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Response surface optimization of pH and coagulant dosage for pharmaceutical wastewater pretreatment using alum and bentonite

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ABSTRACT

Selection of an appropriate coagulant for removal of chemical oxygen demand (COD) and turbidity from wastewater generated in a pharmaceutical industry was demonstrated. The standard jar test procedure was adopted to determine the optimum pH and coagulant dosage needed for enhanced COD and turbidity removal. Alum and bentonite (montmorillonite) were chosen as coagulant and coagulant aid, respectively. Based on the results obtained from experiments, COD removal (COD_{RE}, %) and turbidity removal (T_{RE}, %) were optimized using response surface methodology. Under the optimum conditions, the model predicted a COD_{RE} of 67% and T_{RE} of 90% and COD_{RE} of 55% and T_{RE} of 70% using alum (coagulant dosage = 0.79 g/L, pH 5.91) and bentonite (coagulant dosage = 0.58 g/L, pH 5.61), respectively. Confirmatory experiments conducted on the optimized condition showed experimental findings within 5% of the projected values. Though alum resulted in higher COD_{RE} and T_{RE} as compared to bentonite, bentonite can have the advantage of being environmentally benign when compared to the conventionally used coagulant, alum.

Keywords: Pharmaceutical wastewater; Coagulation; Alum; Bentonite; Response surface methodology

1. Introduction

In pharmaceutical industries, huge amount of water is consumed to meet the requirement of various operations and processes. The raw or partially treated wastewater from pharmaceutical industries ends up in the aquatic environment. Therefore, the possibility of bioaccumulation of the released pharmaceuticals in wastewater cannot be ruled out and may further instigate hazardous and toxic effects on terrestrial as well as aquatic ecosystems [1].

A large number of safe treatment techniques are available for disposal of pharmaceutical wastewater (PWW), while meeting various regulatory standards [2]. Emerging treatments include advanced oxidation processes (AOPs), such as ozonation, photocatalysis, Fenton reaction, and ultrasonic irradiation, which help in removing the pharmaceuticals from wastewater [3]. However, pretreatment with coagulants prior to AOPs

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can improve the quality of water and lowers the cost of wastewater treatment process [4].

The PWW contain relatively high levels of suspended solids and soluble organics, many of which are recalcitrant [5]. The high chemical oxygen demand (COD) value of PWW is due to the presence of pollutants that are susceptible to oxidation. On the other hand, the turbidity of the PWW is largely due to the various compounds present in colloidal form. Removal of turbidity from PWW is, therefore, essential to meet the stringent turbidity standards set by the World Health Organization.

Coagulation is a simple physicochemical technique commonly used for water and wastewater treatment. The basic mechanism of removal is primarily the neutralization of negatively charged colloids by cationic hydrolysis products, followed by hydroxide precipitation which may promote flocculation [6,7]. Inorganic metal salts, such as aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$) or alum, ferrous sulfate, ferric chloride, and ferric chloro-sulfate, are often exploited in the coagulation–flocculation process.

Coagulant aid is an inorganic material, when used along with main coagulant, improves or accelerates the process of coagulation and flocculation by producing quick forming, dense, and rapidly settling flocs [8]. Coagulant aids increase the density and toughness of the slow-settling flocs so that they will not break up during the mixing and settling processes. Alum (aluminum sulfate) is a commercial chemical coagulant that readily dissolves in water and is effective only within a certain pH range. Alum changes the pH and chemical characteristics of the effluent being treated [9]. On the other hand, use of bentonite is eco-friendly and it offers significant improvement in settling characteristics by not altering pH of the effluent [10]. Bentonite, a natural clay, a dioctahedral smectite with general chemical formula, $M_y^+{\cdot}nH_2O\ (Al_{4-y}\ Mg_y)\ Si_8O_{20}\ (OH)_4$, where M ($M = Na^+, Ca^{2+}, Mg^{2+}$, etc.) is the charge balancing interlayer cation. Besides the interlayer cations, the interlayer space of bentonite can absorb large amounts of water [11], which imparts additional weight to flocs and therefore employed in general as a coagulant aid. Bentonite can even provide nuclei to accelerate the coagulation process in low-turbidity water. Furthermore, bentonite is capable of adsorbing some hydrophobic functional group containing long chain organic matter.

The efficiency of coagulation process is regulated by various factors such as the type and dosage of coagulant [12–16], pH [17–20], mixing speed and time [21,22], temperature and retention time [23,24]. The pH at which coagulation occurs is the most important parameter for proper coagulation performance as it affects the surface charge of the colloids, charge of the dissolved-phase coagulant species, surface charge of floc particles, and coagulant solubility. For aluminum-based coagulant, the best coagulation performance is usually observed at pH values close to the pH of the minimum solubility of the coagulant [25]. Coagulant that destabilizes particles by charge neutralization has dosage dependence, in which case sufficient coagulant is usually added to destabilize suspended colloids or to create good settling floc. Coagulant dosage is generally higher when wastewater turbidity increases [26,27]. Coagulant dosage for a typical wastewater is always determined experimentally by jar test. Hence, a proper optimization of various factors influencing the treatment efficiency is always a challenge. In this context, response surface methodology (RSM) provides an efficient way to achieve such an optimization [28–31] by modeling the effects of multiple variables of the process.

