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Application of Response Surface Methodology on Brewery Wastewater Treatment Using Chitosan as a Coagulant

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Abstract: Brewery wastewater (BWW) treatment seems to be challenging for conventional wastewater treatment processes. Hence, different processes (i.e., biological, physical, chemical, and advanced oxidation processes) have been investigated; however, reports on parametric optimization using statistical tools are scant. In this present study, the potential application of chitosan as a biopolymer coagulant in decontaminating BWW was investigated. Operating conditions were optimised using the central composite design in response surface methodology (RSM) with 16 experimental runs. The effect of process variables, i.e., pH (4–8), chitosan dose (2–4) g/L and contact time (15–45 min) on the removal of turbidity, total organic carbon (TOC), and orthophosphates were investigated. Experimental results obtained were statistically analysed using the analysis of variance (ANOVA) and second-order polynomial response predictive models as functions of input variables with a significant regression coefficient of $R^2 > 0.95$ at 95% confidence were obtained. At numerical optimum conditions of pH (8), chitosan dose (2 g/L), and contact time (43 min), validation experimental responses of 91% turbidity, 89% TOC, and 65% orthophosphate removals were obtained at a standard deviation of ±0.588, ±0.395, and ±3.603, respectively. The validation results at optimum conditions suggest that proper adjustment of pH, chitosan dose, and contact time is imperative for maximising the efficiency of chitosan in treating BWW. Moreover, the findings of the current study demonstrate that chitosan can be used as a viable bio-coagulant in BWW treatment prior to being discharged into water receiving bodies.

Keywords: chitosan; brewery wastewater; total organic carbon; orthophosphates; response surface methodology; central composite design

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1. Introduction

For most countries, the brewing industry constitutes a significant segment of the country's economy, which is attributed to the fact that beer is the fifth-most consumed beverage in the world [1]. Despite the high demand for beer, the beer-making process require a substantial amount of fresh water. According to Enitan, et al. [2] an average freshwater consumption of 6 hectoliters is required to produce 1 hectoliter of beer. It was noted that during the beer-making process, water is used for two main distinct processes, i.e., as the main ingredient of the beer itself and as part of the brewing process, which includes steam production, cooling, as well as cleaning of the brewing house between batches [2]. The by-products of the beer-making process (i.e., spent grains from mashing, yeast surplus, etc.), as well as the cleaning of the brewing house, produce significant quantities of organic pollutants such as sugars, starch, and proteins [1,3,4]. Simate, et al. [1] reported that, to produce 1 L of beer, about 3–10 L of wastewater is produced, depending on the production technology and water usage. On the other hand Feng, et al. [4] reported

that the annual wastewater production by the brewing industry in China accounts for up to 2% of the national wastewater production.

Hence, the disposal of untreated or partially treated wastewater emanating from the brewery into water-receiving bodies can constitute potential or severe pollution problems. Moreover, apart from organic contaminants, brewery effluent is also characterised by biological nutrients such as phosphorus and nitrogenous compounds [2,3]. It was noted that the content of the aforementioned biological nutrients is influenced by the chemicals used in cleaning and sanitizing such as caustic soda, nitric acid, and phosphoric acid [1]. Generally, organic pollutants in brewery wastewater require oxygen for degradation. Hence, the discharge of untreated or partially treated brewery effluent to water-receiving bodies result in the depletion of dissolved oxygen by bacteria found in water bodies during the degradation of organic contaminants, thus killing aquatic life as a result of eutrophication.

It is apparent that there is a critical need to treat brewery wastewater prior to being discharged into the environment. The available literature contains extensive reports on the application of biological treatment methods on brewery wastewater. Some of the reported methods include the sequencing batch reactor [5–7], up-flow anaerobic sludge blanket reactors [8–10], anaerobic membrane reactors [11,12], and fluidised bed bioreactors [13]. Moreover, the application of microbial fuel cells and electrochemical methods have been reported as potential technologies in brewery wastewater treatment [13]. Despite the effectiveness of the aforementioned processes in the treatment of wastewater, it is unfortunate that they require high energy input [4], are expensive to set-up [14], and are associated with high retention time and sludge production, which is expensive to handle, particularly biological processes [15], and the addition of chemicals generates considerable quantities of secondary pollutants.

Due to the shortcomings of the reported wastewater treatment processes, the research interest in finding cost-effective and environmentally green wastewater treatment technologies has intensified. The potential application of chitosan-based technologies in wastewater treatment has been widely recognised [14,16–19]. The appetite for chitosan application in wastewater treatment processes is attributed to its properties of being environmentally friendly, non-toxic, bio-degradable, hydrophilic, and recyclable and its ability to remove pollutants with outstanding pollutant-binding capacity [20–23]. Chitosan is characterised as an amino-polysaccharide derived from the N-deacetylation of chitin resulting to the formation of amine groups (-NH_2) from acetamide groups (-$NHCOCH_3$), which are essential for contaminants removal during wastewater treatment processes [22,24]. The free amine and hydroxyl (-OH) groups in chitosan allows for the crosslinking and modification [23–25]. The variety of modifiable positions in chitosan structure allows for its functionalization via N-hydroxylation, O-hydroxylation, carboxymethylation, sulfonation, as well as polymer-grafting to improve chitosan physicochemical properties [25]. Despite the aforementioned attractive properties of chitosan, the modification in chitosan structure is attributed to its low water resistance, limited specific surface area, poor mechanical and thermal properties, and high tendency to agglomerate, as well as its high solubility in acidic environments [22,25].

However, based on the available literature, there have been no studies on the application of chitosan as a bio-coagulant in raw brewery wastewater treatment nor studies focusing on parametric optimization using statistical tools. The current study focused on the potential application of chitosan as a bio-coagulant in brewery wastewater treatment and to optimise the individual and interactive effect of process variables, i.e., pH, chitosan dosage, and contact time, on the percentage removal of turbidity, total organic carbon (TOC), and orthophosphates using the response surface methodology (RSM). It should be noted that the optimisation of any treatment process to maximise pollutant reduction in the context of wastewater treatment processes results in cost reduction and the optimum usage of valuable resources, i.e., energy and materials.

