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Effectiveness of Seafood Shells as Coagulants for the Treatment of Pharmaceutical Wastewater Using Box-Behnken Design

*Anho Lawrence Oghenerivwe, Anwukah Vincent Ifeanyi and Ambrose Onajite Akakabota
Department of Chemical Engineering
Federal University of Petroleum Resources, Effurun, Nigeria
*Corresponding Author: anho.lawrence@fupre.edu.ng

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ABSTRACT

This study evaluates a processed mixture of periwinkle and sea snail shells as an eco-friendly natural coagulant for maximizing Total Dissolved Solids (TDS) removal efficiency from pharmaceutical wastewater. Raw shells were washed, dried, ground, sieved, and characterized using Fourier Transform Infrared Spectroscopy (FTIR). Response Surface Methodology (RSM) via a 17-run Box-Behnken design optimized three parameters: coagulant dosage (1–10 g/L), settling time (30–120 min), and pH (5–9). Statistical analysis revealed settling time as the most dominant factor for TDS reduction, followed by dosage and pH. The derived quadratic predictive model demonstrated exceptional accuracy (R^2 = 0.9936). Three-dimensional response plots showed optimal TDS removal at 7–9 g/L dosage and 90–120 min settling time under neutral-to-slightly alkaline conditions (pH 7–8). Numerical optimization established optimal operating parameters at a dosage of 4.39 g/L, settling time of 98.55 min, and pH of 6.39, successfully minimizing initial TDS content. Therefore, processed seafood shells served as highly viable, biodegradable alternatives to hazardous commercial chemical coagulants. This research validates RSM as a robust framework for parameter optimization, providing a cost-effective, sustainable strategy for industrial pharmaceutical effluent remediation

Keywords: optimization, periwinkle and snail shells, eco-friendly coagulant, pharmaceutical wastewater

INTRODUCTION

Water purifies itself through sedimentation, biochemical breakdown, and dilution, processes that depend on a fragile balance of physical deposition, hydrological dilution, and microbial activity [1-5]. These mechanisms require time and can be overwhelmed when pollutant loads exceed an ecosystem's coping capacity, causing rapid water-quality decline [5-7].

Industrial activity, especially pharmaceutical manufacturing, releases hazardous effluents, often intensely colored and odorous, that threaten aquatic ecosystems and public health [8,9].

Wastewater, or effluent, is the liquid byproduct of industrial processes and varies widely with technology, raw materials, and utilities used. It may include saline streams, wash water, runoff, and acid or alkaline neutralization discharges [10]. Pollution sources are either point sources, single identifiable outlets like discharge pipes, which are easier to monitor, or diffuse sources like agricultural runoff, which are harder to control and require robust land-use measures.

Key pollutants encompass pathogens, oxygen-demanding wastes, synthetic chemicals, microplastics, and heavy metals, all harmful to water quality and aquatic life [11]. Wastewaters are broadly domestic, industrial, or storm-related. Domestic sewage is mostly water with organic impurities and pathogens, industrial sewage contains production-specific chemicals, and storm sewage carries high suspended solids and urban contaminants [11]. Primary indicators of wastewater quality include organic load, measured by biochemical oxygen demand (BOD), and suspended matter. High BOD indicates severe organic pollution. Nutrient loads of nitrogen and phosphorus drive eutrophication, depleting dissolved oxygen and creating septic conditions.

Pharmaceutical wastewater is particularly problematic because active pharmaceutical ingredients (APIs), solvents, and complex organics resist conventional treatments, persist in the environment, and can promote antibiotic-resistant bacteria [12].

Coagulation is a proven primary treatment method. Coagulants neutralize particle charges, allowing colloids to aggregate into flocs for sedimentation [9]. Conventional inorganic coagulants like alum and ferric salts are effective but raise environmental and health concerns due to toxic sludge and residual metals. This has driven research into biodegradable, eco-friendly alternatives from waste biomass. Shell wastes from gastropods, periwinkle, sea snails, and crabs are promising sources of bio-coagulants for treating complex pharmaceutical effluents sustainably [13,14].

Optimized chemical coagulation-flocculation systems can achieve substantial removals. Quintero et al. [15] reported up to 95% colour and 63% Chemical Oxygen Demand (COD) reduction, while single-material bio-coagulants often yield modest results without stabilization or optimization [16,17]. Proper dosing and pH control improved performance for neem and banana leaf powders in dairy effluent, remove 65% turbidity [18].

This study aims to identify the optimal conditions for maximizing TDS removal efficiency using a Box-Behnken design. The objectives are: (i) obtain functional bio-coagulants through the processing and calcination of regional seafood wastes (periwinkle and snail shells). (ii) characterize pharmaceutical wastewater, (iii) analyze coagulant composition and functional groups, (iv) evaluate effects of pH, dosage, and settling time on TDS removal, and (iv) optimize conditions using a Box-Behnken RSM design.