The objective of this work was to investigate the feasibility of PWW pretreatment and optimize the coagulation process by RSM approach. COD and turbidity of the PWW were chosen as the independent variables while their corresponding removal efficiencies were chosen as the dependent variables. Statistical relationships were developed to maximize COD removal (COD_{RE}, %) and turbidity removal (T_{RE}, %) using the results obtained from experiments designed by RSM. Besides, the removal efficiency of the coagulation process using bentonite has been compared with that of alum, which is most often used as a coagulant for treatment of a variety of wastewater [32,33].

2. Materials and methods

2.1. Sample collection

The wastewater sample for the present study was collected from a pharmaceutical industry (Vizianagaram, Andhra Pradesh, India) which produces a wide array of pharmaceuticals viz. Levitracetum, valsartan, quetiapine, and nizatidine. The wastewater treatment methods adopted in the company include pretreatment (screening) of wastewater followed by two-stage aerobic biological treatment. The resulting effluent is passed through two consecutive reverse osmosis (RO) plants; permeate from the first RO plant is used in cooling tower, while that from the second RO plant is used in boilers.

2.2. Materials

The chemicals used for wastewater characterization and regular experiments were of standard grade reagents. The coagulant and the coagulant aid, i.e. alum and bentonite (Balaji Chemicals, Visakhapatnam) were used as purchased. Coagulant solutions of various strengths were prepared based on requirement by weighing the desired amount of coagulant and mixing up with deionized water [34].

2.3. Experimentation

Analysis of total solids (TS), total dissolved solids (TDS) of the sample was carried out in accordance with the procedure outlined in standard methods [35]. The COD of the sample was analyzed using closed reflux titration method. The pH and turbidity of the samples were measured by pH meter and turbidity meter, respectively. The regular coagulation experiments were carried out as per the standard jar testing procedure (10 min rapid stirring, 10 min slow stirring, and 20 min settling) within the working range of pH and coagulant dosage (as per the experimental design) using both alum and bentonite. The pH of the sample was adjusted using 0.1 N/0.01 N HCl or NaOH. All samples were measured in duplicate to ensure data reproducibility, and additional measurements were carried out wherever necessary.

2.4. Experimental design and statistical analysis

The independent variables ($k = 2$) were pH (X_1) and coagulant dosage, g/L (X_2), while the COD removal (Y_1, %) and turbidity removal (Y_2, %) values were chosen as the response variables. The range and levels of independent process variables are given in Table 1. A 2^k full factorial experimental design with five replicates (n_o) at the center point, and thus a total of 13 ($2^k + 2k + n_o$) experiments were performed in this study.

The coded and uncoded values of the individual variables according to the following equation:

$$X_i = \frac{(x_i - x_0)}{\Delta x} \tag{1}$$

where X_i is the coded value of variable i, x_i is the uncoded real value of an independent variable, x_o is the value of X_i at the center point, and Δx is the step change between levels 0 and 1. The behavior of the system was explained by the second-order polynomial equation, Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i,j=1(i \neq j)}^{3} \beta_{ij} X_i X_j \tag{2}$$

where Y is the dependent variable, β_0 is the offset term, β_i is the coefficient of linear effect, β_{ii} is the coefficient of squared effect, β_{ij} is the coefficient of interaction effect, X_i and X are the independent variables. The experimental and model predicted values for Y_1 and Y_2, for alum and bentonite, respectively are shown in Tables 2 and 3.

Analysis of variance (ANOVA) was applied to estimate the main (linear) effects of independent variables and their potential interaction effects on the Y_1 and Y_2 after coagulation with alum and bentonite, respectively. The ANOVA table provides information on the following terms: DF (degrees of freedom); Seq SS (sequential sum of squares); Adj SS (adjusted sum of squares); Adj MS (adjusted mean squares); F (Fischer's variance ratio); and p (probability value). The goodness of fit of the regression model and the significance of parameters estimates were determined through regression analysis. The results of this experimental design were analyzed and interpreted by Minitab® v. 16 (PA, USA) statistical software. For optimizing Y_1 and Y_2 simultaneously, the desirability-based "Response Optimizer" method was used.