2. Materials and Methods

2.1. Materials

Sodium hydroxide (NaOH) pellets, sulphuric acid (H_2SO_4), and chitosan from shrimp shells with a deacetylation of ≥75%, was supplied by Sigma-Aldrich, Johannesburg, South Africa. All materials used were of analytical grade and they were used without any purification.

2.2. Brewery Wastewater Sample

Fresh BWW composite samples were collected from a local South African brewery wastewater treatment plant. Characterisation of the fresh sample was conducted in accordance with the Standard Method for the Examination of Water and Wastewater [26] using a HANNA HI 9828 pH, oxidation reduction potential, electric conductivity, and dissolved oxygen multi-meter probe (HANNA Instruments (Pty) Ltd., Johannesburg, South Africa), a HACH DR900 spectrophotometer (HACH Company, Loveland, CO, USA) for total organic carbon and orthophosphates, and a TB300 IR Turbidimeter (HACH Company, Loveland, USA) for turbidity. Turbidity was measured in nephelometric turbidity units (NTU). The sample composition is presented in Table 1.

Table 1. Composition of brewery wastewater fresh sample.

Physicochemical Property	Value
pH	7.15
Dissolved oxygen	8.33 mg/L
Turbidity	160 NTU
Total organic carbon	176 mg/L
Orthophosphates	139 mg/L
Total dissolved solids	1042 mg/L

2.3. Jar Test Method

Coagulation studies were carried by using the jar test method, which is a standard laboratory technique widely used to assess optimum operating conditions in the wastewater treatment context. The jar test system (i.e., Lovibond Flocculator from United Scientific SA cc, Durban, South Africa) used consists of six 1000 mL graduated beakers with a paddle for stirring each beaker. The jar test unit was incorporated with a stirring regulator to control the mixing speed. Moreover, the unit is also equipped with an automated timer to facilitate the duration of each experimental run with minimal error. Experimental runs were conducted by transferring 1000 mL of raw BWW sample into a beaker with the corresponding chitosan dosage. Jar tests were conducted in a sequence of 2 min rapid mixing at 200 rpm followed by flocculation at 60 rpm for a contact time and pH as indicated in Table 2. Samples were allowed to settle for 30 min; thereafter, the clear supernatant was syphoned using a pipette. The supernatant was immediately analysed for turbidity, total organic carbon, and orthophosphates. The systems' removal efficiency for the aforementioned parameters was calculated based on Equation (1):

$$Y(\%) = \frac{C_{initial} - C_{final}}{C_{final}} \quad (1)$$

where Y (%) is the removal efficiency in terms of turbidity, total organic carbon, and/or orthophosphates, and $C_{initial}$ and C_{final} are the initial and final concentrations of the targeted contaminants, respectively.

Table 2. Codes, ranges, and levels of independent variables of composite design in RSM.

Factor	Code	Range and Level of Factors	
		Low −1	**High +1**
pH	X_1	4	8
Contact time (min)	X_2	15	45
Chitosan dosage (g/L)	X_3	2	4

2.4. Design of Experiment

The central composite design in Design Expert version 11 was used to ascertain the number of experimental runs to be assayed for the optimisation of three independent variables, i.e., pH (X_1), chitosan dose (X_2), and contact time (X_3), on the removal of turbidity (Y_1), total organic carbon (Y_2), and orthophosphates (Y_3). The codes, ranges, and levels of the aforementioned independent variables in RSM design are shown in Table 2.

The quadratic empirical model for predicting the response, i.e., Y, is derived as a function of the levels of the independent variables, expressed according to Equation (2):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k=1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

$$x_i = \frac{z_i - z_0}{\Delta z_i} \quad (3)$$

where x_i and x_j are coded independent variables, i denotes the linear coefficient, j is the quadratic coefficient, β is the coefficient of regression, k denotes the number of factors studied and optimised by the experiment, ε denotes the random error, z_i and z_0 are the code and uncoded values of the ith independent variable, respectively, and Δz_i is the step-change value between the low level (-1) and high level $(+1)$. According to Nair et al. [27], in RSM, codification of variables was conducted to normalise the variables. It is imperative to note that independent variables may have units and orders of magnitude, and codification ensures that all independent variables affect the specified responses evenly.

3. Results and Discussion

3.1. Central Composite Design (CCD)

For the current study, the effect of three independent variables, i.e., pH (X_1), chitosan dose (X_2), and contact time (X_3), was investigated on the removal of turbidity, total organic carbon, and orthophosphates from raw BWW. The percentage removals of the aforementioned responses were selected as dependent variables to identify variables that can influence the reduction of turbidity, total organic carbon, and orthophosphates. The CCD of the current study gave a total of 16 experimental runs, as depicted in Table 3, which were governed by the expression $2k(k-1) + c_p$, where k is the number of factors, and c_p is the number of replicates at the central point [27].

The results obtained were subjected to statistical analysis to validate the predictive ability of the models, i.e., Equations (4)–(6) in terms of percentage removal of turbidity (Y_1), total organic carbon (Y_2), and orthophosphates (Y_3). This was done to ensure that the models provide adequate approximation of the true system. The highest percentage removals in terms of turbidity, total organic carbon, and orthophosphates were found to be 96.39%, 90.91%, and 66.26%, respectively. Moreover, the aforementioned percentage removals were reported at pH 8, chitosan dose of 4 g/L, and a contact time of 45 min for both turbidity and orthophosphates. On the other hand, 89.20% removal of total organic carbon was reported for the aforementioned operating conditions.

$$Y_1 = 88.30 + 3.23X_1 + 0.0626X_2 - 27.17X_3 + 15.53X_1X_3 - 14.85X_3^2 + 27.14X_1X_3^2 + 39.48X_2^2X_3 - 35.99X_1^2X_2^2 \quad (4)$$

$$Y_2 = 90.61 - 0.1689X_1 - 0.0486X_2 - 0.1689X_3 + 0.2131X_1X_3 - 0.5740X_1^2 - 0.6644X_2^2 - 0.5740X_3^2 + 0.3820X_1^2X_3 + 0.3820X_1X_2^2 \quad (5)$$

$$Y_3 = 6.51 + 7.98X_1 + 1.29X_2 + 2.33X_3 + 9.64X_1X_3 + 8.72X_1^2 + 9.99X_1X_2^2 + 17.30X_1^2X_2^2 \quad (6)$$

Table 3. Comparison between experimental response and model predicted response.

