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POTASSIUMFERRATE MODIFIED CHITOSAN SYNTHESIZED AS A NEW ADSORBENT FOR PV ADSORPTION: EXPERIMENTAL STUDY AND MODELLING ANALYSIS

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ABSTRACT
This research finding will be vital and useful in the development of low cost and environmental-friendly technology in the removal of harmful penicillin V from water using waste shrimp shells as adsorbent. The conversion of waste shrimp shells to adsorbent would undoubtedly serve as an economic solid waste management technique. This will immensely contribute to the sound sustainability of environment as one of the sustainable development goals (SDGs).The Chitosan was synthesized through the processes of demineralization, deproteination, and deacetylation and modified with potassium ferrate. Optimization of the adsorption processes using response surface. Methodology (RSM) with regards to the effect of adsorbent dosage, initial concentration, temperature, pH, and contact time was studied. The maximum removal was observed at 92.07% due to the higher concentration of 30mg/L and 0.8g dosage compared to minimum removal efficiency of 85.23% due to the lower dosage and concentration of 0.4g and 20mg/l. The findings of this study suggested that synthesized Chitosan can be applied successfully to remove PV from aqueous solutions.

Keywords: *chitosan, shrimp shells, adsorption and penicillin V.*

1.0 Introduction

Water is an essential component of life, both in terms of food production and population increase. Pharmaceutical wastewater is one of the most significant sources of pollution in emerging and underdeveloped countries. Textile, pharmaceutical, leather, food, plastic, rubber, cosmetics, and paper sectors all released diverse types of effluents. Antibiotics, synthetic dyes, and petroleum additives are all found in the aforementioned firms' effluent, and they have high molecular weights and complex chemical structures, making them non-biodegradable Pharmaceuticals are toxic and dangerous, and they must be removed from aquatic sources as soon as possible, or they will have a major detrimental influence on human health as well as the preservation of a diverse flora and aquatic animals (Adeyi, et al., 2018). In the past, wastewater treatment procedures such as anaerobic decomposition, membrane separation, precipitation, coagulation, and flocculation were extensively utilized for the treatment of effluents containing phenoxymethyl penicillin (PV-$C_{16}H_{18}N_2O_5S$), However, this method is quite costly, and it is not suitable for the treatment of big flows-industry effluents. Many studies have been conducted on the use of adsorbents, such as activated carbon, peat, chitin, rice husk, soy meal hull, and agro wastes as adsorbents. The adsorption capacity of the adsorbents, on the other hand, is insufficient to improve adsorption performance. Due to a variety of features,

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including their polyelectrolyte and cationic nature, the presence of reactive groups, high adsorption capabilities, and bacteriostatic and fungi-static impacts, chitosan is a viable bio-material for biotechnological enterprises. Shrimp shells, which are a waste, pollute the environment due to inappropriate disposal from the seafood sector. It would be a promising and effective technique to treat wastewater using chitosan adsorbents made from waste shrimp shells, and in this study, the applicability of chitosan adsorbents made from shrimp shells for the adsorptive removal of penicillin V from aqueous solution was evaluated.

2.0 METHODOLOGY:

(a) **Materials, reagents and chemicals**:
The shrimp shells used in this study were obtained from the University of Lagos lagoon and a local market in Lagos State, Nigeria. The shells were processed into powder. All chemicals are of analytical grade and were used as received. They include; Hydrochloric acid (HCl-37%) by Loba Chemie PVT.ltd, sodium hydroxide pellets (NaOH-97%) by Trust Chemical Laboratories, Potassium ferrate by Central Drug House(P) ltd, India. which were purchased from Top jay medical and science laboratory shop in Ado-Ekiti, Ekiti State, Nigeria.

(b) Equipment
The equipment used for this experimental work were obtained from the Chemical reaction laboratory, Afe Babalola University and National Research Institute, Zaria, Kaduna State, Nigeria. They include; electronic grinder, separating funnel, test tubes, conical flask, beakers, programmable Rheometer, muffle furnace, pH indicator (scale), Fourier transform infrared spectrometer, water bath, hot plate and Energy diffractometer.

