Comparison of chitosan based nano-adsorbents for dairy industry wastewater treatment through response surface methodology and artificial neural network models

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ABSTRACT

The present investigation was focused to compare chitosan based nano-adsorbents (CZnO and CTiO2) for efficient treatment of dairy industry wastewater using Response Surface Methodology (RSM) and Artificial Neural Network (ANN) models. The nano-adsorbents were synthesized using chemical precipitation method and characterized by using scanning electron microscope with elemental detection sensor (SEM-EDS) and atomic force microscope (AFM). Maximum %RBOD (96.71 and 87.56%) and %RCOD (90.48 and 82.10%) for CZnO and CTiO2 nano-adsorbents were obtained at adsorbent dosage of 1.25 mg/L, initial biological oxygen demand (BOD) and chemical oxygen demand (COD) concentration of 100 and 200 mg/L, pH of 7.0 and 2.00, contact time of 100 and 60 min, respectively. The results obtained for both the nano-adsorbents were subject to RSM and ANN models for determination of goodness of fit in terms of sum of square errors (SSE), root mean square error (RMSE), R² and Adj. R², respectively. The well trained ANN model was found superior over RSM in prediction of the treatment effect. Hence, the developed CZnO and CTiO2 nano-adsorbents could be effectively used for dairy industry wastewater treatment.

Key words | dairy industry, optimization, modelling, nano-adsorbents, wastewater treatment

HIGHLIGHTS

- Operational parameters effect on adsorption of BOD and COD were investigated.
- Cost-effective and environmental friendly effluent treatment processes developed.
- Process parameters were optimized by RSM and ANN models.
- Desirability function resulted to 0.981 and 0.965 for CZnO and CTiO2 nano-adsorbents.
- Modelling, prediction and generalization capabilities are investigated.

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INTRODUCTION

The dairy industry (DI) is one of the major economic sectors for many nations due to their resourceful products, but they generate a lot of wastewater (effluent) (Pathak et al. 2016). Constituents of DI wastewater include total dissolved solids (TDS), total suspended solids (TSS), low pH, high electrical conductivity (EC), turbidity, biological oxygen demand (BOD), chemical oxygen demand (COD), oil, grease, phosphate, sulphate, nitrate-nitrogen, ammoniacal-nitrogen and chloride (Biancani et al. 2014).

Various environmental regulations and emission standards have been formulated to address water pollution issues to defend the non-toxic global freshwater inventory (Teh et al. 2014). To meet the wastewater discharge limits set by the state as well as central pollution control boards, the DI started treating the effluents before discharging into the environment (Qasim & Mane 2016). Dairy industry wastewater (DIWW) could be treated with various biological and physicochemical processes. However, the performance of the biological treatment process is low due to the high organic load and the toxic nature of the DIWW (Sarkar et al. 2016). The traditional physicochemical treatment processes have been able to reduce BOD and COD but to a lesser extent (Thirugnanasambandham & Sivakumar 2015). Hence, secondary pollution occurs due to a low reduction in BOD and COD after being treated by existing DI effluent treatment plants.

There are several traditional treatment methods used for DIWW treatment. Preliminary treatment is used to remove large solids such as rags, sticks, grit and grease (Verma & Singh 2017) whereas primary treatment is used for removal of floating and settle-able materials, i.e. suspended solids and organic matter. Secondary treatment includes both biological and chemical methods used to remove biodegradable organic matter and suspended solids (Tikariha & Sahu 2014). Tertiary or advanced treatment process are used to remove residual suspended solids or dissolved solids by using any one or more of these techniques – membrane techniques (micro and ultrafiltration), reverse osmosis, ozone technology, electrocoagulation and activated sludge treatment. Some of the promising wastewater treatment techniques or tools introduced by nanotechnology are photocatalysis, nanofiltration, and nano-adsorbents (Abdessemed & Nezzal 2002; Balannec et al. 2002; Sarkar et al. 2006; Achak et al. 2009; Bora & Dutta 2014; Stoller et al. 2016).