3. Results and discussion

3.1. PWW characterization

The characteristics of the PWW investigated in this study are pH 7.34, TS: 10,018 mg/L, TSS: 910 mg/L, TDS: 9,108 mg/L, Turbidity: 998 NTU, COD: 2,240 mg/L. Ghafari et al. [36] demonstrated

Table1
Experimental range and levels of independent process variables

	Range and level				
Independent variable	−1.414	−1.000	0.000	+1.000	+1.414
pH (X_1)	4.17	5	7	9	9.83
Coagulant dosage, g/L (X_2)	0.29	0.5	1.0	1.5	1.71

Table 2
Full factorial central composite design matrix for alum

Run order	pH (X_1)	Coagulant dosage (g/L) (X_2)	COD (Y_1)		T_{RE} (Y_2)	
			Experimental	Predicted	Experimental	Predicted
1	−1 (5)	−1 (0.5)	71.428	64.711	84.569	84.095
2	+1 (9)	−1 (0.5)	67.857	70.225	92.68	93.001
3	−1 (5)	+1 (1.5)	60.714	53.41	74.849	76.71
4	+1 (9)	+1 (1.5)	60.714	62.496	94.881	97.544
5	$-\alpha$ (4.17)	0 (1.0)	55.357	64.243	73.146	72.597
6	$+\alpha$ (4.83)	0 (1.0)	78.571	74.572	95.29	93.637
7	0 (7)	$-\alpha$ (0.293)	60.714	62.746	92.985	93.55
8	0 (7)	$+\alpha$ (0.707)	46.428	49.292	94.28	91.541
9	0 (7)	0 (1.0)	67.857	67.846	95.49	95.051
10	0 (7)	0 (1.0)	67.857	67.846	94.889	95.051
11	0 (7)	0 (1.0)	67.857	67.846	94.489	95.051
12	0 (7)	0 (1.0)	67.857	67.846	95.49	95.051
13	0 (7)	0 (1.0)	67.857	67.846	94.889	95.051

Table 3
Full factorial central composite design matrix for bentonite

Run order	pH (X_1)	Coagulant dosage (g/L) (X_2)	COD (Y_1)		T_{RE} (Y_2)	
			Experimental	Predicted	Experimental	Predicted
1	−1 (5)	−1 (0.5)	60.714	57.605	67.435	64.859
2	+1 (9)	−1 (0.5)	50	45.889	77.154	73.753
3	−1 (5)	+1 (1.5)	42.857	42.948	68.838	67.609
4	+1 (9)	+1 (1.5)	50	49.088	74.048	71.995
5	$-\alpha$ (4.17)	0 (1.0)	51.786	53.089	60.822	62.54
6	$+\alpha$ (4.83)	0 (1.0)	46.828	49.144	69.078	71.936
7	0 (7)	$-\alpha$ (0.293)	46.828	50.702	68.236	71.51
8	0 (7)	$+\alpha$ (0.707)	42.857	42.601	70.842	72.211
9	0 (7)	0 (1.0)	46.828	49.499	75.852	77.858
10	0 (7)	0 (1.0)	51.786	49.499	79.358	77.858
11	0 (7)	0 (1.0)	51.071	49.499	78.857	77.858
12	0 (7)	0 (1.0)	46.828	49.499	75.852	77.858
13	0 (7)	0 (1.0)	51.786	49.499	79.358	77.858

coagulation–flocculation treatment of landfill leachate with average COD of 1,925 mg/L and turbidity of 347 FAU using alum and polyaluminum chloride. At the optimum condition of 9.5 g/L alum and a pH of 7, COD removal of 62.8% was achieved. Al-Malack et al. [37] investigated coagulation of polymeric wastewater with high turbidity (up to 5,400 NTU) and COD (up to 13,500 mg/L) values using alum, ferric chloride, and ferrous sulfate. They observed the turbidity and COD removal efficiencies up to about 96% at the optimum conditions. Syafalni et al. [38] focused on coagulation of wastewater with an average COD of 134 mg/L and turbidity of 68 NTU using bentonite, combinations of bentonite–zeolite, bentonite–alum, and bentonite–limestone as adsorbent and coagulant. They compared the removal efficiencies in terms of COD and turbidity at the optimum coagulant dosages.

3.2. Development and validation of regression model

3.2.1. Using alum as coagulant

The experimental results were analyzed in the form of ANOVA by using COD_{RE} (Y_1, %) and T_{RE} (Y_2, %) as the response variables (Table 4). ANOVA subdivides the total variation into component associated with specific sources of variation for the model. As shown in Table 4, the F values for T_{RE} were higher than those observed for COD_{RE}. The p values were used to judge whether F is large enough to indicate

Table 4
ANOVA for COD_{RE} (Y_1) and T_{RE} (Y_2)

Source	DF		Seq SS		Adj MS		F		p	
	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2
(a) Using alum as coagulant										
Linear	2	2	288.08	446.08	29.796	148.16	0.97	46.28	0.424	0
Square	2	2	260.46	248.72	130.23	124.364	4.25	38.85	0.062	0
Interaction	1	1	3.18	35.57	3.189	35.575	0.1	11.11	0.756	0.013
Residual error	7	7	214.55	22.41	30.65	3.2				
Total	12	12	766.29	752.8						
(b) Using bentonite as coagulant										
Linear	2	2	81.13	88.59	22.79	113.51	1.84	12.92	0.288	0.004
Square	2	2	21.1	233.4	10.55	116.7	0.85	13.28	0.466	0.004
Interaction	1	1	79.71	5.083	79.71	5.08	0.45	0.58	0.039	0.472
Residual error	7	7	86.57	61.49	12.36	8.78				
Total	12	12	268.52	388.57						

Notes: DF: degree of freedom; Seq SS: sequential sum of squares; Adj MS: adjusted mean squares; F: fischer's variance ratio; P: probability value.

statistical significance [39]. Thus, high F and low p values (<0.05) indicate that the effect is significant at 95% confidence level. The p values of the linear, squared, and interaction effects were <0.05 for T_{RE}, while only the squared effects for COD_{RE} were found to be statistically significant. The residual error in Table 4(a) indicates the amount of variation in the response data left unexplained by the model.

