Decolorization of reactive dye Remazol Brilliant Blue R by zirconium oxychloride as a novel coagulant: optimization through response surface methodology

Sonalika Sonal, Astha Singh and Brijesh Kumar Mishra

ABSTRACT

The aim of the present study was to investigate the performance of a novel coagulant, i.e. ZrOCl₂, for the removal of anthraquinone-based reactive dye from aqueous solution. An ideal experimental setup was designed based on central composite design using response surface methodology to determine the individual and interactive effects of different operational variables (i.e. pH, coagulant dose and dye concentration) on treatment performance in terms of dye and chemical oxygen demand (COD) removal efficiencies. Total 92.58% dye and 85.33% COD removal were experimentally attained at optimized conditions at low coagulant dose, i.e. 156.67 mg/L for the dye concentration of 105.67 mg/L at pH 2. To validate the working pH of the metal coagulant, the static charge of ZrOCl₂ was measured using Eh value. The performance of the coagulant was validated with experimental and predicted values in the selected data set, and R² values for both responses were found to be 0.99 and 0.95 respectively, which shows the reliability of the experimental design. Further, the toxicity of the coagulant was assessed and no such toxicity was found even up to the concentration of 500 mg/L, proclaiming the disposal of sludge may not exhibit any threat to humans. Experimental results suggested that the ZrOCl₂ could be used as an eco-friendly coagulant for dye wastewater treatment.

Key words | COD, reactive dye, response surface methodology, toxicity, zirconium oxychloride

HIGHLIGHTS

- 92.58% dye removal was achieved at optimized conditions for anthraquinone based reactive dye by using ZrOCl₂ as a coagulant.
- The low Eh value attributed higher charge on ZrOCl₂.
- ZrOCl₂ did not exhibit any toxicity even for 500 mg/L.
- The boundary condition of operational parameters was validated with response surface methodology (RSM), which confirms the accessibility of ZrOCl₂ as a coagulant.

INTRODUCTION

Industrialization and commercialization results in an enormous expansion and exploration of textile industries. These textile industries require plenty of water among all industries for their various dyeing processes, which eventually generates a huge amount of effluents and pollutants (Correia et al. 1994; Malik et al. 2017). The dyeing process of wet processing textile mills is the most polluting one, and is characterized by high biological oxygen demand (BOD), chemical oxygen demand (COD), pH, suspended solids (SS), alkalinity, residual dyes and auxiliary chemicals that make the effluents more toxic and cause serious threats to aquatic flora and fauna, when
discharged untreated into the water environment (Correia et al. 1994). Because of its high colour and COD content, dyeing wastewater even at very low concentrations, cannot be released directly into water bodies and thus has been listed as one of the most polluting industrial wastewaters that are difficult to treat (Verma et al. 2012). Dyes are mainly complex organic molecules having chromophores (colour imparting compounds) and auxochrome (colour intensifier) groups (Verma et al. 2012; Stawiński et al. 2017). These possess high photochemical stability and a low degradation rate, which prevents light penetration in the water bodies, causing instability in the aquatic environment (Natarajan et al. 2017; Srivastava & Sillanpaa 2017). Depending upon the groups and their characteristics, dyes are categorized as reactive, acid, basic, anionic, direct, azo, anthraquinone etc. Among all groups, reactive dyes are used extensively in textile industries (Zhao et al. 2017), especially in cotton and wool industries because of their high stability during washing, bright colours and simple dyeing application techniques with low energy consumption (Chen et al. 2010). Subsequently, these dyes have become an environmental concern because of their high concentration in effluents due to the low fixation rate on fabrics and resistance to being degraded (Verma et al. 2012). Remazol Brilliant Blue R has been chosen as a representative anthraquinone based reactive dye for the present study, as it represents the most important dyes used commonly in the textile industry, possessing high toxicity and recalcitrant nature (Eichlerová et al. 2007).