Std	Run	Factors			Actual Values			RSM Predicted Values		
		Factor 1	Factor 2	Factor 3	Response 1	Response 2	Response 3	Response 1	Response 2	Response 3
		pH, (X_1)	Coagulant Dosage, g/L (X_2)	Time, Minutes (X_3)	Turbidity Removal, % (Y_1)	TOC Removal, % (Y_2)	PO_4^{3-} Removal, % (Y_3)	Turbidity Removal, % (Y_1)	TOC Removal, % (Y_2)	PO_4^{3-} Removal, % (Y_3)
14	1	6	3	55	0.625	88.64	1.00	0.6250	88.71	10.43
9	2	3	3	30	82.88	89.20	17.77	82.86	89.27	17.77
11	3	6	1	30	88.00	88.69	3.60	88.20	88.82	4.34
16	4	6	3	30	89.88	90.34	4.32	88.30	90.61	6.51
7	5	4	4	45	4.00	88.64	7.19	3.94	88.54	8.55
6	6	8	2	45	94.99	89.77	62.23	95.62	89.49	61.18
5	7	4	2	45	3.75	88.64	11.22	3.81	88.64	5.97
10	8	9	3	30	93.75	88.64	44.60	93.74	88.71	44.60
4	9	8	4	15	41.38	88.64	35.83	40.06	88.54	39.82
1	10	4	2	15	11.88	88.64	20.22	10.25	88.64	20.59
15	11	6	3	5	87.56	90.91	12.59	88.30	90.61	6.51
8	12	8	4	45	96.39	89.20	66.62	95.75	89.39	63.76
13	13	6	3	5	92.00	89.20	2.45	92.00	89.27	2.59
2	14	8	2	15	38.63	88.64	37.34	39.94	88.64	37.24
12	15	6	5	30	87.75	88.64	15.11	88.41	88.65	8.68
3	16	4	4	15	8.75	88.64	19.64	10.38	88.54	23.17

3.2. Analysis of Variance (ANOVA)

The significance of the predictive models (i.e., Equations (4)–(6)) obtained for the current study were subjected to statistical analysis using the analysis of variance (ANOVA) approach, as presented in Table 4. For the current work, the overall significance of each model is explained by the coefficient of determination (R^2), which measures the total variation of predicted values to the mean. The R^2 values reported in Table 4 suggest a good prediction efficiency on the removal of turbidity, total organic carbon, and orthophosphates. According to Montgomery [28], for a model with good prediction efficiency, the value of the coefficient of determination must be close to 1. However, the efficiency of a model cannot be tested by the coefficient of determination alone due to the fact that the value of R^2 increases with an increase in the number of terms in the model regardless of its statistical significance [27]. Hence, the R^2 value was compared with the adjusted R^2 value to determine the models' prediction significance.

Table 4. ANOVA statistical results for response models.

Response	Turbidity	TOC	PO_4^{3-}
p-values	<0.0001	0.0023	<0.0001
F-values	1604.51	13.80	29.90
Mean of squares	2988.77	0.7822	896.25
Sum of squares errors	23,910.18	0.7822	896.25
Standard deviation	1.36	0.2381	5.48
Mean	57.64	89.07	22.61
Coefficient of variance (C.V., %)	2.37	0.2673	24.22
Coefficient of determination (R^2)	0.9995	0.9539	0.9632
Adjusted R^2	0.9988	0.8848	0.9310
Adequate precision	92.9304	11.0195	15.800

It is worth noting that the value of $R^2_{adjusted}$ decreases with an increase in the number of insignificant variables added in the model. Therefore, a significant difference between R^2 and $R^2_{adjusted}$ denotes the presence of non-significant terms in the prediction model.

From Table 4, it is apparent that there is no significant difference between R^2 and $R^2_{adjusted}$ suggesting that nonsignificant variables are not included in the systems' prediction models.

Furthermore, the significance of each factor (i.e., pH, chitosan dose, and contact time) and their interactions were checked by applying a Fisher test. In principle, a larger magnitude of the F-value and correspondingly, the smaller the *p*-value (i.e., $p > F$), the more significant is the corresponding model together with the individual coefficients. Hence, from the ANOVA results presented in Table 4, the *p*-values for all three responses are less than the F-values and less than 0.05. This suggests that all three response prediction models are significant, at 95% confidence intervals and at F-values of 1604.51, 13.80, and 29.90 for turbidity, total organic carbon, and orthophosphates, respectively. As such, the ANOVA results suggest that there is only a 0.01% chance that the models' F-values will be significant due to noise; therefore, the lack of fit for the current system is insignificant.

The prediction efficiency of the reported models, i.e., Equations (4)–(6), were evaluated by the plot of experimental response values versus the predicted response values, as depicted in Figure 1. From the plots depicted in Figure 1, it is apparent that the predicted response values are distributed near to the actual response values, which suggests a significant correlation between the independent variables and the responses. The consistent distribution of data along the straight line in Figure 1 demonstrates insignificant errors within the bounds of the operating parameters for the current system. However, for total organic carbon (Figure 1b) and orthophosphates (Figure 1c), a few points are above and below the line, which suggests minor error margins of over and/or under predictions of the responses within the bounds of operating parameters.