Furthermore, the students t-test was used to determine the regression coefficients of the parameters. The corresponding p values were used as a tool to check the significance of each of the interactions among the variables, which in turn may indicate the patterns of interactions between the variables [40]. The regression coefficient, t and p values for all the linear, squared, and interaction effects of the parameter are given in Table 5, for COD_{RE} and T_{RE}, respectively. The regression model equations for COD_{RE} and T_{RE} are given in Eqs. (3) and (4), respectively.

$$COD_{RE} : Y_1 = 56.73 - 1.79X_1 + 31.55X_2 + 0.195X_1^2 - 23.66X_2^2 + 0.893X_1 \times X_2 \quad (3)$$

$$T_{RE} : Y_2 = 13.30 + 21.59X_1 - 12.27X_2 - 1.49X_1^2 - 5.01X_2^2 + 2.98X_1 \times X_2 \quad (4)$$

From Table 5, it is evident that the coefficient for the linear effects due to pH (X_1) for turbidity removal showed less p value ($p = 0.0$), which indicated that this effect was more pronounced as compared with COD removal.

Among the squared effects, coagulant dosage (X_2) was significant for COD_{RE} ($p = 0.026$) while pH was significant for T_{RE} ($p = 0.0$). The coefficients of

Table 5
Estimated regression coefficients and corresponding t and p values for COD_{RE} and T_{RE} using alum as coagulant

Term	Coefficient		SE coefficient		t		p	
	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2
Constant	56.73	13.30	33.64	10.87	1.68	1.22	0.136	0.261
X_1	−1.79	21.59	7.91	2.55	−0.22	8.44	0.827	0.0
X_2	−31.55	−12.27	25.93	8.38	1.21	−1.46	0.263	0.187
X_1^2	0.195	−1.49	0.52	0.16	0.37	−8.78	0.721	0.0
X_2^2	−23.66	−5.01	8.39	2.71	−2.81	−1.84	0.026	0.107
$X_1 \times X_2$	0.893	2.98	2.76	0.89	0.32	3.33	0.756	0.013

interaction effects appeared to be significant ($p = 0.013$) for T_{RE} but insignificant at 95% confidence limit for COD_{RE} ($p > 0.05$). The positive terms of the coefficients given in Table 5 indicate a significant effect of these parameters on the COD_{RE} and T_{RE} values. Only the squared effect of coagulant dosage ($p = 0.026$) showed a significant effect on COD_{RE}. For T_{RE}, the coefficients of linear effect of pH and the interaction effect between pH and coagulant dosage were significant with p values 0.0 and 0.013, respectively. The experimental and predicted values of COD_{RE} and T_{RE} (Table 2) indicated good fitness of the model with coefficient of determination (R^2) values 0.72 and 0.97, respectively. Thus, only less that 28% variation in COD_{RE}, and 3% in the case of T_{RE}, was not statistically explained by the model equation, reflecting the goodness of fit of the regression model to analyze trends in the responses. Though the value of $R^2 = 0.72$ would be considered low in applied statistics, it can be accepted due to complex interactions observed between COD_{RE}—pH—coagulant dosage, which could not be reasoned by the model equation. These variations in the model predictions are highlighted in Table 4(a), when F values of regression (3.6 and 45.63) were less than the F from the effects. It is noteworthy to remember here that such observations on the significance of different statistical terms, the main effects and interactions amongst different process parameters, i.e. pH and coagulant dosage, would go unnoticed if experiments were to be carried out by conventional methods.

3.2.2. Using bentonite as coagulant

As shown in Table 4(b), the F values for T_{RE} (Y_2) were higher than those observed for COD_{RE} (Y_1) except for the interaction effect. The p values for the linear and squared (quadratic) effects were <0.05 for T_{RE}, while only the interaction effects for COD_{RE} were found to be statistically significant. Besides, the F values of regression (2.94 and 7.45) for COD_{RE} and T_{RE} were less than the maximum F of the effects (6.45 and 13.28). The residual error in Table 4(b) indicates the amount of variation in the response data left unexplained by the model.