MATERIALS AND METHODS

The pharmaceutical wastewater effluent sample was collected from an industrial production facility in Benin City, Edo State, Nigeria. Seafood waste materials, periwinkle (*Tympanotonus fuscatus*) and snail shells were sourced from the New Benin Market. The chemicals/reagents for this experiment were of high analytical grade are as follows:

- Hydrochloric acid; 98% pure, produced by Fisons, Loughborough, England
- Phenolphthalein indicator; produced by Kermel Chemicals Reagent Company, Ltd, Tianjin, China.
- Sodium hydroxide; 96% pure, produced by CDH, New Delhi, India
- Buffer solution; 99.0% pure, produced by Spectrum Chemical MGF Corp, California and New Jersey, U.S.A.

Other specific instruments are presented in Table 1:

T able 1: Instruments and Apparatus used during the course of this experiment;

S/n	Property Instrument and manufacturer
1	Weighing balance AND (A&D) FX-3000i electronic balance, Hanoi, Vietnam
2	Functional groups FTIR-8400S, Shimadzu, Japan
3	Spectrophotometer Model 530 Infrared Spectrophotometer, Buck Scientific Instruments, LLC, United States (Hand-built in Norwalk/Ansonia, Connecticut)
4	pH Meter / TDS & EC Meter / Salinity Meter HI98192 (for EC/TDS/Salinity) and HI98191, Hanna Instruments, Romania / United States.
5	Turbidimeter 2100Q Portable Turbidimeter, Hach Company, United States (Loveland, Colorado)
6	Oven (Drying Oven) Heratherm General Protocol Oven, Thermo Fisher Scientific, Germany

Preparation of Coagulant

Washing and Drying of the Seafood Shells

The harvested shells were washed with clean tap water and distilled water to remove dirt, mud, flesh residues, and organic impurities. The washed shells were then dried in a laboratory oven at 105 °C for 24 h to eliminate all internal moisture, a crucial step to inhibit microbial activity and embrittle the matrices for efficient mechanical pulverization. This thermal drying phase matches baseline conditioning standards for raw biowaste precursors before chemical or thermal activation [19].

Grinding, Calcination, and Sieving

Following drying, the shell matrices were mechanically crushed and ground into a fine powder using a laboratory pulverizer. The resulting powder was then calcined in a muffle furnace at elevated temperatures to convert $CaCO_3$ into highly reactive CaO, which significantly enhances coagulation. The calcined powder was passed through a standard 150 sieve to guarantee a uniform particle size distribution, optimizing specific surface area and particle reactivity during subsequent treatment runs [8].

Characterization of the Pharmaceutical Wastewater

The baseline physicochemical properties of the crude pharmaceutical wastewater, including pH, TDS, Electrical Conductivity (EC), Salinity, Turbidity, and Dissolved Oxygen (DO), were determined using standard water analysis meters. These parameters established the framework required to assess subsequent coagulation and filtration efficiencies via RSM [20].

Physicochemical Characterization of Wastewater Effluents

To establish the characteristics of the pharmaceutical wastewater (PWW), a comprehensive suite of physicochemical parameters, including pH, EC, TDS, salinity, turbidity, and DO, was systematically evaluated [21]. The analytical procedures were based on the *Standard Methods for the Examination of Water and Wastewater* [22]. Because of the volatile and chemically reactive nature of pharmaceutical matrices, electrochemical parameters and DO were quantified immediately on-site upon sample collection to prevent artefacts arising from biological activity or temperature shifts during transport [23].

Potentiometric determination of pH was achieved using a calibrated digital pH meter (Model HI98191, Hanna Instruments) following a rigorous three-point calibration against standard

reference buffers pH 4.01, 7.01, and 10.01 [24]. Simultaneously, a benchtop conductivity meter (Model Seven Compact, Mettler Toledo) equipped with a platinum four-pole cell was utilized to measure EC and salinity [25]. To ensure data reproducibility across varying ambient conditions, the instrument automatically normalized all EC readings to a reference temperature of 25 °C, as shown in Table 2.

Given the high concentration of mobile organic and inorganic constituents typical of pharmaceutical streams, TDS was determined gravimetrically using APHA Method 2540 C (25). A well-mixed 100 mL sample aliquot was filtered through a 1.2 μm glass-fibre filter (Whatman GF/C) to remove suspended matter. The remaining filtrate was then transferred to a pre-weighed porcelain dish, evaporated to dryness, and thermally cured in a laboratory oven at 180 $\pm$ 2 °C until a constant weight was achieved ($\pm$0.5 mg) as presented in Table 2.

Optical characteristics were monitored via the nephelometric method using a Hach 2100Q turbidimeter [26]. Samples were analyzed in optical glass cuvettes, measuring the light scattered at a 90 ° angle relative to the incident beam against certified Formazin standards to yield values in Nephelometric Turbidity Units, as presented in Table 2 [27].

DO concentrations were mapped using a luminescent dissolved oxygen meter (HQ40D, Hach) equipped with an optical sensor (LDO101) calibrated via water-saturated air [21].