3.3. Response Surface Plots

Figure 2 presents 3D plots on the relationship between pH and the contact time on the removal of turbidity (Figure 2a), total organic carbon (Figure 2b), and orthophosphates (Figure 2c), while chitosan dosage was set as an actual factor (3 g chitosan/L) in RSM. The pH was found to be the most significant factor in the reduction of turbidity, total organic carbon, and orthophosphates. The point of predictions showed maximum and minimum points within the experimental regions for optimization in Figure 2. Chitosan proved to be an effective coagulant, recording the highest removals of 96%, 91%, and 66% for turbidity, total organic carbon, and orthophosphates, respectively. The response peaks in Figure 2 imply that the optimum conditions for the maximum values of the responses are highly dependent on pH and contact time in the design space.

3.4. Numerical Optimization

Numerical optimisation was employed to maximise the percentage removal of turbidity, total organic carbon, and orthophosphates using Design Expert version 11. The system attained gave 30 conditional solutions, and the best optimal conditions with a desirability of 64.2% were achieved at pH 8, chitosan dosage of 2 g/L, and at a contact time of 43 min, as depicted by the ramp plots in Figure 3. Experimental studies for the model validation at 95% confidence prediction level were conducted under the aforementioned optimum conditions, and removal efficiencies of 91%, 89%, and 65% were recorded for turbidity, total organic carbon, and orthophosphates, respectively.

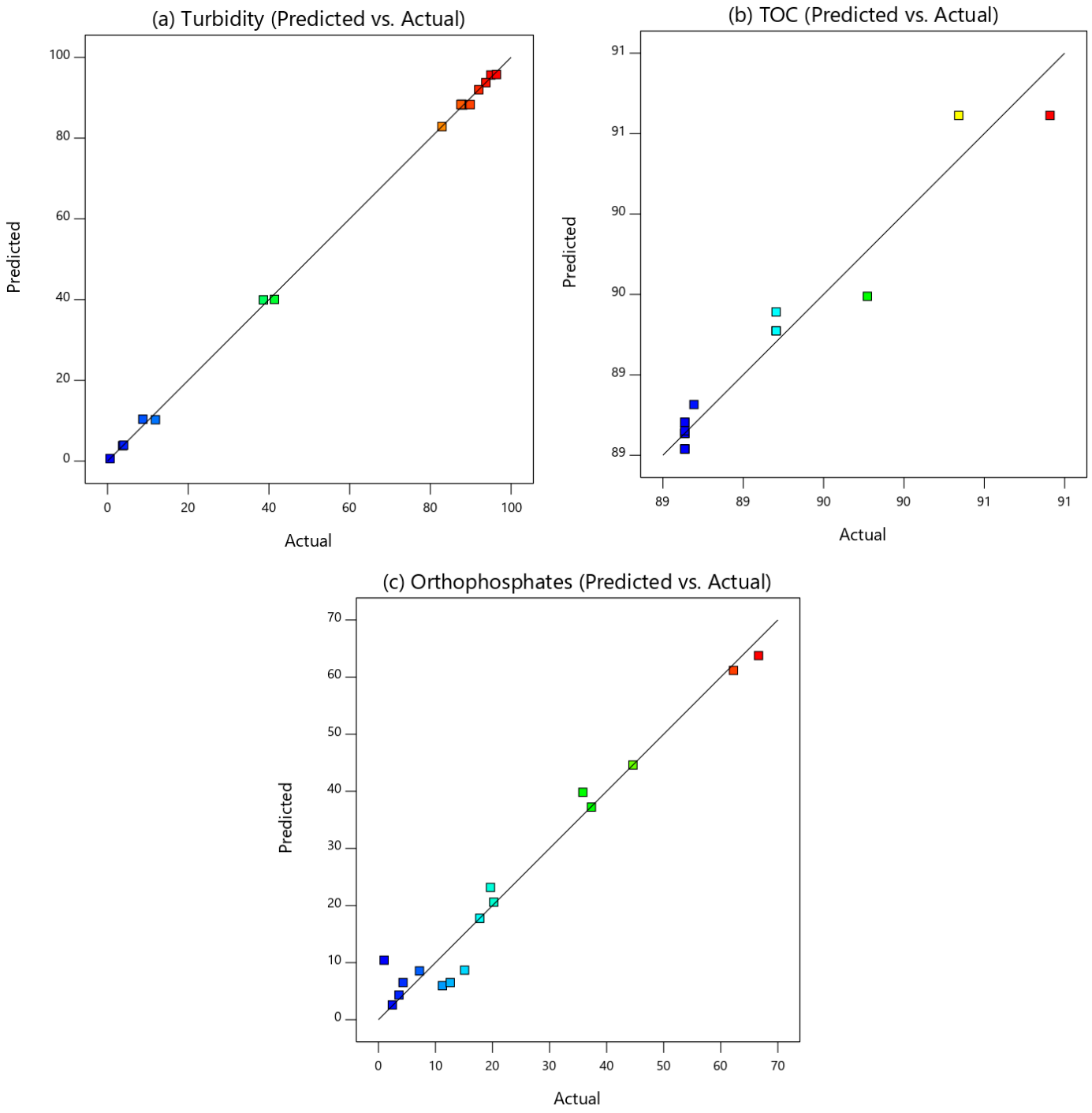
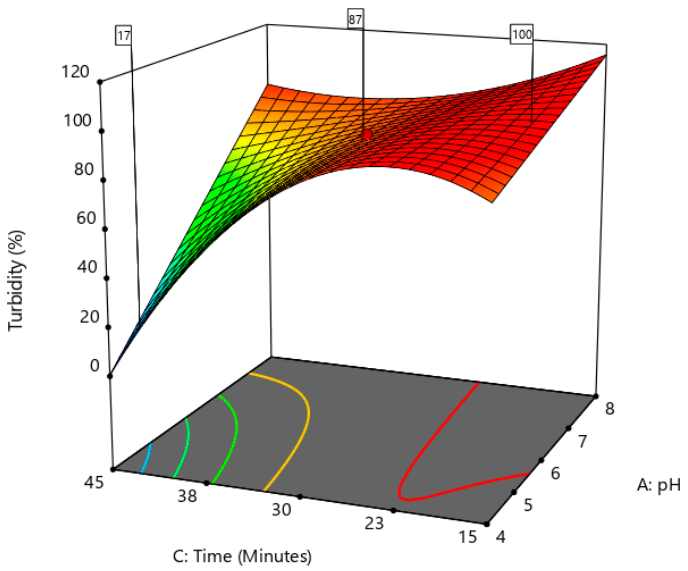
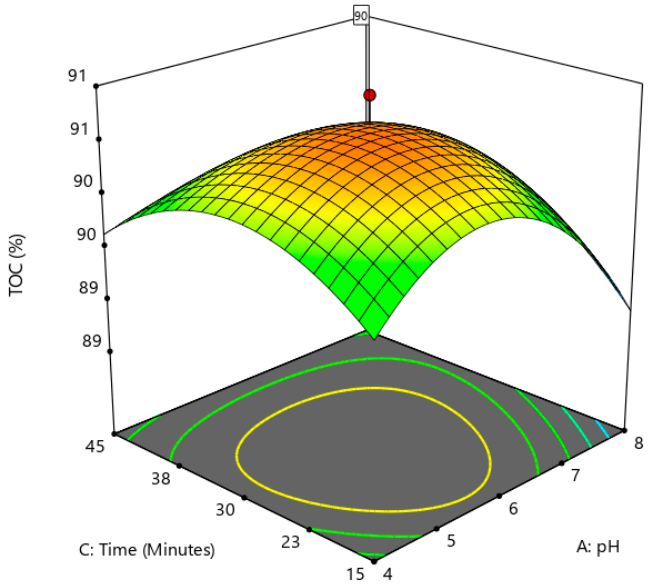