The regression model equations for COD_{RE} and T_{RE} are given in Eqs. (5) and (6), respectively.

$$COD_{RE} : Y_1 = 95.55 - 7.98X_1 - 25.58X_2 + 0.20X_1^2 - 5.69X_2^2 + 4.46X_1 \times X_2 \tag{5}$$

$$T_{RE} : Y_2 = -19.12 + 21.35X_1 + 32.38X_2 - 1.32X_1^2 - 11.99X_2^2 - 1.127X_1 \times X_2 \tag{6}$$

From Table 6, it is evident that the coefficient for the linear effects due to pH (X_1) for T_{RE} showed less p value (p = 0. 001), indicating that this effect was more pronounced for T_{RE} than for COD_{RE}. Both the squared effects were significant for T_{RE} with p value 0.002 and 0.032, respectively, while for COD_{RE} they were statistically insignificant ($p > 0.05$). The coefficients of interaction effects appeared to be significant between pH and coagulant dosage ($p = 0.039$) for COD_{RE} but insignificant at 95% confidence limit for T_{RE} ($p > 0.05$). The positive coefficients for the squared effect due to pH and interaction effect showed a significant effect on COD_{RE} with the interaction effect being significant ($p = 0.039$). Similarly, the linear effect due to pH and coagulant dosage showed significant effects on T_{RE}, but are statistically insignificant at 95% confidence interval while the squared effects (significant at $p < 0.05$) and the interaction effect showed an insignificant effect on T_{RE}.

The experimental and predicted values of COD_{RE} and T_{RE} are shown in Table 5. The predicted values were not statistically different from the experimental ones, yielding coefficient of determination (R^2) values

Table 6
Estimated regression coefficients and corresponding t and p values for COD_{RE} and T_{RE} using bentonite as coagulant

	Coefficient		SE coefficient		t		p	
Term	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2
Constant	95.55	−19.12	21.37	18.01	4.47	−1.06	0.003	0.324
X_1	−7.98	21.35	5.026	4.23	−1.59	5.04	0.156	0.110
X_2	−25.58	32.38	16.47	13.88	−1.55	2.33	0.164	0.052
X_1^2	0.20	−1.32	0.333	0.28	0.60	−4.72	0.564	0.002
X_2^2	−5.69	−11.99	5.334	4.49	−1.06	−2.66	0.321	0.032
$X_1 \times X_2$	4.46	−1.127	1.758	1.48	2.53	−0.76	0.039	0.472

of 0.68 and 0.84, for COD_{RE} and T_{RE} respectively. Thus, only 32 and 16% variation in COD_{RE} and T_{RE}, respectively, were not statistically explained by the model equation, reflecting the goodness of fit of the regression model to analyze trends in the responses. Though $R^2 = 0.68$ would be considered low in applied statistics, it can be accepted due to complex interactions observed between COD Removal – pH – coagulant dosage, which could not be reasoned by the model equation.

3.3. Response surface optimization

The response surface plots (Figs. 1(a) and 2(a)) provide a three-dimensional (3D) view of the COD_{RE} (Y_1) and T_{RE} (Y_2) surface over different combinations of independent variables, i.e. pH (X_1) and coagulant dosage (X_2) and also explain their interactive effects on COD and turbidity removal. The contour plots (Figs. 1(b) and 2(b)) are represented as a function of two factors at a time.

3.3.1. Using alum as coagulant

The response surface plots for COD_{RE} and T_{RE} using alum as coagulant (Fig. 1) show the interaction effect between pH and coagulant dosage. It can be seen that the nature of the surface plots depends on the sign and magnitude of the coefficients for COD_{RE} and T_{RE} as in Table 5. The response surfaces show the COD_{RE} and T_{RE} to be 67.26 and 90%, respectively, at optimum conditions. This type of two-dimensional plot of the responses on pH–coagulant dosage passes through the steepest ascent of COD_{RE} or T_{RE}, and the optimum conditions are in the direction of maximum decline of response with respect to increasing or decreasing values of independent variables [38].