To safeguard against potential optical or chemical interferences from complex pharmaceutical surfactants or solvents, the digital probe results were periodically cross-verified using the classic azide-modified Winkler titration method (APHA Method 4500-O C) as presented in Table 2.

Characterization of the Seafood Shells

FTIR Analysis

The surface functional groups and structural bonds governing the performance of the shell-derived coagulant blend were investigated using a Buck Scientific Infrared Spectrophotometer (Model 530, Buck Scientific, USA) scanning within the mid-infrared range of 4000 to 400 cm^{-1}. Analyzing the composite periwinkle and snail shell matrix via FTIR allows researchers to confirm the presence of key surface functional groups, such as –OH and carbonate linkages, which provide active adsorption and charge-neutralization sites during the flocculation process [19].

Experimental Setup and Parameter Adjustment

The sieved, calcined powder blend was precisely weighed out into distinct portions to execute the 17 independent experimental runs dictated by the Box-Behnken design matrix. RSM was employed to systematically model and evaluate the individual and interactive effects of coagulant dosage, settling time, and system pH on maximum contaminant reduction [20].

pH Measurement and Adjustment

The raw pharmaceutical wastewater sample exhibited an initial pH of 6.80. To examine how solution chemistry influences the natural coagulation mechanism, the effluent samples were adjusted to test pH boundaries at acidic (pH 5) and alkaline (pH 9) levels. Adjustments were made by dropwise addition of 0.1M HCl to lower the pH or 0.1M NaOH to raise it. Maintaining precise control over system pH is critical, as solution acidity or alkalinity fundamentally alters the surface charge characteristics of natural shell coagulants, with slightly alkaline boundaries often accelerating floc formation [8].

Coagulation and Separation

Preparation of Coagulant Mixture

Measured quantities of the pulverized periwinkle and snail shell powder blend were introduced into a series of 1000 mL glass beakers containing the corresponding wastewater volumes according to the requirements of the Box-Behnken design matrix

Agitation and Settling

To initiate coagulation, the wastewater-shell mixture was subjected to rapid mechanical agitation on a laboratory jar tester/shaker apparatus for 10 minutes [28]. This controlled agitation phase promotes rapid particle-coagulant collision and subsequent bridging [29]. Following agitation, the suspension was left undisturbed to settle, allowing the newly formed dense particulate flocs to precipitate out of the liquid phase under gravity [30].

Filtration and Analysis

Following the designated settling period, the supernatant liquid layer was carefully decanted and cleared of residual macro-flocs via filtration through Whatman No. 1 filter paper. The resulting treated filtrate was immediately collected and subjected to analytical testing to measure residual TDS, Turbidity, and DO values, validating the overall removal efficiency of the natural shell coagulant blend [20].

Testing Parameters

The treated wastewater filtrate was analyzed for TDS, turbidity, and DO to evaluate the overall treatment and contaminant removal efficiency of the shell-derived bio-coagulant. Monitoring these specific parameters aligns with standard regulatory frameworks for industrial effluent discharge and follows established protocols for environmental water quality assessment [10,22]

RESULTS AND DISCUSSION

The wastewater was characterized to determine physical and chemical properties, including pH, TDS, turbidity, and DO (Table 2). These parameters are crucial for evaluating treatment efficiency.

Table 2: Physicochemical properties of Untreated and Treated Pharmaceutical Wastewater

Property	Untreated P. W	Treated P.W (Optimized)
pH	6.80	7.40
TDS (mg/L)	2484	1392
Salinity (ppt)	2.96	1.40
E.C. (μS/cm)	4906	2770
Turbidity (NTU)	9.60	1.20
DO (mg/L)	2.67	4.85

This characterization and optimization framework aligns with established practices in studies that utilize RSM to model and optimize coagulation processes [31,32].

The raw effluent exhibited a heavy pollutant load, characterized by a high initial total dissolved solids concentration of 2484 mg/L and a correspondingly high EC of 4906 μS/cm. These elevated baselines are typical of industrial pharmaceutical discharges, which often carry high concentrations of dissolved chemical processing salts, active ingredients, and inorganic ions. This intense chemical presence is further highlighted by a depressed dissolved oxygen level of 2.67 mg/L, indicating a heavily strained aquatic environment.

Following treatment with the processed seafood shell bio-coagulant, a significant reduction in the overall pollution matrix was achieved. The TDS concentration dropped by 43.9% down to 1392 mg/L. This sharp decrease suggests that active functional groups within the shell matrix, such as chitin-derived amine and hydroxyl units, effectively destabilized the dissolved particles through charge neutralization and polymer bridging, pulling them out of solution into heavy, settleable

flocs as shown in Table 3. This mechanism is mathematically validated by the simultaneous reductions observed in electrical conductivity (from 4906 to 277μS/cm) and salinity (from 2.96 to 1.4 ppt), as both parameters directly correlate with the density of ionized dissolved solutes. Furthermore, the mild shift in pH from a slightly acidic 6.8 to a neutral 7.2 is highly advantageous. It demonstrates that the natural coagulant avoids the post-treatment acidification typical of commercial chemical alternatives, eliminating the need for expensive neutralizing agents before effluent discharge, as presented in Table 3.