In today’s perspective, the growing environmental concern all over the world forbids us to discharge the highly polluted effluent directly into the environmental surroundings. Conventional coagulation/flocculation is one of the well-established efficient, widely used and cost-effective pretreatment methods because of its advantages of decolorization of dye bath effluent by removal of dye, but not by partial decomposition of dyes, which can lead to the formation of potentially more toxic and harmful aromatic compounds (Golob et al. 2005). Some conventional aluminium and ferric salt based chemical coagulants are practised widely but have some limitations such as high dose requirement, low colour removal efficiency (being 50–80% especially for the reactive dyes), huge sludge generation and their great disposal cost, creating the need for a new, efficient coagulant for overcoming these limitations (Kim et al. 2004a, 2004b; Butt et al. 2005). Moreover, the high dose requirement of metal coagulants causes excess metal concentrations in the effluent beyond the permissible limits. Some authors had also reported that these conventional coagulants have serious long-term residual health effects such as Al intake, which may cause several neuropathological diseases, including percentile dementia and Alzheimer’s diseases (Miller et al. 1984; Gauthier et al. 2000; Schintu et al. 2000; Szygula et al. 2009) and Fe-based coagulant has increased the corrosiveness of the treated water (Matilainen et al. 2010) and its health effect is not guaranteed still (Jeon et al. 2009). Some workers also have reported Ti and Zr salts as good coagulants for removal of natural organic matter (NOM) from drinking water (Jarvis et al. 2012; Hussein et al. 2014). Zirconium oxychloride can be used as an alternative metal-based coagulant for the treatment of dye wastewater, as WHO has reported that zirconium compound (for use as a coagulant) is non-toxic and does not possess any known risk to health and the environment. Zirconium also validates the Schulze-Hardy rule, which suggests that the higher the valency of metal-based counter ions, the better the efficient destabilization of colloidal particles (Hussain et al. 2014). Because of all these advantages, in this study the potential and effectiveness of zirconium has been studied as an alternative and efficient coagulant for the removal of reactive dyes.

To find out the effectiveness of a novel coagulant, process optimization is required and for that, the selection of coagulant dose and operational conditions are very important. Some recent publications have demonstrated the effectiveness of RSM modelling for dye removal. In fact, RSM is an aggregation of mathematical and statistical techniques that helps in developing, improving and optimizing different processes and therefore assessing the comparative meaning of interaction effects between various factors (Arslan-Alaton et al. 2009; Zaroual et al. 2009; Bashir et al. 2010). In the present study, RSM has been applied to optimize all the parameters in lieu of conventional optimization methods as the traditional method demands more time-consuming experimental runs without showing any interaction between the operational parameters (Khayet et al. 2011).

Based on the above literature, it has been found that iron and aluminium based metallic coagulants cannot be a good choice for the dye industry. To overcome this issue, the foremost attempt has been commenced to assess the feasibility of a highly charged novel metallic coagulant, zirconium oxychloride octahydrate, as a coagulant for the treatment of reactive dye (RBBR). The execution of the coagulant has been assessed on the basis of dye removal, COD removal and its toxicity test, to support its environmental suitability.
MATERIALS AND METHODS

Chemical and materials

An anthraquinone based dye, Remazol Brilliant Blue R (Commercial name: Reactive Blue 19), was supplied by Sigma Aldrich, USA (Table 1). Other chemical reagents such as zirconium oxychloride, sodium hydroxide, hydrochloric acid, etc., were purchased from Merck, Mumbai, India. Milli-Q, RO water (Millipore, USA) was used for the preparation of the stock solution and other sample preparation as per the experimental requirement. In this study, all reagents were of analytical grade and were used as received without any further purification.

Experimental procedure

A stock solution of dye mass was prepared in Mili-Q, RO water to the desired concentration and diluted accordingly with tap water for the desired working concentrations. A stock solution of coagulant at a desired concentration was freshly prepared. The predetermined pH was adjusted by using 0.1–1.0 N NaOH and HCl. pH and Eh were measured by using a multiparameter pH meter (Hanna Instrument Model HI 5521). COD measurement was carried out by the open reflux method as per the standard method of APHA (2012).