2.1 Synthesis of Chitosan.

The shrimp shell wastes were thoroughly scrubbed, washed, cleaned and dried. The powdered shrimp shell was made to undergo demineralization, deproteinization and deacetylation processes to produce Chitosan. The details of the above three steps are discussed below:

2.1.1 Demineralization:

150g of shrimp shell powder was immersed in 500 ml HCl for a period of 24 hours at room temperature, and then the remaining powder was washed with distilled water till constant pH was attained. The resulting powder was sieved and then dried in the oven at 60 ^oC till constant mass was attained.

2.1.2 Deproteination:

The shell from demineralization was immersed in 1.0 M NaOH solution followed by boiling in water bath for 1hour to remove protein. The mixture was cooled at room temperature for 30 minute, sieved and washed with distilled water until it became neutral. Thereafter, it was dried in the oven at 60 ^{o} C till constant mass was attained.

2.1.3 Deacetylation:

The deacetylation (partial removal of acetyl groups from chitin) process was carried out by adding 1.0 M NaOH and boiling at a temperature of 120 ^{o} C for 2hours on a hot plate. The sample was cooled for 15minute at room temperature. After that, it was washed continuously with distilled water to get neutralized and filtered to retain its solid mater, which was the Chitosan. The resulting Chitosan was oven-dried at 60 ^{o} C till constant mass was attained.

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Figure 1.0 Prepared potassium ferrate modified chitosan (PMFC)

3.0 RESULTS AND DISCUSSIONS

3.1 Response surface methodology (RSM)

Response surface methodology (RSM) was used to optimize the removal percentage of PV. Besides, the impacts of each independent variables (pH, adsorbent dosage, initial concentration of adsorbate, temperature and time) on the removal efficiency of PV were determined. As obtained from the Taguchi design of experiments; a total of 16 experiments was conducted to check the influence of process parameters. The maximum removal was observed at 92.07% due to the higher concentration of 30mg/L and 0.8g dosage compared to minimum removal efficiency of 85.23% due to the lower dosage and concentration of 0.4g and 20mg/l. The central composite design of experiments is the regression model obtained from the software for future prediction of percentage removal of PV, the exactness of this model was determined by its degree of fitness of the experimental data as presented in table 1.0 below:

Table 1.0 The Taguchi design for the removal of PV

Run	dosage(g)	pH	Concentration mg/L	Temp t ^{0}C	Time (mins)	Absorbance	Ce (mg/l)	% Removal
1	0.2	3	10	25	20	0.789	1.211	87.89
2	0.2	9	40	55	80	1.764	3.867	90.33
3	0.8	9	10	45	40	0.759	1.129	88.71
4	0.2	7	30	45	60	1.235	2.426	91.91
5	0.6	9	20	25	60	1.135	2.153	89.23
6	0.6	5	40	45	20	1.618	3.469	91.33
7	0.4	9	30	35	20	1.265	2.507	91.64
8	0.6	3	30	55	40	1.359	2.764	90.79
9	0.4	7	40	25	40	1.534	3.240	91.90
10	0.4	3	20	45	80	1.429	2.954	85.23
11	0.8	7	20	55	20	1.156	2.211	88.95
12	0.2	5	20	35	40	1.128	2.134	89.33
13	0.8	5	30	25	80	1.218	2.379	92.07
14	0.4	5	10	55	60	0.675	0.900	91.00
15	0.6	7	10	35	80	0.842	1.355	86.45
16	0.8	3	40	35	60	1.569	3.336	91.66

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3.2 Model fitting and statistical analysis

3.2.1 Developed Model for Prediction

The mathematical model shows coefficients of each factor which could be used to determine the response at various experimental conditions.

$$\% \ Removal = 89.90 - 0.036A1 + 0.041A2 + 0.45A2 - 0.45A3 - 1.01B1 + 1.03B2 - 0.099B3 - 1.39C1 - 1.72C2 + 170C3 + 0.37D1 - 0.13D2 - 0.61D3 + 0.051E1 + 0.28E2 + 1.05E3 \quad \text{Equation} \quad (1)$$

A = Dosage, B = pH, C = Concentration, D = Temperature, E = Time

The experimental data fitness was used to determine correlation coefficient (R^2).A plot of experimental and predicted values against each other gave the R^2 value of 0.9179; R^2 value of close to 1 suggests better correlation between experimental and predicted data (Figure 2.0). This signifies that the model could represent approximately 92% of the dependent variables viability. This implies that less than 9% of the total PV removed could not be explained by the model.