Table 3: Comparative Physicochemical Profiles and Effluent Treatment Efficiency

Water Quality Parameter	Untreated Industrial Effluent	Post-Treatment Optimized State	Net Preservation / Removal Efficiency
pH	6.80	7.40	Normalized to Neutral
Total Dissolved Solids	2484 mg/L	1392 mg/L	43.96% Reduction
Salinity	2.96 ppt	1.40 ppt	52.70% Reduction
Electrical Conductivity	4906 μS/cm	2770 μS/cm	43.54% Reduction
Turbidity	9.60 NTU	1.20 NTU	87.50% Reduction
Dissolved Oxygen (DO)	2.67 mg/L	4.85 mg/L	81.65% Re-oxygenation Increase

The experimental steps and procedures were followed to achieve the results, which show the experimental runs with the combined effect of the three different variables of coagulant dosage, settling time and pH on the removal efficiency of TDS. Using a model, a Box-Behnken Design. In this study, 17 experimental runs were carried out. The experiments were conducted at random to prevent systematic errors. The experimental results are presented in Table 4.

Table 4: Experimental Design matrix and Total dissolved Solids removal efficiency results for the optimization of pharmaceutical wastewater coagulation using Box-Behnken Design

	Coagulation dosage (g/L)	Settling Time (minutes)	pH	Total Dissolved Solids
1	10	75	5	3548
2	5.5	75	7	2995
3	10	120	7	3478
4	10	75	9	3204
5	5.5	75	7	2895
6	1	30	7	4013
7	5.5	75	7	2895
8	5.5	120	9	3161
9	5.5	120	5	3082
10	1	75	5	3174
11	1	120	7	3062
12	5.5	75	5	2895
13	5.5	30	7	3870
14	5.5	75	7	2895
15	5.5	30	9	3639
16	1	75	9	3222
17	10	30	7	3790

Characterization of the Seafood Shells

FTIR analysis

FTIR was used to identify key organic and inorganic functional groups in the shell-derived coagulant that drive the wastewater treatment process. The spectral peaks revealed a highly reactive surface with distinct roles in pollutant removal. FTIR spectra obtained are shown in Figures 1-3.

Organic Groups (Adsorption Sites): Peaks at 3474.90 cm^{-1} (O-H stretching) and 2922.15 cm^{-1} (C-H stretching) indicate hydroxyl and aliphatic groups, which provide hydrophilic binding properties. The peak at 1531.54 cm^{-1} (N-H bending) suggests amine groups or proteins, while 1081.85 cm^{-1} (C-O stretching) points to polysaccharides; both enhance coagulation through their chemical binding capabilities.

Inorganic & Carbonate Groups (Charge-Neutralization): Peaks around 2521.02 cm^{-1} and 1786.53 cm^{-1} (C=O stretching), alongside lower-frequency fingerprint peaks at 707.34 cm^{-1} and 416.54 cm^{-1}, confirm a heavy presence of carbonates and calcium-rich inorganic structures.

The FTIR spectrum proves the material acts via a dual mechanism: the organic groups act as active adsorption sites to catch complex pharmaceutical compounds, while the inorganic carbonate components provide the necessary surface charges to neutralize and settle suspended particles.

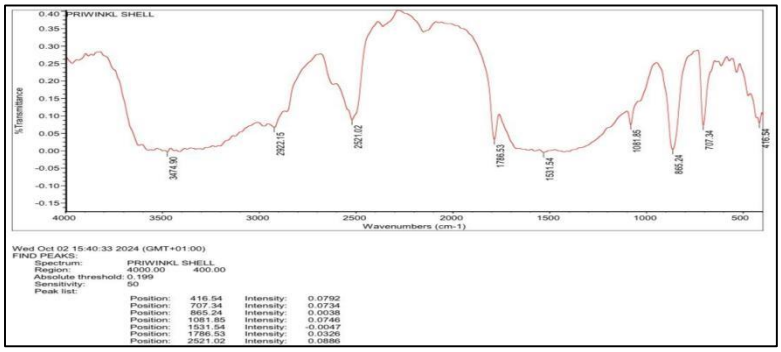


Figure 1: FTIR for seafood shells (A)