Jar test experiments

1 L dye solution at the required concentration was filled in 1 L jar beakers and the required pH was adjusted using 0.1–1 N HCl and NaOH. After a while, the required dose of the coagulant was added to each beaker. A standard digital six jar test apparatus (M/s Labard Instru Chem, India), equipped with stainless steel paddles, was used to perform the coagulation/flocculation experiment. The coagulation/flocculation procedure involved 2 min of rapid mixing at 200 rpm, followed by 30 min of slow mixing at 40 rpm and 120 min of settling time. After settling, the supernatant liquid was withdrawn from each beaker by using a water syringe from a height of about 2 cm below the liquid surface. Simultaneously, the dye concentration was measured using a UV/Vis spectrophotometer (Labtech, Model UV 9100/A) at 595 nm, and COD was measured by the standard protocol as prescribed by APHA (2012). The dye concentration was calculated by using the standard curve, and removal percentages for dye and COD were calculated by using the following formula:

\[
\text{Removal(\%)} = \frac{C_0 - C_f}{C_0} \times 100
\]  

(1)

where, \(C_0\) and \(C_f\) are the initial and final concentration respectively.

All the experiments and measurements were conducted at room temperature and done in triplicate form for more authentic outcomes.

Toxicity test by culture media preparation

Further, the toxicity of the coagulant was examined to ensure the reliability and environmental friendliness of the coagulant. The set nutritional agar (HI Media) Petri plates were dried at 37 °C in a laminar air flow chamber under UV light and inoculated with stock Escherichia coli ATCC 25922. The inoculated plates had three 6 mm dia. cut outs of Whatman filter paper-42 (cat. no. 1442-125) into the surface of the agar. The cut outs were dipped with ZrOCl2 and the plates were incubated (34 °C) overnight (Holder & Boyce 1994).

Statistics and experimental design

Jar test experiments were conducted based on RSM (Design-Expert software version 7.0), which has been used for structured and systematized experimentation designing. RSM involves the statistical design of experiments (DoE) in which all factors varied concurrently over a set of experimental runs, to understand the relationship between factors, affecting the process and output from each beaker by using a water syringe from a height of about 2 cm below the liquid surface. Simultaneously, the dye concentration was measured using a UV/Vis spectrophotometer (Labtech, Model UV 9100/A) at 595 nm, and COD was measured by the standard protocol as prescribed by APHA (2012). The dye concentration was calculated by using the standard curve, and removal percentages for dye and COD were calculated by using the following formula:

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<table>
<thead>
<tr>
<th>Name of the dye</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>Supplier’s purity (%)</th>
<th>Type of dye</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remazol Brilliant Blue R</td>
<td>595</td>
<td>~50%</td>
<td>Reactive dye</td>
<td>C(<em>{22})H(</em>{16})N(_2)Na(<em>2)O(</em>{11})S(_3)</td>
<td>626.54 g/mol</td>
<td></td>
</tr>
</tbody>
</table>

\( \lambda_{\text{max}} \) = maximum wavelength.
responses (Khayet et al. 2011). Before designing experimen-
tal runs through RSM, a narrow range of all the variables 
was determined manually at first, by keeping two factors 
constant at a specific set of conditions. Based on manual 
observation with regard to operational conditions, the 
desired ranges of experimental conditions were selected, 
as shown in Table 2 and analysed for optimum conditions 
with respect to the defined responses. Later, a second 
order three-level full factorial CCD (central composite 
design) was employed to develop a mathematical corre-
lation between the operating variables (i.e. initial pH, 
coagulant dosage and initial dye concentration) to 
assess the dye and COD removal efficiency by zirconium oxy-
chloride as a novel coagulant. A total of 20 exper-
iments were run for face centred full factorial CCD 
design, which consists of eight factorial points, six axial 
points and six central points. For statistical calculations, 
the variables $z_i$ (the real values of independent variables) 
were coded as $x_i$ (dimensionless value) by using the 
following equations:

$$X_i = \left(\frac{z_i - z_i^0}{\Delta z_i}\right)\beta_d$$

(2)

where, $\Delta z_i$ is the distance between the real value in the 
central point and the real value in the superior or the 
inferior level of a variable, $\beta_d$ is the major coded limit 
value in the matrix for each variable, and $z_i^0$ is the real 
value in the central point (Bezerra et al. 2008).