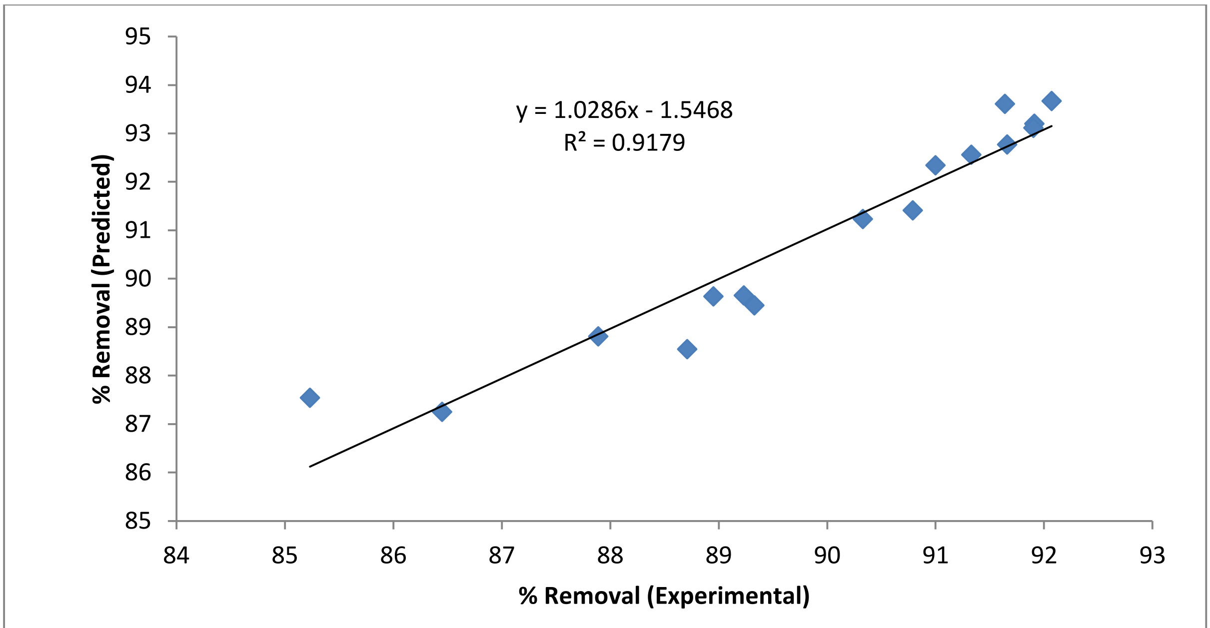

Figure 2. 0 predicted versus experimental percentage PV removal by PFMC.

3.2.2 Analysis of Variance (ANOVA) for the quadratic polynomial model

In ANOVA for selected factorial model the sum of square is classical. The obtained F-value of 11.69 implies that the model is highly significant as shown in Table 2.0. The P-value of 0.0071 is <0.05 indicating that the model term is significant and can be very good for the design of the model. However, the most significant model terms were X_4 and X_5,their prob>F values were less than 0.05.Their lack of fit was significant as F-value of 11.69 was recorded. This suggests that only 7.1% chance of large lack of fit F-value for the response could occur as a result of noise. Significant lack of fit is bad and thus, the model must fit adequately well. Also, the difference between the predicted R^2(=0.6718) and the adjusted R^2(=0.471)

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was 0.2 which signifies small difference between the two, signaling small block effect with developed model and data for the percentage PV removal. Finally, positive "Adeq precision" value was observed suggesting the current model was better predictor of the response than the overall mean. Adeq precision is a measure of signal to noise ratio which is desirable at a ratio greater than 4.Thus, a ratio of 6.370 indicates adequate signals.