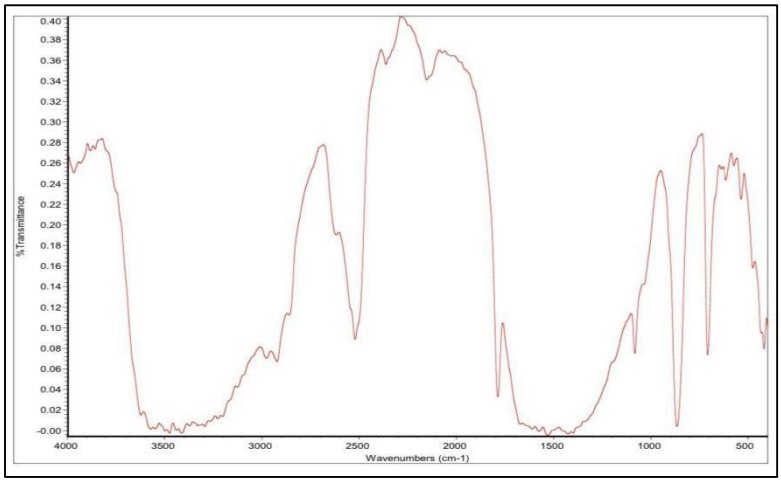
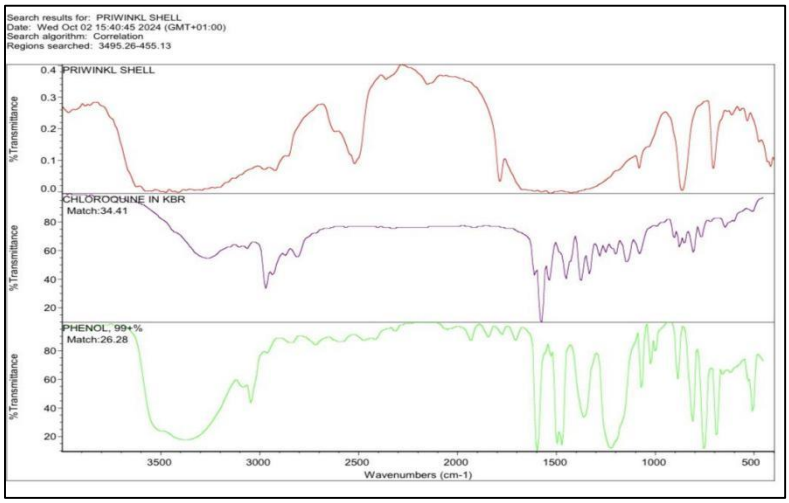
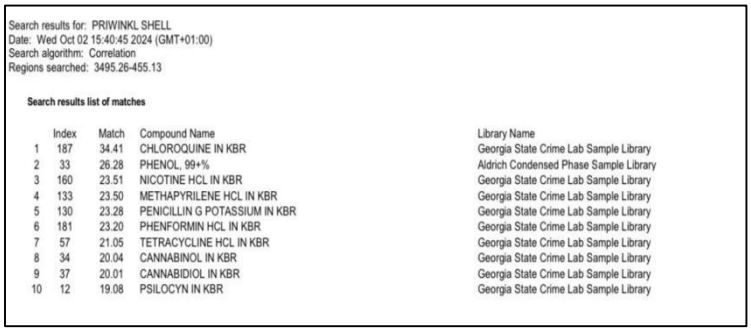


Figure 2: FTIR for seafood shells (B)





Search results for: PRIWINKL SHELL
Date: Wed Oct 02 15:40:45 2024 (GMT+01:00)
Search algorithm: Correlation
Regions searched: 3495.26-455.13

Search results list of matches

	Index	Match	Compound Name	Library Name
1	187	34.41	CHLOROQUINE IN KBR	Georgia State Crime Lab Sample Library
2	33	26.28	PHENOL, 99+%	Aldrich Condensed Phase Sample Library
3	160	23.51	NICOTINE HCL IN KBR	Georgia State Crime Lab Sample Library
4	133	23.50	METHAPYRILENE HCL IN KBR	Georgia State Crime Lab Sample Library
5	130	23.28	PENICILLIN G POTASSIUM IN KBR	Georgia State Crime Lab Sample Library
6	181	23.20	PHENFORMIN HCL IN KBR	Georgia State Crime Lab Sample Library
7	57	21.05	TETRACYCLINE HCL IN KBR	Georgia State Crime Lab Sample Library
8	34	20.04	CANNABINOL IN KBR	Georgia State Crime Lab Sample Library
9	37	20.01	CANNABIDIOL IN KBR	Georgia State Crime Lab Sample Library
10	12	19.08	PSILOCYN IN KBR	Georgia State Crime Lab Sample Library

Figure 3: FTIR for seafood shells (C)

Model Fitting and Analysis of Variance (ANOVA) for TDS Removal

The ANOVA results indicated that the model was significant in predicting TDS removal. The Analysis of Variance confirms that the developed quadratic model is highly significant (F-value = 121.11$, $p < 0.0001$). The **Lack of Fit** ($p = 0.4839$) is not statistically significant, indicating that the model fits the experimental data well. The ANOVA results are shown in Table 5.