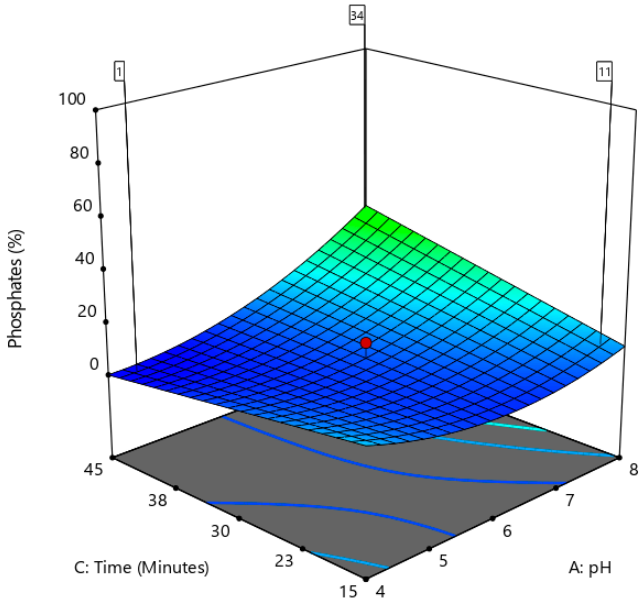
Figure 1. RSM predicted versus actual values of (**a**) turbidity removal, (**b**) total organic carbon (TOC) removal, and (**c**) orthophosphates removal.



(**a**) Turbidity removal



(**b**) Total organic carbon removal



(**c**) Orthophosphates removal

Figure 2. Response on the interactive effect of contact time and pH on the removal of (**a**) turbidity, (**b**) total organic carbon, and (**c**) orthophosphates.

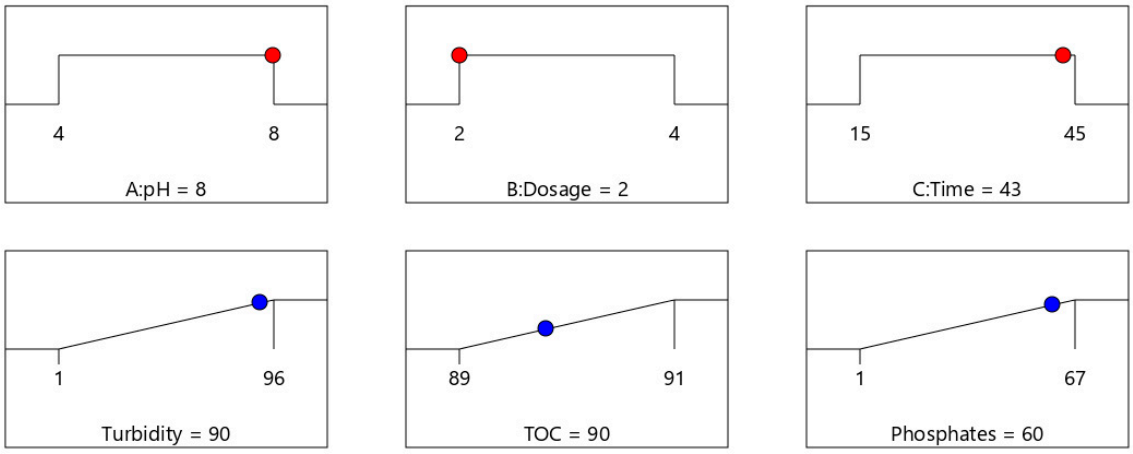


Figure 3. Ramp plot for numerical optimization conditions.

The experimental results presented in Table 5 are congruent to the responses predicted by the response models, i.e., Equations (4) and (5). The low standard deviation values of less than 5% is a clear indication that the RSM demonstrated a good correspondence between experimental values and predicted values. Hence, the results obtained demonstrate the feasibility of the application of chitosan for treating BBW prior to being discharged into water-receiving bodies.

Table 5. Model prediction response values versus experimental values at optimum conditions.