Table 2. 0 ANOVA for % Removal Response Surface Quadratic Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2847.51	14	176.39	1.51	0.0341	
X_1 - Dosage	408.08	1	278.08	4.21	0.0380	
X_2 - pH	319.38	1	299.38	3.15	0.0564	
X_3 - Cconcentration	934.17	1	114.17	8.32	0.0143	
X_4 - Temperature	1020.22	1	120.22	16.39	0.0011	
X_5 - Time	1820.22	1	1850.22	16.39	0.0011	
X_1X_2	11.38	1	19.38	0.17	0.6821	
X_1X_3	3.57	1	6.57	0.06	0.8112	
X_1X_4	1.43	1	2.43	0.02	0.8645	
X_1X_5	3.43	1	2.43	0.02	0.8345	
X_2X_3	10.48	1	12.48	0.11	0.7321	
X_2X_4	11.43	1	15.43	0.14	0.7646	
X_3X_4	22.60	1	23.60	0.21	0.6215	
X_1^2	1.30	1	1.30	0.01	0.9754	
X_2^2	21.95	1	26.95	0.24	0.6295	
X_3^2	26.80	1	25.80	0.23	0.6368	
X_4^2	219.06	1	247.06	2.13	0.1647	
X_5^2	222.06	1	287.06	2.13	0.1647	
Residual	1646.00	15	111.07			
Lack of Fit	1597.66	10	159.77	11.69	0.0071	significant
R^2 = 0.9824	Adj R^2 = 0.4711		Pred. R^2 = - 0.6718	Adeq Precision = 6.370		

3.2.3. Effect of parameter interaction on penicillin V removal:

The 3D surface plot showing effects of parameter interactions of pH and dosage (Fig.3.0 a), pH and concentration (Fig.3.0 b), temperature and concentration (Fig.3.0 c), temperature and time (Fig.3.0d) time and dosage (figure3.0e), on penicillin V

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adsorption from aqueous solution using chitosan. A high level of complementary interactive effects was exhibited among the investigated factors at different levels for the adsorption process. The plots were executed via plotting any two independent variables against each other while other variables were held constant. All actual factors were kept constant as Level 1, such that pH, temperature, time, dosage and initial concentration values were 5, 298 K, 20 minutes, 0.8g/l and30mg/L, respectively. It was shown that the higher the initial concentration, the higher the percentage total removal of PV as revealed in figure 3.13(b and c), this affirmed that the initial concentration and PH were key factors in the removal of the PV by PFMC.Also, figure 3.0(a, and e) show that the higher the dosage, the higher the percentage PV removal though increased in temperature shows decrease but as the time is increased the percentage removal rises to 88.9% (figure 3.0 d). The percentage of penicillin V removed from aqueous solution was greater than 86% in each of the plots. This affirms the high efficiency of chitosan as an effective adsorbent for PV removal from aqueous solution.

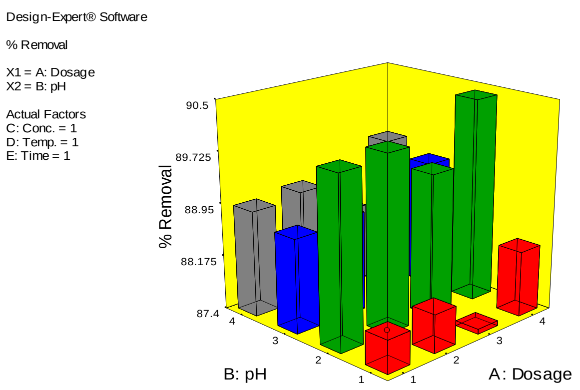

Figure 3.0(a)

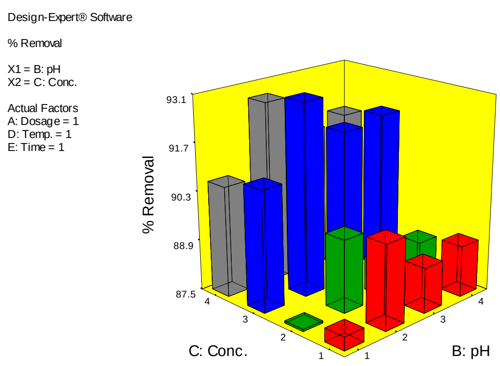

Figure3.0 (b)

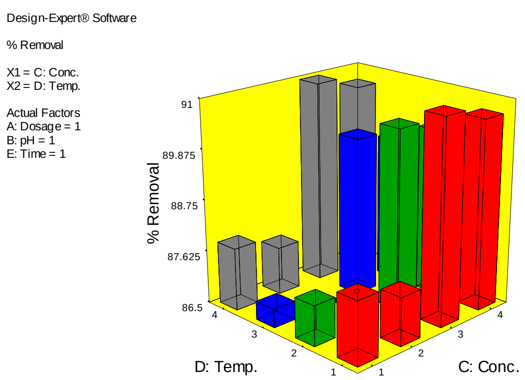

Figure3.0 (c)