Table 5: TDS ANOVA for quadratic model

Source	Sum of Squares	DF	Mean Square	F-Value	P-Value	
Model	2.167E+06	9	2.407E+05	121.11	< 0.0001	Significant
A-Coagulant dosage	37675.13	1	37675.13	18.95	0.0033	

B-Settling time	7.995E+05	1	7.995E+05	402.20	< 0.0001	
C-pH	25088.00	1	25088.00	12.62	0.0093	
AB	1.021E+05	1	1.021E+05	51.35	0.0002	
AC	38416.00	1	38416.00	19.33	0.0032	
BC	24025.00	1	24025.00	12.09	0.0103	
A^2	2.844E+05	1	2.844E+05	143.06	< 0.0001	
B^2	7.108E+05	1	7.108E+05	357.60	< 0.0001	
C^2	52934.80	1	52934.80	26.63	0.0013	
Residual	13914.25	7	1987.75			
Lack of fit	5914.25	3	1971.42	0.9857	0.4839	Not significant
Pure error	8000.00	4	2000.00			
Cor total	2.181E+06	16				

Factor Coding is coded

The Sum of Squares is Type III Factors, such as Coagulant dosage, settling time and pH, were statistically significant.

Fit summary

The fit summary describes how well the model explains the variation in the answer. Key measures, including R-squared, Adjusted R-squared, and Predicted R-squared, demonstrate the model's accuracy and predictive capabilities, with higher values indicating a better fit. Moreover, p-values for each term show which factors and interactions have a substantial impact on the response, guiding improvements for better model accuracy and relevance. The Fit summary is shown in Table 6.

Table 6: Fit Statistics

R^2	Adjusted R^2	Predicted R^2	Adeq Precision	Std. Dev.	Mean	C.V. %
0.9936	0.9854	0.9509	31.5355	44.58	3283.41	1.36

The model displays exceptional predictive capacity and reliability based on its fit statistics:

- **R^2 = 0.9936$:** The model explains 99.36% of the variability in TDS removal.
- **Adjusted R^2= 0.9854 & Predicted R^2= 0.9509:** The close agreement between these values (difference < 0.2) indicates excellent predictive power for new observations.
- **Adequate Precision = 31.54:** Far exceeding the minimum desirable threshold of 4, confirming a strong signal-to-noise ratio.
- **Coefficient of Variation (C.V. %) = 1.36%:** Demonstrates high experimental precision and reproducibility.
- **Regression Equation for TDS Removal**

  The final predictive mathematical model, expressed through the coded regression equation, is presented below: TDS = +2915.00 + 68.63A - 316.12B - 56.00C + 159.75AB - 98.00AC + 77.50BC + 259.87A^2 + 410.87B^2+ 112.13C^2

The final quadratic model equation in terms of coded factors for predicting TDS is presented in Table 7:

Table 7: Final equations in terms of coded factors

TDS = +2915.00	
A	+68.63
B	-316.12
C	-56.00
AB	+159.75
AC	-98.00

BC	+77.50
A^2	+259.87
B^2	+410.87
C^2	+112.13

The regression equation indicates that settling time (B) has the strongest influence on TDS removal, as seen by the large negative coefficient (-316.12). Coagulant dosage (A) and pH (C) also impact TDS removal, but their effects are less pronounced. The positive interaction between coagulant dosage and settling time (AB = 159.75) suggests that optimizing these parameters together leads to enhanced TDS reduction, as shown in Table 7

Factor Effects

Coagulant Dosage

From Table 7, the results show that increasing the coagulant dosage from 1 g/L to 10 g/L leads to a decrease in TDS, as indicated by the positive linear coefficient of 68.63. However, the non-linear (quadratic) term A^2, with a significant positive coefficient of 259.87, suggests diminishing returns at higher dosages. This is likely due to the saturation of active binding sites, beyond which further addition of coagulant may not improve TDS removal efficiently.

Settling Time

Settling time was found to have the most significant effect on TDS removal, with a high F-value of 402.20. The negative linear coefficient of -316.12 indicates that increasing the settling time from 30 minutes to 120 minutes significantly reduces TDS. However, the positive quadratic term B^2 (410.87) suggests that there is an optimal settling time beyond which the efficiency plateaus or even worsens. This could be attributed to re-suspension or re-aggregation of particles after an optimal time, as presented in Table 7.

pH

From Table 7, pH also had a significant but less pronounced effect on TDS reduction. The linear coefficient of -56.00 suggests that a decrease in pH (from 9 to 5) slightly improves TDS removal. The quadratic term C^2 (112.13) suggests a nonlinear relationship, with an optimal pH range where

TDS removal is maximized. This is likely because pH influences the charge and solubility of particles in the wastewater, thus affecting coagulation efficiency.

Interactions Between Factors

The significant interaction between coagulant dosage and settling time (AB = 159.75) indicates that their combined effect is greater than their individual contributions. This suggests that adjusting both factors simultaneously can lead to improved TDS removal. The negative interaction between coagulant dosage and pH (AC = -98.00) suggests that increasing coagulant dosage at higher pH levels may reduce efficiency. Conversely, the positive interaction between settling time and pH (BC = 77.50) suggests that a higher settling time improves TDS removal at different pH levels, as shown in Table 7.

Model Validation

An accuracy check is indispensable to get an adequate model. The model accuracy was checked by comparing the predicted and experimental TDS values. Figure 4 shows the linear relationship between them. The straight line means that no response transformation was required, and there was no apparent problem with normality.