Response	Experimental Values (%)	RSM Predicted Values (%)	Standard Deviation
Turbidity	91	90.168	0.588
TOC	89	89.559	0.395
Orthophosphates	65	59.904	3.603

3.5. pH Optimisation

From the results obtained, it is evident that the pH of BWW is the most influential factor in terms of model contaminant removal. Studies were conducted under acidic (pH range 3–6) and basic (pH range 8–9) conditions with varying dosage of chitosan (1–5 g/L) to investigate the effect of pH on contaminants reduction. From the results presented in Table 3, it is apparent that turbidity removal increased with an increase in pH while TOC removal remained relatively constant. The findings of the current study suggest that turbidity removal by chitosan as a bio-coagulant can be attributed to both polymer-bridging and the charge-neutralisation mechanism. According to Cheng et al. [29], when chitosan dosage exceeds the saturation point of polymer bridging or charge neutralisation, the excess chitosan compromises the polymer bridging between particles and/or reverses the particle charge, thus restabilising them, resulting in an increase in residual turbidity. Therefore, the low turbidity removal efficiencies at pH 4 can be attributed to the excess dosage of chitosan, causing the reversal of surface charge and thus restabilising colloidal particles. It is worth noting that at pH 4, a slight improvement on turbidity removal of 12% was recorded at a coagulant dose of 2 g/L compared to the removal percentage of 4% for a coagulant dose of 4 g/L.

On the other hand, a significant turbidity removal of 82.88% was recorded at a pH of 3 and coagulant dose of 3 g/L as indicated in Table 3. The high turbidity removal is attributed to the fact that, at low pH values of less than 4, about 90% of the chitosan functional groups of NH_2 are protonated [30,31], hence charge neutralisation dominated the destabilisation

of colloidal particles by chitosan. Moreover, it is worth nothing that as the pH increases up to 6 and above, the protonated chitosan functional groups decrease to about 50% [31], thus rendering the charge neutralisation mechanism ineffective, but dominating the polymer-bridging mechanism in turbidity reduction. Hence, the results presented in Table 3 suggest that turbidity removal at pH 8 and 9 were dominated by polymer bridging, and the systems' efficiency was not hindered by the chitosan dosage. Instead, it improved with an increase in contact time. The findings of the current study on the effect of pH on turbidity removal are congruent with the findings reported by Cheng et al. [29]. Furthermore, it is worth noting that the isoelectric point of chitosan was reported by Cheng, et al. [29] to be pH 8.7, thus confirming that polymer bridging is likely to be favoured for a pH range of 8 to 9; hence, turbidity removal efficiencies improved with an increase in chitosan dosage at pH 8 (Table 3). Furthermore, the highest orthophosphates removal of 66.62% was achieved at a pH of 8, while TOC maintained relatively high percentage removals, despite the variation in pH.

3.6. Comparison with Previous Studies

Table 6 presents studies from the literature on the treatment of BWW using different treatment processes such as the application of sequencing batch reactors (SBR) [5,32,33], chemical coagulation (CC) [34], and electro-chemical coagulation (ECC) [35]. In the studies by Khumalo, et al. [5] and Khan, et al. [32] on the application of SBR in BWW remediation, it is apparent that good removal efficiencies for both chemical oxygen demand (COD) and orthophosphates (PO_4^{3-}) were achieved. However, it should be noted that the good removal efficiencies were achieved at a hydraulic retention time (HRT) of at least 18 h, which is higher than the HRT reported by Swain et al. [35] and the current work, at 30 min and 43 min, respectively. High HRTs suggest high operational costs in terms of energy usage for agitation, aeration, and process variable monitoring in the context of the application of SBR. The low COD removal efficiency reported by Swain et al. [35] suggests that the BWW effluent had a high composition of dissolved organic pollutants, which can be successfully removed by biological processes, as demonstrated by Khan et al. [32]. On the other hand, Shao et al. [33] reported a high COD removal efficiency of 90% for an HRT of 8 h and sludge retention time of 200 days. The high COD removal efficiency can be attributed to the acclimation of microbial population.

Ferral-Pérez et al. [36] investigated the application of chitosan, Cosmedia guar, algarrobo seed, and guar gum as biopolymer coagulants for the treatment of wastewater emanating from the tequila-producing plant. Among all the aforementioned investigated bio-coagulants, only chitosan proved to be effective in terms of COD, turbidity, and colour reduction, recording removal efficiencies of 84%, 90%, and 75%, respectively. The findings of the current study demonstrate that high removal efficiencies in terms of turbidity, TOC, and orthophosphates can be achieved at lower HRT compared to biological and chemical coagulation treatment processes. This suggests that the application of chitosan as a bio-coagulant in BWW treatment is a viable green technology on the basis that chitosan is characterised to be an environmentally green polymer.

Table 6. Summary of studies on BWW treatment.

Treatment Process	Removal Efficiency				HRT	Reference
	Turbidity (%)	TOC, (%)	COD, (%)	PO_4^{3-} (%)		
SBR	-	-	54	69	18 h	[5]
	-	-	87	85	19.5 h	[32]
	-	-	90	-	8 h	[33]
CC	91	-	59	-	-	[34]
	75	-	50	-	-	
	-	-	66	-	40 min	[37]

Table 6. *Cont.*

Treatment Process	Removal Efficiency				HRT	Reference
	Turbidity (%)	TOC, (%)	COD, (%)	PO_4^{3-} (%)		
ECC	-	-	26	74	30 min	[35]
	-	-	68	-	6 h	[38]
	-	-	72	-	2 h	[39]
Chitosan coagulation	90	-	84	-	60 min	[36]
	91	89	-	65	43 min	Current study