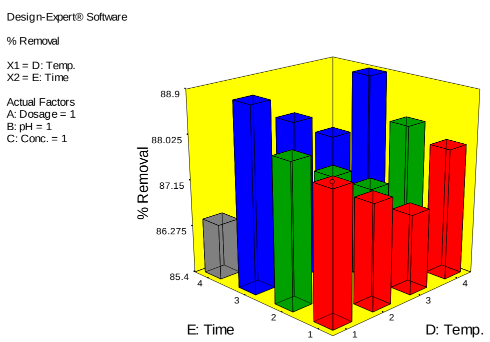

Figure 3.0(d)

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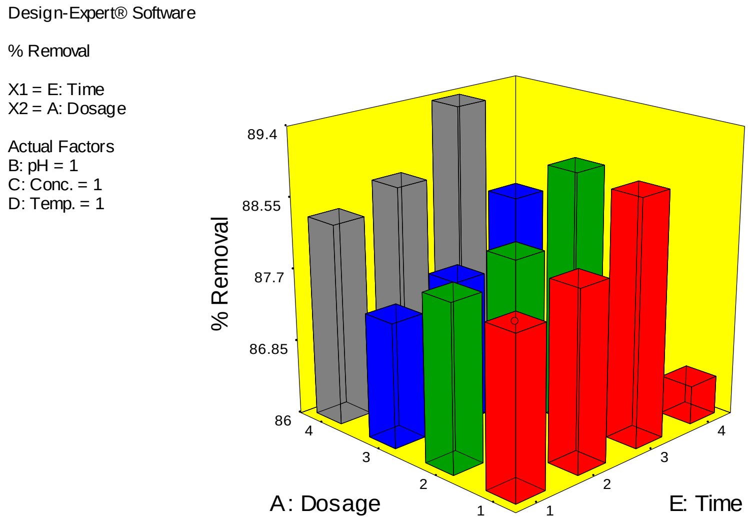

Figure 3.0 (e)

3.3. Optimization study from Response surface methodology

A re-run percentage removal of PV by PFMC laboratory experiment was conducted. Optimum point predicted by the central composite design of the design expert software was studied. This was to affirm the developed polynomial model accuracy and PFMC effectiveness to remove PV in the waste water. Optimum point prediction was observed at 93.50% while the laboratory result revealed 92.07%.A relative error of 1.43% between the values strongly indicated the accuracy of developed model to excellently predict influence of examined process parameters on the response.

Table 3. 0: Optimum Point Prediction and Validation for % Removal of PV

Factor	Name	Level	Pred.	Exp.
X_1	Dosage	0.8	93.50	91.78
X_2	pH	5		
X_3	Concentration	30		
X_4	Temperature	25		
X_5	Time	20		

4.0 CONCLUSION.

In conclusion, the present study has shown that shrimp shells can be used to produce chitosan adsorbent for the removal of penicillin (v) contaminant in the pharmaceutical effluent. Chitosan are amazing amino polysaccharides that have so many applications in several fields. They are found in abundance in nature as a renewable resource, especially in the exoskeleton of crustaceans, principally crabs and shrimps. Chitosan are biopolymers with interesting chemical and biological properties, such as biodegradability, biocompatibility, non-toxicity, and antibacterial and antimicrobial

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activities. For the adsorption of penicillin V antibiotics from pharmaceutical wastewater. The Optimum point prediction was observed at 93.50% while the laboratory result revealed 92.07%.A relative error of 1.43% between the values strongly indicated the accuracy of developed model to excellently predict influence of examined process parameters.

4.1 RECOMMENDATIONS

In view of the above results, I/we hereby recommend that shrimp shells can be used to produce low cost chitosan adsorbent for the removal of penicillin (V) in the industrial sewage. Further studies include investigating its effectiveness on other contaminants present in the industrial effluent. Other obstacles to overcome, includes:

(1)Future research can be focused on the production of long-lasting adsorbents using simple, low-cost, and easier-to-implement modification techniques.

(2) The need for innovative large-scale, low-cost chitosan-based adsorbents for real-world water treatment situations with numerous pollutants rather than just a single antibiotic contaminant.

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