The experimental data were fitted to a second order 
polynomial equation to predict the optimum conditions of 
factors such as pH, coagulant dose and dye concentration. 
The quadratic equation model for predicting the optimal 
condition through 3D contour plots can be expressed with 
the help of Equation (3).

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_i^2 X_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} X_i X_j + \varepsilon$$

(3)

where, $y$ is the predicted response, $\beta_0$ is the constant coef-
icient, $\beta_i$ is the linear coefficient, $\beta_{ij}$ represents the 
coefficients of a quadratic parameter, $\beta_{ij}$ is the interaction 
coefficient of second-order terms, $k$ is the number of fac-
tors studied, $X_i$ and $X_j$ are the coded values of the 
variables, and $\varepsilon$ is the random error. The adequacy of the 
proposed model is examined by ANOVA (analysis of 
variance) inbuilt within the Design-Expert software to 
obtain the interaction between the independent and 
dependent variables. The quality of the fit polynomial 
model was expressed by the $R^2$ (coefficient of 
determination), which describes the proportion of total 
variation in the response predicted by the model. The stat-
istical significance of the $R^2$ value was determined by 
checking the Fisher’s F-test model. The model terms 
were evaluated by the $P$-value (probability) with a 95% 
confidence level (Montgomery 2001). Eventually, three 
dimensional plots with respective contour plots were 
obtained from the results of the experiments for all the par-
eters and then lastly the optimum region was identified.

RESULTS AND DISCUSSION

The study was conducted to evaluate the efficiency of a 
novel coagulant (i.e. zirconium oxychloride) for removal of 
a reactive dye (RBBR) by a full factorial CCD design using 
the RSM tool and a relation between output responses, i.e. 
dye and COD removal and the input factors (pH, coagulant 
dose and dye concentration) were established using a 
second order polynomial regression equation (Equation 
(3)) developed by RSM.

Statistical evaluation of the data with fitted models

Based on CCD experimental design, all the output results 
of the coagulant were obtained and depicted in Table 3. 
The quadratic model was selected for both the responses, 
i.e. dye and COD removal, as suggested by the software 
(Stat-Ease Design-Expert). In the present study, it was 
observed that the actual experimental data of dye and 
COD removal efficiency of the coagulant from the 
model have an adequate agreement with the predicted 
values (Figure 1(a) and 1(b)), which revealed that the model 
has reliability in terms of prediction accuracy. The 
regression equation was fitted with the removal effi-
ciency results and obtained in terms of coded factors.
Dye removal \(= 74.61 - 7.73A + 11.09B - 11.32C - 3.82AB + 3.48AC + 15.98BC + 5.39A^2 - 4.11B^2 - 2.99A^2 \) (4)

COD removal \(= 64.24 - 10.00A + 13.10B - 5.90C - 3.87AB + 3.62AC + 14.38BC + 11.06A^2 - 11.44B^2 - 6.44C^2 \) (5)

where A is initial pH, B is coagulant dose and C is dye concentration.

The positive and negative sign in front of the terms indicates synergistic and antagonistic effects respectively.

The equations clearly show that pH and dye concentration have an antagonistic effect, whereas coagulant dose has a synergistic effect for dye as well as COD removal within the optimized condition. The adequacy of the model responses was validated statistically by ANOVA, which is
mainly a statistical tool that subdivides the total variance in a set of data into component parts associated with specific sources of variation for the function of testing hypotheses on the parameters of the model (Ravikumar et al. 2007). The ANOVA results of the present study have been presented in Table 4, which shows the modified quadratic models in terms of coded variables and other statistically significant parameters. The table data clearly show that dye and COD removal efficiencies of the coagulant were significant, i.e. their F-value is less than the probability value (P-value) (i.e. F value < 0.0001) which suggests that there is only 0.01% chance that a model F-value deviates from the experimental values. The larger value of the F-value implies that the regression equation can explain most of the variation in the response (Ravikumar et al. 2007) and its associated P-value is used to judge whether F_{stat} is large enough to indicate statistical significance or not. Also, the significance of the model terms was evaluated with respect to their associated P-values. Model terms are significant at a 5% confidence level (P < 0.05), and it was found in the present study that all model terms were significant in the case of dye removal, while in case of COD removal A, B, C, AB, BC, A^2 and B^2 were the significant model terms. Another model validating parameters is the lack of fit (LoF) test, which explains the variation of data around the fitted model. If a P-value of LoF is larger than 0.05, it suggests that the F-test is insignificant, implying significant model correlation between the variables and process responses. Thus, based on the P-value of regression and LoF test, it has been affirmed that the model was well fitted to the experimental data, as the results showed significant regression and non-significant lack of fit in the developed model.