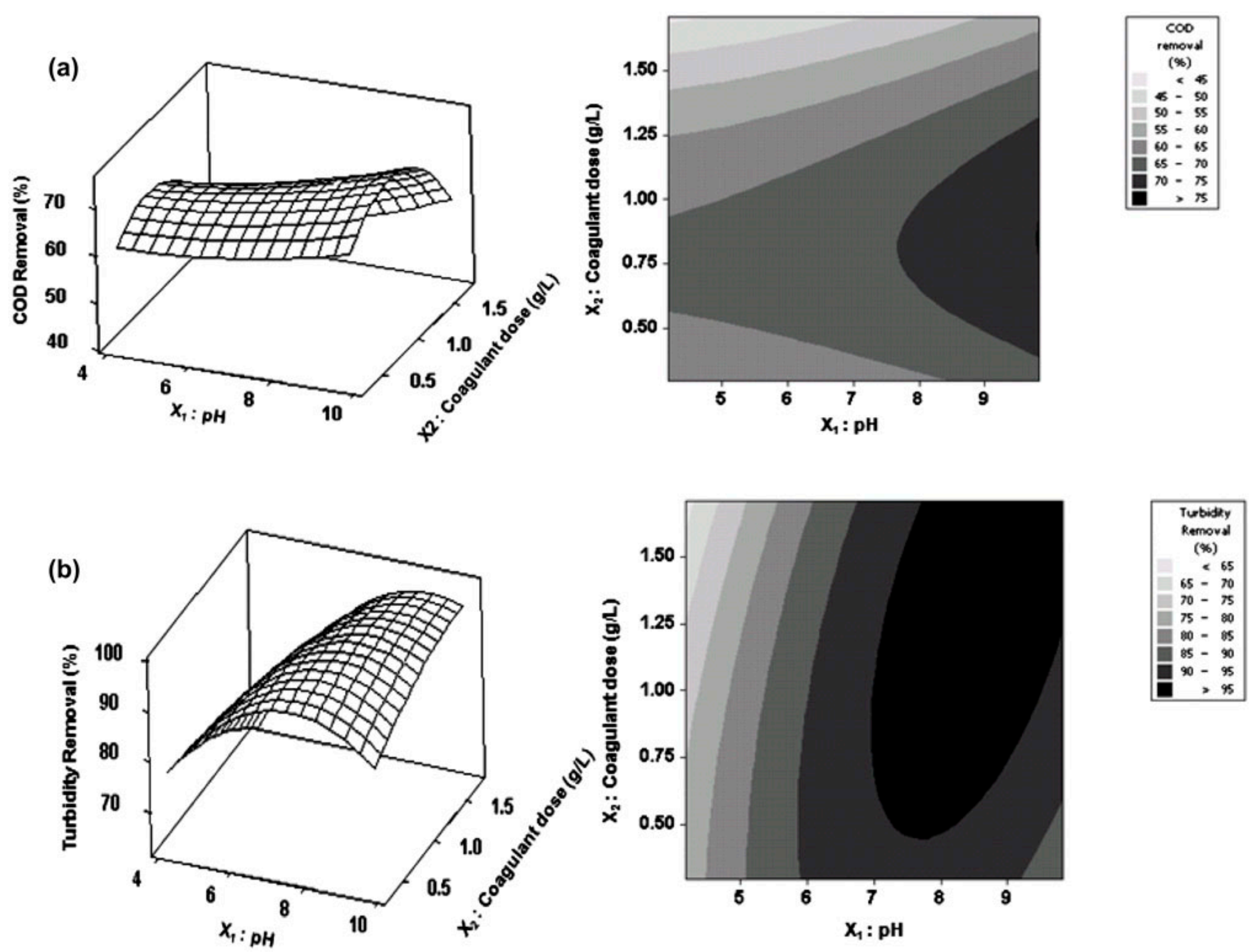

Fig. 1. Response surface (a) and contour plots (b) using alum as coagulant.