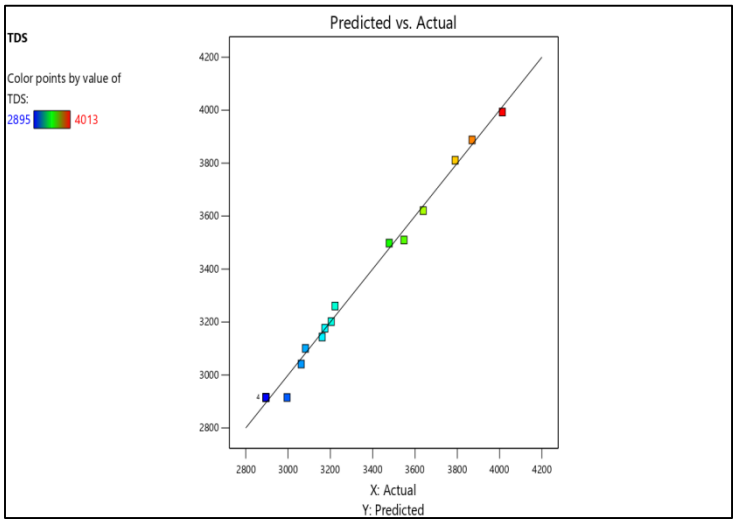


Figure 4: Predicted Vs actual total dissolved solids values for pharmaceutical wastewater treatment.

Response Surface and Contour Plots

To visualize how the process variables, interact and influence the response, 3-D surface plots and their corresponding contour plots are presented in Figures 5 to 8. These plots offer a clear picture of how the experimental design behaves across the tested design space, with the peaks visible in the 3-D plots pinpointing the conditions that produce the highest response values.

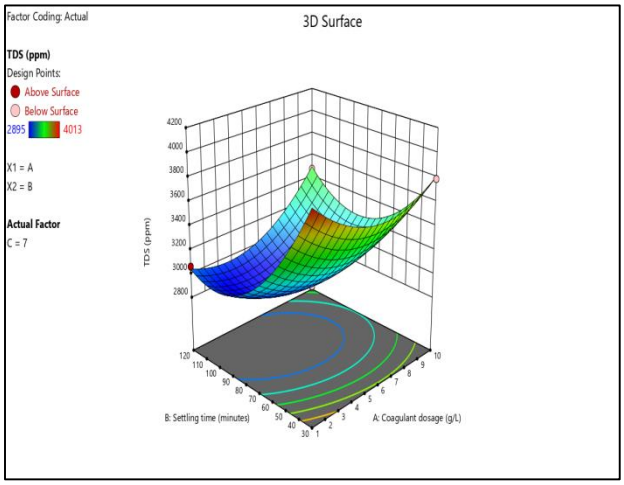


Figure 5: 3D Response surface plot showing the interaction between coagulant dosage and settling time on TDS removal

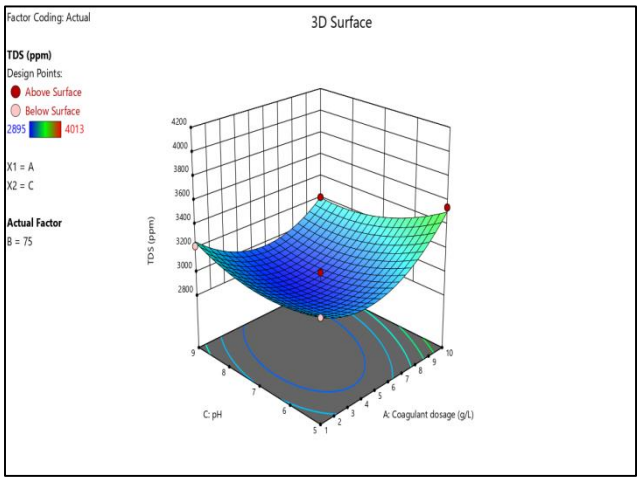


Figure 6: 3D Response surface plot showing the interaction between coagulant dosage and pH on TDS removal**.**

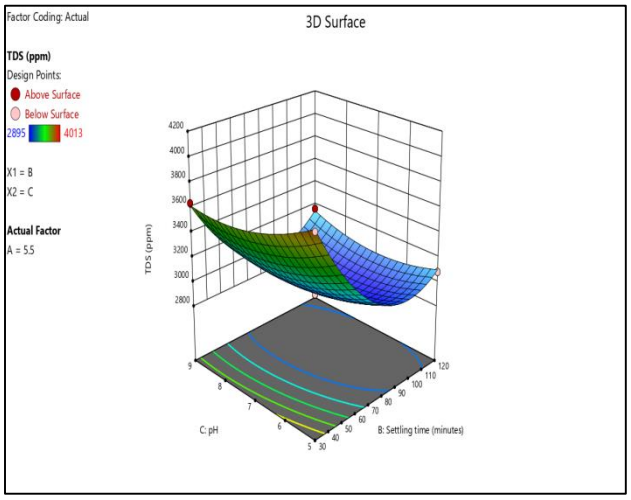


Figure 7: 3D Response surface plot showing the interaction between TDS, pH and Settling Time.