4. Conclusions and Future Perspectives

Chitosan is characterised by the presence of amine and hydroxyl groups on its surface, which are essential for pollutants removal in aqueous environments [22,24]. The potential application of chitosan as a bio-coagulant for BWW treatment was investigated by employing the RSM model for parametric optimisation for the reduction of turbidity, total organic carbon, and orthophosphates. The CCD in RSM was used to design experiments, investigate the interactive effects of the input variables (i.e., pH, chitosan dose, and contact time) on the responses (i.e., turbidity, total organic carbon, and orthophosphates). Results obtained from the ANOVA produced quadratic prediction models at a 95% confidence level for the removal of turbidity, total organic carbon, and orthophosphates. Under optimised conditions of pH 8, coagulant dose of 2 mg/L, and contact time of 43 min, a system desirability of 64% removal of model responses was achieved. Moreover, the quadratic response prediction models were experimentally validated and found to be congruent with the RSM predicted results at 95% confidence with a standard deviation of less than 5% in all responses. It is worth noting that the pH and contact time were found to affect the reduction efficiency of turbidity, total organic carbon, and orthophosphates from BWW; however, pH was found to be the most influential factor. Based on the results obtained, it is apparent that high removal efficiencies in terms of turbidity, TOC, and orthophosphates were recorded for a low HRT when compared to similar work in the literature (Table 6). The findings of the current study suggest that the application of chitosan for the reduction of turbidity, total organic carbon, and orthophosphates seem to be viable for BWW treatment prior to being discharged into water-receiving bodies.

Despite the high-percentage removal of the model contaminants that we achieved, more work is needed to investigate the possibilities of upscaling chitosan-based wastewater treatment processes and its associated operational costs. Hitherto, there are no studies in the literature that conducted techno-economic analysis of chitosan-based wastewater treatment processes. Moreover, the existing studies on chitosan-based processes were conducted at laboratory scale.

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References

1. Simate, G.S.; Cluett, J.; Iyuke, S.E.; Musapatika, E.T.; Ndlovu, S.; Walubita, L.F.; Alvarez, A.E. The treatment of brewery wastewater for reuse: State of the art. *Desalination* **2011**, *273*, 235–247. [CrossRef]
2. Enitan, A.M.; Adeyemo, J.; Kumari, S.K.; Swalaha, F.M.; Bux, F. Characterization of brewery wastewater composition. *Int. J. Environ. Ecol. Eng.* **2015**, *9*, 1073–1076. [CrossRef]
3. Khumalo, S.M.; Bakare, B.F.; Rathilal, S.; Tetteh, E.K. Characterization of South African Brewery Wastewater: Oxidation-Reduction Potential Variation. *Water* **2022**, *14*, 1604. [CrossRef]
4. Feng, Y.; Wang, X.; Logan, B.E.; Lee, H. Brewery wastewater treatment using air-cathode microbial fuel cells. *Appl. Microbiol. Biotechnol.* **2008**, *78*, 873–880. [CrossRef]
5. Khumalo, S.M.; Bakare, B.F.; Tetteh, E.K.; Rathilal, S. Sequencing Batch Reactor Performance Evaluation on Orthophosphates and COD Removal from Brewery Wastewater. *Fermentation* **2022**, *8*, 296. [CrossRef]
6. Bakare, B.; Shabangu, K.; Chetty, M. Brewery wastewater treatment using laboratory scale aerobic sequencing batch reactor. *S. Afr. J. Chem. Eng.* **2017**, *24*, 128–134. [CrossRef]
7. Wang, S.-G.; Liu, X.-W.; Gong, W.-X.; Gao, B.-Y.; Zhang, D.-H.; Yu, H.-Q. Aerobic granulation with brewery wastewater in a sequencing batch reactor. *Bioresour. Technol.* **2007**, *98*, 2142–2147. [CrossRef]
8. Moe, N.S.; Aung, E.M. A laboratory scale up-flow anaerobic sludge blanket (UASB) reactor for distillery wastewater treatment. *Int. J. Sci. Eng. Technol. Res.* **2014**, *3*, 4050–4055.
9. Basandorj, D. Anaerobic Treatment of Brewery Wastewater Using UASB (Up Flow Anaerobic Sludge Blanket) Reactors Seeded with Activated Sludge. In Proceedings of the 2007 International Forum on Strategic Technology, Ulaanbaatar, Mongolia, 3–6 October 2007; pp. 630–631.
10. Joshi, A. Performance Evaluation of Up-flow Anaerobic Sludge Blanket Reactor and Aerobic Digestor of Raj Brewery, Bhairahawa, Nepal. Master's Thesis, Pulchowk Campus, Patan, Nepal, 2019.
11. Meshksar, M.; Roostaee, T.; Rahimpour, M.R. Membrane technology for brewery wastewater treatment. In *Current Trends and Future Developments on (Bio-) Membranes*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 289–303.
12. Deschamps, L.; Merlet, D.; Lemaire, J.; Imatoukene, N.; Filali, R.; Clément, T.; Lopez, M.; Theoleyre, M.-A. Excellent performance of anaerobic membrane bioreactor in treatment of distillery wastewater at pilot scale. *J. Water Process. Eng.* **2021**, *41*, 102061. [CrossRef]
13. Werkneh, A.A.; Beyene, H.D.; Osunkunle, A.A. Recent advances in brewery wastewater treatment; approaches for water reuse and energy recovery: A review. *Environ. Sustain.* **2019**, *2*, 199–209. [CrossRef]
14. Thirugnanasambandham, K.; Sivakumar, V.; Maran, J.P. Application of chitosan as an adsorbent to treat rice mill wastewater—Mechanism, modelling and optimization. *Carbohydr. Polym.* **2013**, *97*, 451–457. [CrossRef] [PubMed]
15. Shabangu, K.P.; Bakare, B.F. Study of an SBR Treating Brewery Wastewater: Case of COD-HRT and BOD Removal. In Proceedings of the World Congress on Engineering and Computer Science, San Francisco, CA, USA, 22–24 October 2019; pp. 22–24.
16. Desbrières, J.; Guibal, E. Chitosan for wastewater treatment. *Polym. Int.* **2018**, *67*, 7–14. [CrossRef]
17. Hassan, M.A.; Li, T.P.; Noor, Z.Z. Coagulation and flocculation treatment of wastewater in textile industry using chitosan. *J. Chem. Nat. Resour. Eng.* **2009**, *4*, 43–53.
18. Onsøyen, E.; Skaugrud, O. Metal recovery using chitosan. *J. Chem. Technol. Biotechnol.* **1990**, *49*, 395–404. [CrossRef] [PubMed]
19. Nechita, P. Applications of chitosan in wastewater treatment. *Biol. Act. Appl. Mar. Polysacch.* **2017**, *1*, 209–228.
20. Abd El-Monaem, E.M.; Eltaweil, A.S.; Elshishini, H.M.; Hosny, M.; Abou Alsoaud, M.M.; Attia, N.F.; El-Subruiti, G.M.; Omer, A.M. Sustainable adsorptive removal of antibiotic residues by chitosan composites: An insight into current developments and future recommendations. *Arab. J. Chem.* **2022**, *15*, 103743. [CrossRef]
21. De Farias, B.S.; Grundmann, D.D.R.; Rizzi, F.Z.; Martins, N.S.S.; Junior, T.R.S.A.C.; de Almeida Pinto, L.A. Production of low molecular weight chitosan by acid and oxidative pathways: Effect on physicochemical properties. *Food Res. Int.* **2019**, *123*, 88–94. [CrossRef]
22. Omer, A.M.; Dey, R.; Eltaweil, A.S.; Abd El-Monaem, E.M.; Ziora, Z.M. Insights into recent advances of chitosan-based adsorbents for sustainable removal of heavy metals and anions. *Arab. J. Chem.* **2022**, *15*, 103543. [CrossRef]
23. Surgutskaia, N.S.; Di Martino, A.; Zednik, J.; Ozaltin, K.; Lovecka, L.; Bergerova, E.D.; Kimmer, D.; Svoboda, J.; Sedlarik, V. Efficient Cu2+, Pb2+ and Ni2+ ion removal from wastewater using electrospun DTPA-modified chitosan/polyethylene oxide nanofibers. *Sep. Purif. Technol.* **2020**, *247*, 116914. [CrossRef]
24. Dong, L.; Shan, C.; Liu, Y.; Sun, H.; Yao, B.; Gong, G.; Jin, X.; Wang, S. Characterization and mechanistic study of heavy metal adsorption by facile synthesized magnetic xanthate-modified chitosan/polyacrylic acid hydrogels. *Int. J. Environ. Res. Public Health* **2022**, *19*, 11123. [CrossRef]
25. Eltaweil, A.S.; El-Tawil, A.M.; Abd El-Monaem, E.M.; El-Subruiti, G.M. Zero valent iron nanoparticle-loaded nanobentonite intercalated carboxymethyl chitosan for efficient removal of both anionic and cationic dyes. *ACS Omega* **2021**, *6*, 6348–6360. [CrossRef] [PubMed]
26. Rice, E.W.; Bridgewater, L.; American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*; American Public Health Association: Washington, DC, USA, 2012; Volume 10.