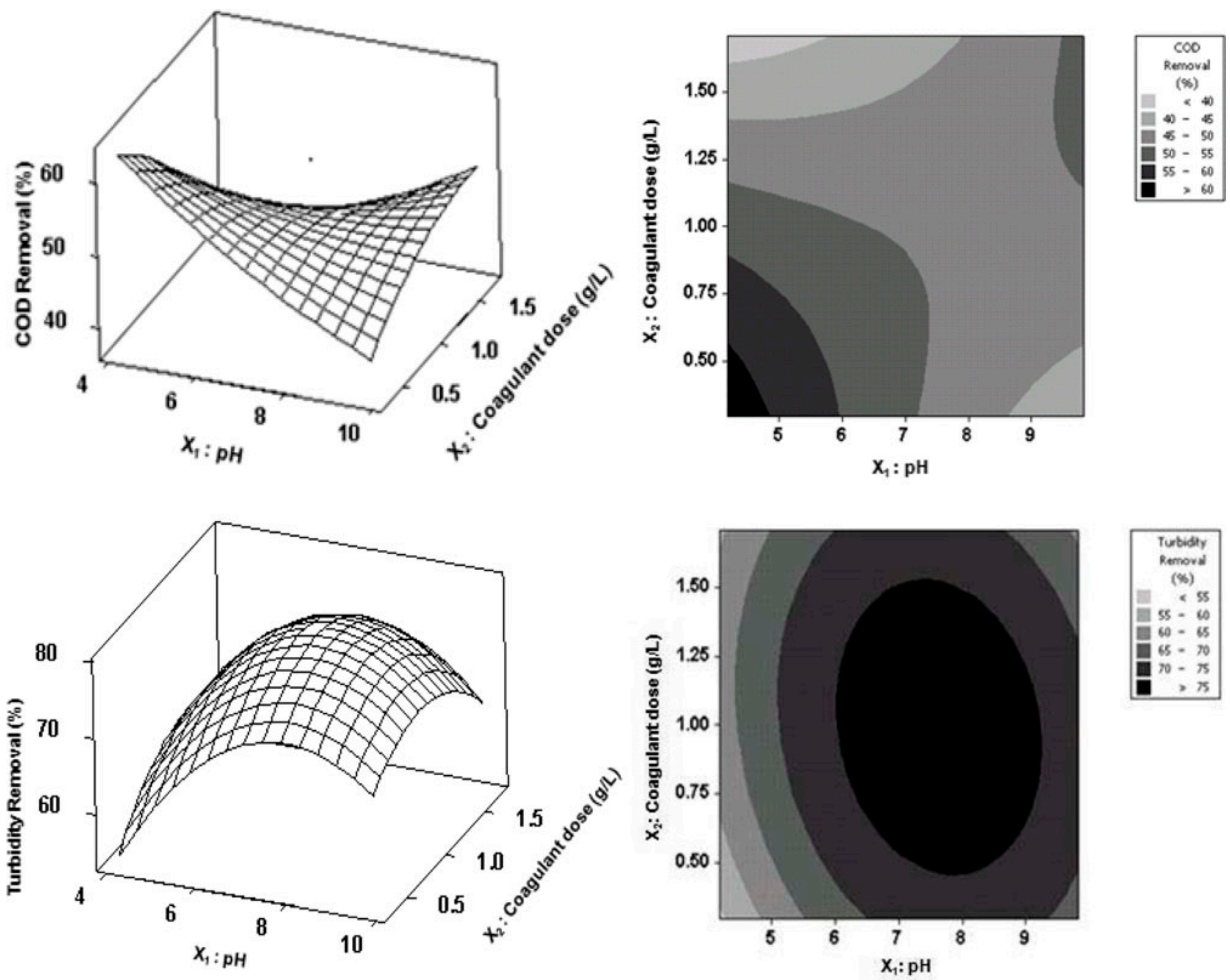

Fig 2. Response surface (a) and contour plots (b) using bentonite as coagulant.

The RSM plot based on the Eq. (3) with a variation of pH and coagulant dosage (within the experimental range) does not have a clear peak, which indicates that the optimum condition falls outside the design boundary and COD_{RE} is confined to the small curve of the contour plot whereas the 3D plot based on Eq. (4) shows a relatively clearer peak and the elliptical contours give the maximum T_{RE}.

The data obtained from batch coagulation experiments in this study collectively displayed the synergistic and antagonistic effects on COD_{RE} and T_{RE} values (Figs. 1 and 2), thereby affecting coagulation of PWW by alum and bentonite. As observed from the Fig. 1(a), COD_{RE} gradually increased when the coagulant dosage was increased from 0.29 to 0.9 g/L and further increase in the dosage decreased the removal efficiency. The possible explanation for the observed phenomenon might be the fact that usually coagulants form hydroxide when dissolved in water. These metal hydroxide polymers have amorphous structure as well as large surface area and possess positive charge. These hydroxides are hydrophobic due to which they are adsorbed into the organic anionic particle surface and become insoluble due to the increased production of hydroxide ions competing for the adsorption sites [40–42]. This is supported by ANOVA results as explained in Section 3.2.1. The elliptical contours in the 3D surface graphs in Fig. 1(b) indicate that the T_{RE} percentage increases at the center of the region, which involves the interaction between coagulant dosage and pH [43]. The effect of pH is found to be significant and the range of 5.5–7.5 gives optimum T_{RE}. Beyond the given range, T_{RE} falls down, perhaps due to reverse stabilization of charges [44]. This could be due to the formation of amorphous solid-phase $Al(OH)_3$ at pH 5.0–8.0 which reduced the turbidity through

Table 7
Comparison of treatment of different wastewaters using various coagulants

		Characteristics of the effluent			Coagulant used	Optimum condition		% Removal		References
S.No	Type of wastewater	pH	Turbidity (NTU)	COD (mg/L)		pH	Coagulant dosage (mg/L)	COD	Turbidity	
1	Emulsified polymeric wastewater	7.5	1,000	2,500	Alum, $FeCl_3$	9	250 (Alum), 200 ($FeCl_3$)	96	96	[37]
2	Beverage industry wastewater	7.66	NS	3,470	$Fe(SO_4)_3{\cdot}3H_2O$ + PE	3–8	500	93	NS	[54]
3	Pulp mill wastewater*	6.99	1,209	1,358	Starch-based biodegradable resin	8.35	871	NS	83.5	[55]
4	Pulp mill wastewater#	6.99	1,209	1,358	starch-g-PAM g-PDMC	7.1	1,017	90.7	99.4	[57]
5	Black liquor from Paper mills	6.73	NS	28,270	$AlCl_3$, PAC and various PE	<3	0.2–1.2	76	NS	[56]
6	Landfill leachate	8.3–8.45	58–74	2,950–4,050	Laterite soil, alum	2 (Laterite soil), 4.8 (alum)	14,000 (Laterite soil), 10,000 (alum)	65.7 Laterite soil), 85.4 (alum)	NS	[38]
7	PWW	7.34	998	2,240	Alum, bentonite	5.91 (alum),5.61 (bentonite)	790 (alum), 580 (bentonite)	67 (alum), 55 (bentonite)	90 (alum), 70 (bentonite)	This study

Notes: COD: chemical oxygen demand; PAC: polyaluminum chloride; PE: polyelectrolyte; PWW: pharmaceutical wastewater; NS: Not specified.
Starch-g-PAM-g-PDMC: polyacrylamide and poly (2-methacryloyloxyethyl) trimethyl ammonium chloride.
*Flocculant (22.3 mg/L) was added with coagulant.
#Flocculant (17.8 mg/L) was added with coagulant.

adsorbing the colloids onto its surface in the so-called sweep floc process [45].