The coefficient of determination, i.e. R^2, was used to express the quality of the fitted model and its value, close to 1, has been desirable for the best-suited model. In the present study, the R^2 value was found to be 0.99 and 0.95 for dye and COD removal respectively, which ensured acceptable modification of the quadratic model to the experimental data. For more precise regression model judgment, the adjusted R^2 was used for comparing the residual per unit degree of freedom (Amago 2002). Moreover, the predicted R-squared values of both responses were in reasonable agreement with the adjusted R^2 value, which suggests significant terms have been included in the model. Similarly, adequate precision (measurement of signal to noise ratio) for a significant model requires a value greater than 4, and in the present study the adequate precision value was found to be above 4 (Table 4) for both the responses, which indicates the model can be used to navigate the design space. In a similar fashion, less than 10% CV value represents the reproducibility of the model and in the present study the CV values in both cases, i.e. dye and COD removal, were 2.48% and 8.01% (Table 4) respectively, which shows the model has a better reproducibility capacity.

**Coagulant activity**

Graphical representation of the response surface was plotted based on the model equation as described in the Materials and methods section (Equation (3)), and the removal efficiency of dye and COD were examined under different operational conditions. The effects of operational parameters for dye removal were monitored by varying two independent variables while keeping a single factor fixed at a specific set of conditions, as shown in

**Table 4 | Summary of ANOVA results for response parameters**

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Response</th>
<th>Source</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F-value</th>
<th>P &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrOCl₂</td>
<td>Dye</td>
<td>Model</td>
<td>5,483.03</td>
<td>9</td>
<td>609.23</td>
<td>182.79</td>
<td>&lt;0.0001 (significant)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Residual</td>
<td>33.33</td>
<td>10</td>
<td>3.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lack of fit</td>
<td>26.84</td>
<td>5</td>
<td>5.37</td>
<td>4.14</td>
<td>0.0725 (not significant)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pure error</td>
<td>6.48</td>
<td>5</td>
<td>1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD removal</td>
<td></td>
<td>Model</td>
<td>5,671.32</td>
<td>9</td>
<td>630.15</td>
<td>26.57</td>
<td>&lt;0.0001 (significant)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Residual</td>
<td>237.16</td>
<td>10</td>
<td>23.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lack of fit</td>
<td>159.06</td>
<td>5</td>
<td>27.81</td>
<td>1.42</td>
<td>0.3555 (not significant)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pure error</td>
<td>98.10</td>
<td>5</td>
<td>19.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SD = 1.83, C.V. = 2.48, PRESS = 174.82, R^2 = 0.9940, R^2_{adj} = 0.9885, Adequate Precision = 48.517

SD = 4.87, C.V. = 8.01, PRESS = 1486.04, R^2 = 0.9599, R^2_{adj} = 0.9237, Adequate precision = 19.660

SD: standard deviation; CV: coefficient of variance; PRESS: predicted residual error sum of squares; R^2: correlation coefficient; R^2_{adj}: adjusted R^2.
From Figure 2(a), it was distinctly established that the dye removal enhances to more than 94% when the pH was adjusted from 5 to 2 for the dye concentration of 100 mg/L. The results revealed that, in the case of ZrOCl₂, good destabilization of the colloidal occurred mostly in a highly acidic condition. Several researchers reported that the pH plays an eminent role during the coagulation/flocculation process, as a charge on hydroxide products and the destabilization of the colloidal particles are highly pH dependent in an aqueous medium (Li et al. 2017). The potential mechanism behind the working phenomenon of ZrOCl₂ at this low pH may be due to increase in the static charge of attraction between anions of dye molecules and cationic species of metallic coagulant.