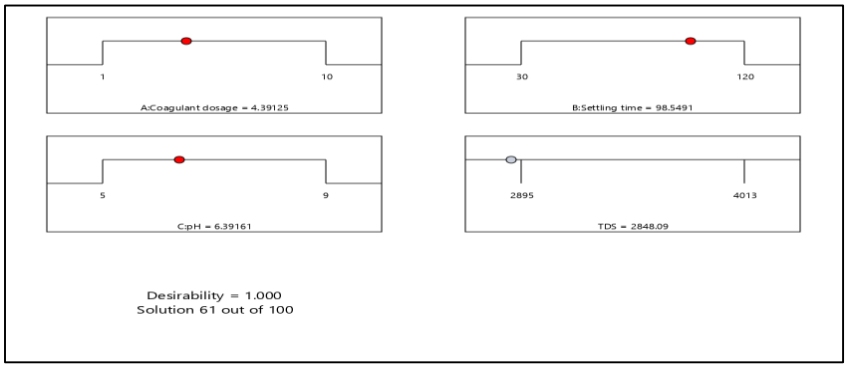


Figure 8: Showing the Ramp plot for the optimization.

The set of four individual plots above represents the optimized solution for the parameters involved in the study. Each plot illustrates the range of the respective factor:

- (A) Coagulant dosage is optimized at 4.39125 g/L.
- (B) Settling time is near its upper limit, at 98.5491 minutes.
- (C) pH is set at 6.39161 for optimal performance.
- (D) TDS is minimized at a value of 2848.09 ppm.

A desirability score of 1.000 confirms that the identified conditions represent the best possible outcome for TDS reduction while keeping operational parameters balanced. The results clearly show that RSM is a reliable and effective tool for optimizing pharmaceutical wastewater treatment using natural coagulants. The three variables tested, settling time had the greatest influence on

performance, followed by coagulant dosage and pH. The quadratic model proved highly accurate, with an R^2 of 0.9936, meaning it accounts for 99.36% of the variation in TDS removal. In practical terms, carefully tuning these three parameters within the tested ranges is sufficient to achieve efficient and consistent treatment outcomes.

CONCLUSION

This study puts the circular economy into real-world practice by repurposing discarded seafood shells, specifically periwinkle *(Tympanotonus fuscatus)* and snail shells, as an eco-friendly bio-coagulant for treating industrial pharmaceutical wastewater. The raw effluent was heavily polluted: EC stood at 4,906 µS/cm, DO was low at 2.67 mg/L, and TDS reached 2,484 mg/L. After optimized treatment, conditions improved significantly, and EC dropped to 2,770 µS/cm, DO rose to 4.85 mg/L, and TDS fell to 1,392 mg/L. FTIR analysis confirmed that calcinating the shells produces a highly reactive biopolymer surface that cleans water through two complementary mechanisms. On the organic side, surface functional groups, including O–H at 3,474.90 cm^{-1}, C–H at 2,922.15 cm^{-1}, and N–H at 1,531.54 cm^{-1}, act as active sites that capture complex pharmaceutical compounds. On the inorganic side, dominant C=O at 2,521.02 cm^{-1} and 1,786.53 cm^{-1}) generate surface charges that drive charge neutralization and coagulation. RSM using a 17-run BBD was used to model the interactions among process variables. ANOVA confirmed the quadratic model was highly significant (F-value = 121.11, $p < 0.0001$), with a non-significant Lack of Fit, and excellent predictive performance ($R^2 = 0.9936$, Adjusted $R^2 = 0.9854$, Predicted $R^2 = 0.9509$). The resulting regression equation is:

$$TDS = +2915.00 + 68.63A - 316.12B - 56.00C + 159.75AB - 98.00AC + 77.50BC + 259.87A^2 + 410.87B^2 + 112.13C^2$$

Among the three factors tested, settling time (B) had the greatest influence on clarification (F-value = 402.20), followed by coagulant dosage (A) and solution pH (C). Notably, the positive quadratic terms for both dosage (A^2) and settling time (B^2) point to non-linear behaviour: too much coagulant saturates the available binding sites, while excessively long settling times can cause particle re-suspension due to shear stress. These findings highlight the importance of optimizing each variable rather than simply maximizing them.

Recommendations

Building on this study's findings, four key directions stand out for future work. First, the process should be scaled up from lab beakers to continuous-flow pilot systems that reflect real industrial conditions. Second, adding a secondary polishing step, such as activated carbon from agricultural waste, would help bring the residual TDS (1,392 mg/L) down to regulatory standards. Third, the nutrient-rich sludge left after treatment could be explored as a soil conditioner or building material. Finally, a formal cost and life cycle assessment would quantify the economic and environmental savings of replacing synthetic chemicals with locally sourced seafood shell coagulants.

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