3.3.2. Using bentonite as coagulant

Fig. 2(a) reveals saddle-type contour plot producing stationary points that have the maximum estimated response or an approximate maximum on a line within the design region [46]. It is clearly evident from the RSM plot depicting the pH and coagulant dosage that the pH level of wastewaters plays an important role in the COD_{RE}. With low pH ($-\alpha$) and an increase in coagulant dosage from low (0.3 g/L) to high (1.7 g/L) levels, there was a significant increase in the COD_{RE}. On the other hand, with a high pH ($+\alpha$) and increase in coagulant dosage COD_{RE} decreased from a high value (>70%) to lower values. Within the range of pH tested, significant interactions were produced between coagulant dosage and pH as evident from their low p values (0.039) for COD_{RE}. This indicates that the extent of pH value does not only depend on the type and concentration of coagulants but also depend on the characteristics of wastewater itself [36]. The squared effects due to pH and coagulant dosage were also insignificant ($p = 0.228$, $p = 0.466$) indicating that the COD_{RE} and T_{RE} were inhibited by mutual interaction rather than the linear or squared effects.

The response surface and contour plots for the T_{RE} (Fig. 2(b)) show that the T_{RE} was less (70%) as compared to that of alum (90%). The possible explanation for this observation could be the fact that the moderate surface charge on the smectite clay platelets [47–51] allows the exchange of intercalated cation with other cations [52,53]. Furthermore, such a moderate surface charge allow the penetration of water or other polar molecules in the interlayer space between platelet, causing smectite grains to swell. ANOVA results (Table 4) justified the adequacy of the regression model. The interactions were highly significant with $p < 0.05$ for the regression model equation which implies that the second-order polynomial model fitted well to the experimental data.

3.4. Optimization and confirmation experiment

The numerical point prediction tool of Minitab® v. 16 was used to find the optimum values of the test variables to maximize the COD_{RE} (>75%) and T_{RE} (>90%) using alum and the COD_{RE} (>55%) and T_{RE} (>70%) for coagulation using bentonite. The optimum values of the test variables were obtained when pH and coagulant dosage were 5.91 and 0.79 g/L for alum and 5.61 and 0.58 g/L, for bentonite. Under optimal conditions, the model predicted a COD_{RE} of 67.26% and T_{RE} of 90% for alum. Similarly, using bentonite a COD_{RE} of 54.87% and a T_{RE} of 70% was predicted.

In order to confirm the validity of the regression equations, experiments were performed under optimal conditions in duplicate. The calculated optima can be acknowledged with the observed values of COD_{RE} of 72.14% and T_{RE} of 91.68% for alum within 5%, which can be attributed to experimental error. For bentonite, the observed values of COD_{RE} and T_{RE} (53.57 and 73.85%, respectively) were in close agreement to predicted values with a deviation of less than 5%. The optimum conditions for the variables pH and coagulant dosage were found using a desirable function (D). The composite desirability value (D) of the predicted removal at optimized levels of variables was close to 1 ($D = 0.882$ using alum as coagulant, and $D = 0.996$ using bentonite as coagulant aid). Thus, the regression model developed in this study resulted in good compatibility between the actual and predicted responses.

The results obtained at the optimal condition are compared with results from the literature wherein various coagulants are used for wastewater treatment (Table 7). The COD_{RE} and T_{RE} obtained in this study were found to be comparable with those in the literature, and the differences found are obvious, which could be attributed to the type of wastewater treated and the coagulant used for the treatment of wastewater. As the regression equations have proven to be accurate to calculate the operational conditions of the coagulation–flocculation process, they might be useful to select appropriate process parameters in a wide range of environmental engineering applications [44].

4. Conclusion

This study compares the treatment efficiency of PWW by coagulation–flocculation process using alum and bentonite as coagulant and coagulant aid, respectively. The influence of two key operating variables viz. pH and coagulant dosage was analyzed, and the optimization of these two parameters for simultaneous improvement in the COD_{RE} and T_{RE} was carried out using RSM approach. The results indicated that the optimum conditions for maximizing COD_{RE} and T_{RE} were pH 5.91 and coagulant dosage = 0.78 g/L when alum was used as the coagulant. While for bentonite, the pH and coagulant dosage were 5.61 and 0.58 g/L, respectively. The predicted COD_{RE} and T_{RE} were 67.26 and 90%, respectively, for alum and, for bentonite the predicted COD_{RE} and T_{RE} were 54.87 and 70%, respectively. Accurate prediction of the maximum value of the experimental responses indicates that the quadratic models had been adequately selected to describe the response surface within the experimental region. Though the use of bentonite does not show any remarkable gain in enhancing the removal efficiency compared to alum, its use in coagulation–flocculation process has advantage of being biodegradable and environment friendly, and thus can be used as a potential alternative to alum for PWW treatment.

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