-} removal by IL-PP

Figure 3 plots the interactions of the studied parameters. If the interaction lines are not parallel, this implies that the interaction has a strong effect, whereas parallel interaction lines indicate a weak effect Interpretation of interaction plot implies that if the interactions lines are not parallel, the interaction under control is strong and vice versa [9]. The most important interaction for PO_4^{3-} removal by IL-PP appears to be (pH × adsorbent dose), followed by (adsorbent dose × temperature). The least important interaction was (pH × temperature), which had almost parallel interaction lines.

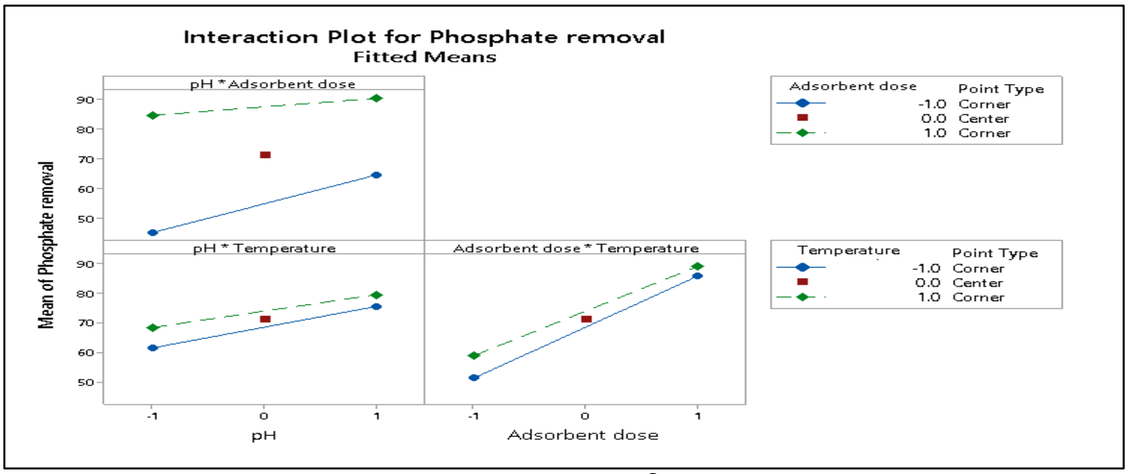

Figure 3. Interaction plot for PO_4^{3-} removal by IL-PP

A Pareto chart can be used to evaluate the significance of effects on the basis of how much they exceed the reference line [10]. Figure 4 shows that (A), (B), their interaction (AB), and (C) had a significant effect because their values exceeded that of the reference line (12.7, in red). However, the effects of interactions (B × C), (A × C) and (A × B × C) are not significant as their values didn't exceed the red line.

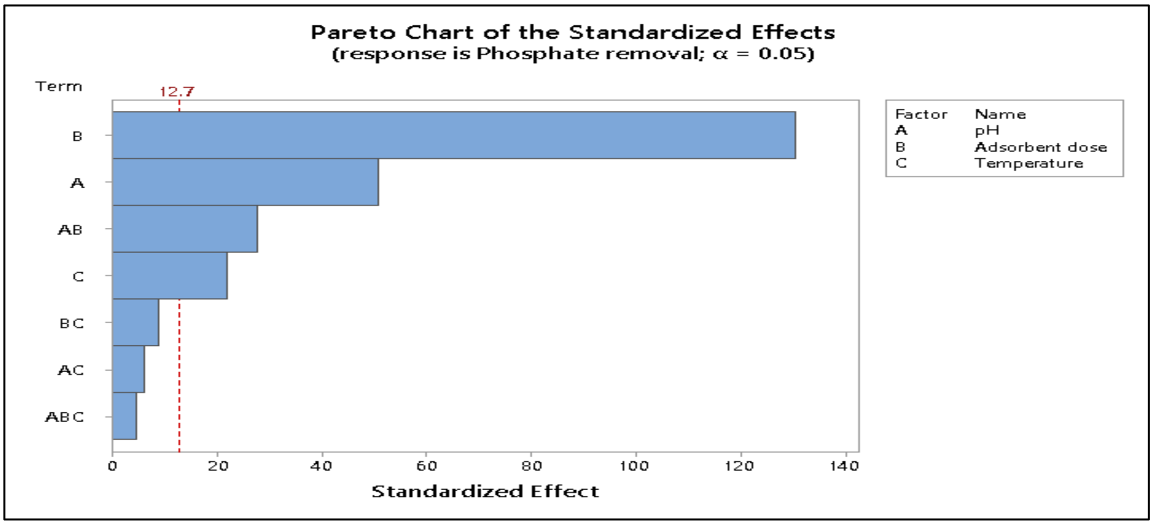

Figure *4*. Pareto chart of the standardized effects for PO_4^{3-} removal by IL-PP

The results of 2^3 factorial design have showed that pH (A), adsorbent dose (B), their interaction (AB), and temperature (C) are the factors with significant effect on the PO_4^{3-} removal from Na_2HPO_4 solution using IL-PP. On the other hand, the effect of temperature between high and low level was very weak and tends to be negligible (0.25%) when using optimum pH (9) and adsorbent dose (150 mg), therefore for technical and cost-effectivity reasons, a reduced model that take in consideration only the significant factors and neglect temperature is suggested. The new model is 2^2 factorial model with two factors (pH and adsorbent dose) at two levels and can be described using Eq. (2):

$$\text{Phosphate removal\%} = 71.19 + 6.33\,A + 16.28\,B - 3.43\,A \cdot B + 0.06\,Ct\,Pt \qquad (2)$$

Conclusion

The efficiency of IL-PP to remove PO_4^{3-} from aqueous solution was evaluated in this study. Results introduce IL-PP as an efficient bio-adsorbent which could be used in a green technology for wastewater treatment, waste biomass management and phosphate recovery.

Acknowledgements

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