To interpret the electrostatic charge of the metallic coagulant, the Eh value of Zr in aqueous solution at room temperature was determined and was found to be in the range of 0.27 to 0.37 V. The lowest value of Eh was found at pH 2, and the corresponding Eh value was compared with Pourbaix diagram (Source: GSJ 2005, F No. 419) which showed that at this low pH the Zr has a maximum static charge, i.e. +3, which may be one of the reasons behind the high removal of dye at this low pH (Figure 3). Ruihua Li et al. (2017) and Demirbas & Nas (2009) had also reported the removal of reactive dye at a highly acidic condition, i.e. pH < 2 (Demirbas & Nas 2009; Li et al. 2017). The performance of ZrOCl₂ in terms of NOM removal was carried out by some researchers and it has been reported that the ZrOCl₂ coagulant activity is always predominant in acidic conditions (Jarvis et al. 2012; Priya et al. 2017).

Further, the interaction of coagulant dose with respect to dye removal was also monitored at a dye concentration of 100 mg/l as shown in Figure 2(a), and from the figure it was observed that the increase in coagulant dose increases the removal efficiency of dye without further re-stabilization effect up to 160 mg/L coagulant dose. Contrary to this, Patel & Vashi (2010) reported 70,000 mg/L of alum as an optimized dose for the 74% removal of reactive dye (Patel & Vashi 2010), whereas Kim et al. (2004a, 2004b) reported 293 mg/L dose of ferric chloride to achieve 71% removal efficiency (Kim et al. 2004a, 2004b). The optimized dose of ZrOCl₂ shows better efficiency at a low dose, which may be because of the dye protonation process, which could lead to a reduction of the charge density and cause self-agglomeration of anionic dye molecules at decreasing pH (Shi et al. 2007; Moghaddam et al. 2010). This low dose of coagulant may be attributed the theory of high charge on coagulant, as ZrOCl₂ has highly charged hydrolysis products of ZrOCl₂ i.e. Zr(OH)₂₄H₂O)⁺⁺⁺, Zr₄(OH)₂₈(OH₂)₁₆⁺⁺⁺, Zr₃(OH)₈⁺⁺⁺, Zr(OH)(OH₂)₇⁺⁺, which play a significant role in destabilizing the anionic nature of the functional group of the organic dye (Hussain et al. 2014). In Figure 2(b) and 2(c) it was found that the dye removal efficiency of ZrOCl₂ metal increases with a decrease in dye concentration from 150 to 50 mg/L, this may be because of the charge neutralization along with sweep flocculation as, at low concentration of dye, metals counter ions gets enough surface to neutralize the charge and sufficient degree of oversaturation of metal hydroxide occurs which enmeshes the colloidal particles and subsequently leads to precipitation of the dye molecules (Peavy et al. 1985).
Figure 3 | (a)–(c) Design-Expert plot; response surface plot for the dye and COD removal % for ZrOCl$_2$. 

(a) Effect on pH and coagulant dose at dye concentration of 100 mg/L for Dye and COD removal (%)

(b) Effect on pH and Dye concentration at coagulant dose of 120 mg/L for Dye and COD removal (%)

(c) Effect on Coagulant dose and Dye concentration at initial pH 3.5 for Dye and COD removal in percentage
Many researchers have validated the performance of coagulant activity during the coagulation/flocculation process with the help of COD removal efficiency (Kim et al. 2004a, 2004b; Papic et al. 2004). In the present study, COD removal efficiency was also accorded to be similar to that of dye removal efficiency by changing two variables while keeping one variable constant at one time as shown in Figure 2(a)–2(c), and almost similar trends were found for the COD removal as discussed above. The maximum removal efficiency of COD found more than 80% of the coagulant dose of 160 mg/l at pH 2, while previous studies have reported 44–82% and 23–63% removal of dye and COD respectively, for reactive dyes (Kim et al. 2004a, 2004b; Butt et al. 2005).