27. Nair, A.T.; Makwana, A.R.; Ahammed, M.M. The use of response surface methodology for modelling and analysis of water and wastewater treatment processes: A review. *Water Sci. Technol.* **2014**, *69*, 464–478. [CrossRef] [PubMed]
28. Montgomery, D.C. *Design and Analysis of Experiments*; John Wiley & Sons: Hoboken, NJ, USA, 2017.
29. Cheng, W.P.; Chi, F.H.; Yu, R.F.; Lee, Y.C. Using chitosan as a coagulant in recovery of organic matters from the mash and lauter wastewater of brewery. *J. Polym. Environ.* **2005**, *13*, 383–388. [CrossRef]
30. Huang, C.; Chen, Y. Coagulation of colloidal particles in water by chitosan. *J. Chem. Technol. Biotechnol.* **1996**, *66*, 227–232. [CrossRef]
31. Domard, A.; Rinaudo, M.; Terrassin, C. Adsorption of chitosan and a quaternized derivative on kaolin. *J. Appl. Polym. Sci.* **1989**, *38*, 1799–1806. [CrossRef]
32. Khan, N.A.; Morabet, R.E.; Khan, R.A.; Alsubih, M.; Gaurav, G.K.; Klemeš, J.J.; Thakur, A.K. Modelling and parameter optimisation for performance evaluation of sequencing batch reactor for treating hospital wastewater. *Biomass. Convers. Biorefin.* **2022**, 1–16. [CrossRef] [PubMed]
33. Shao, X.; Peng, D.; Teng, Z.; Ju, X. Treatment of brewery wastewater using anaerobic sequencing batch reactor (ASBR). *Bioresour. Technol.* **2008**, *99*, 3182–3186. [CrossRef] [PubMed]
34. Shabangu, K.P.; Bakare, B.F.; Bwapwa, J.K. The treatment effect of chemical coagulation process in South African brewery wastewater: Comparison of polyamine and aluminum-chlorohydrate coagulants. *Water* **2022**, *14*, 2495. [CrossRef]
35. Swain, K.; Abbassi, B.; Kinsley, C. Combined electrocoagulation and chemical coagulation in treating brewery wastewater. *Water* **2020**, *12*, 726. [CrossRef]
36. Ferral-Pérez, H.; Torres Bustillos, L.; Méndez, H.; Rodríguez-Santillan, J.; Chairez, I. Sequential treatment of tequila industry vinasses by biopolymer-based coagulation/flocculation and catalytic ozonation. *Ozone Sci. Eng.* **2016**, *38*, 279–290. [CrossRef]
37. Wagh, M.P.; Nemade, P. Treatment of distillery spent wash by using chemical coagulation (CC) and electro-coagulation (EC). *Am. J. Environ. Prot.* **2015**, *3*, 159–163.
38. Farshi, R.; Priya, S.; Saidutta, M. Reduction of color and COD of anaerobically treated distillary wastewater by electrochemical method. In Proceedings of the National Conference on Women in Science & Engineering (SCWSE), Dharwad, India, 5 July 2013.
39. Krishna, B.; Murthy, U.N.; Manoj Kumar, B.; Lokesh, K. Electrochemical pretreatment of distillery wastewater using aluminum electrode. *J. Appl. Electrochem.* **2010**, *40*, 663–673. [CrossRef]