Toxicity level of ZrOCl2 as coagulant

Generally, metal-based coagulants have toxic impacts on the aquatic environment and have a tendency to leave a residual effect in the effluent which causes the fatal effect on aquatic and human life (Miller et al. 1984; Gauthier et al. 2000; Schintu et al. 2000). Thus, pretreatment with metal coagulant may possess a hazard quotient (HQ) towards the aquatic environment and have a tendency to leave a residual effect on the environment and the sludge generated with this metal coagulant may not be going to impact the groundwater on its disposal, unlike traditional coagulants.

Process optimization

The RSM was used to determine the values of the independent variables that produce optimum values of the responses i.e. dye and COD removal. To maximize the responses in terms of dye and COD removal, all independent variables were individually arranged in a sequence of increasing or decreasing order. Subsequently, the combination of these optimum variables was selected for the conditions to obtain the best results (Bezerra et al. 2008). In this work, the responses of each process were chosen to be maximized and the independent variables were selected to be within range. After maximization for the responses in terms of dye and COD removal, the following independent variables were recorded by a model as described in Table 5.

The maximum dye and COD removal at optimized independent variables as suggested by the model was 96.79% for dye and 89.75% for COD. Ultimately, the optimum values were further validated with experiments actually carried out at the estimated optimal conditions to confirm the satisfactoriness of the model. The experimental results were found to be in full agreement with the RSM results, which suggests the soundness of the optimization procedures.

### Table 5 | Optimization results for decolorization of Remazol Brilliant Blue R by using ZrOCl2

<table>
<thead>
<tr>
<th>Variables</th>
<th>Unit</th>
<th>Optimum values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH of the dye solution (A)</td>
<td>–</td>
<td>2.08</td>
</tr>
<tr>
<td>ZrOCl2 dose (B) mg/L</td>
<td></td>
<td>156.72</td>
</tr>
<tr>
<td>Initial dye concentration (C) mg/L</td>
<td></td>
<td>105.67</td>
</tr>
<tr>
<td>Dye removal efficiency (predicted) %</td>
<td></td>
<td>96.79</td>
</tr>
<tr>
<td>Dye removal efficiency (experimental) %</td>
<td></td>
<td>92.58</td>
</tr>
<tr>
<td>COD removal efficiency (predicted) %</td>
<td></td>
<td>89.75</td>
</tr>
<tr>
<td>COD removal efficiency (experimental) %</td>
<td></td>
<td>85.33</td>
</tr>
</tbody>
</table>

CONCLUSION

In the present study, a coagulation/ flocculation experiment was conducted to study the performance of a novel coagulant ZrOCl2 for the removal of reactive dye Remazol Brilliant Blue R. The correlation coefficient, i.e. the R2 value for dye and COD removal, was found to be 0.99 and 0.95 respectively, which clearly described the soundness of the modelling approach for the optimization process. The experimental results at model optimized conditions disclosed that the ZrOCl2 coagulant has huge potential in terms of dye and COD removal efficiency, i.e. 92.58% and 85.33%, respectively, at a low coagulant dose, i.e. 156.72 mg/l for the dye concentration of 105.67 mg/l. The possible mechanism for higher removal of reactive dye at low coagulant doses from the synthetic dye wastewater may be attributed because ZrOCl2 has a tendency towards a dye protonation process which leads to the reduction of charge density and causing self-agglomeration of anionic dye molecules at decreasing pH. The low Eh value attributed higher charge on ZrOCl2, which facilitates charge neutralization during the coagulation process that accredited the low dose requirement of coagulant. ZrOCl2 as coagulant offers advantages over traditional coagulant such as a low dose requirement,
high removal efficiency, nontoxic effect on effluent etc., hence, makes its use reasonable and effective in dye wastewater treatment. Thus, it is concluded that ZrOCl₂ has properties that are of interest in dye wastewater treatment.

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