Generally, BOD and COD adsorption approaches include the traditional and novel physico-chemical methods. Among these methods, adsorption is an efficient method for the removal of inorganic and organic pollutants from wastewater. There are several advantages in adsorption process such as effectiveness (low contaminant concentrations), higher selectivity (tailored adsorbents), regenerability and cost-efficiency (Oladipo et al. 2017). In this contest, to meet the global environmental sustainability, the synthesis and characterization of novel adsorbents with high adsorption capacity and high rate give more importance (Pathak et al. 2016). Previous studies reported that metal oxide-based materials were highly efficient adsorbents for adsorption of organic pollutants (Qu et al. 2013). Recently, metal oxide-based nano-adsorbents gained demand in environmental and biological engineering due to their charming intrinsic properties such as high surface area and adsorption capacity (Thirumavalavan et al. 2015). The development of an eco-friendly and energy-efficient approach for the synthesis of these nano-adsorbents on a large scale is still a challenge (Thirugnanasambandham et al. 2014b). Synthesis of nano zinc oxide (ZnO) and titanium dioxide (TiO₂) for
photocatalytic and biological activities have been reported by several researchers (Thirumavalavan et al. 2013; Haldorai & Shim 2014). These nano-adsorbents are eco-friendly and do not affect the environment through leaching of particles in a treatment system (Thirugnanasambandham & Sivakumar 2015).

Chitosan is derived from the exoskeleton of crustaceans, which is one of the important polymers made from the alkaline deacetylated product of chitin (Thirumavalavan et al. 2013). Chitosan is a non-poisonous, hydrophilic, biocompatible, biodegradable and antibacterial polymer (Raut et al. 2016). In the area of wastewater treatment, the chitosan and its byproducts have greater potential applications due to its chemical structure, stability, biologically compatible, very good oxidation-reduction potential and non-toxicity (Thirugnanasambandham et al. 2014b). Chitosan-containing amino groups can serve as chelation sites for adsorption of BOD and COD from DIWW. Thus, the binding of chitosan into ZnO and TiO2 will probably yield novel nano-adsorbents for the efficient removal of BOD and COD from DIWW (Vaseeharan et al. 2013; Haldorai & Shim 2014; Thirugnanasambandham & Sivakumar 2015). Therefore, it was decided to synthesize chitosan-zinc oxide (CZnO) and chitosan-titanium dioxide (CTiO2) nano-adsorbents for DIWW treatment.

Performance of the adsorption process at an insignificant state could be the highest reagent consumption, and it may take more time. Hence, the process optimization for adsorption of BOD and COD is very important. One Factor at a Time (OFAT), Response Surface Methodology (RSM) and the Artificial Neural Network (ANN) modelling approaches are generally used for optimization. There are several disadvantages in the OFAT method, such as operational parameters between interaction effects are not considered for optimization and not used for validation (Youseffi et al. 2009; Karimi et al. 2012). To solve these problems, RSM and ANN models are used for the prediction of nonlinear systems. RSM and ANN are excellent empirical modelling tool used for combined mathematical and statistical analysis. The aim of optimization using RSM and ANN method is dependent variables or responses will be verified by independent parameters (operational parameters). Input, output and hidden layers of neurons are the part of the multilayered perceptron (MLP) in ANN based models. The mathematical problems underlying process are generally predict the modelling data. In conventional modelling technique, the relationships between linear and nonlinear variables are directly drawn from a set of examples. However, ANN is a data-driven technique used to compute the relationship between input and output variables (Sarve et al. 2015; Yadav et al. 2018). Therefore, in the present study, optimization of process parameters were achieved for percent reduction of BOD (%R_BOD) and percent reduction of COD (%R_COD) from DIWW using CZnO and CTiO2 nano-adsorbents.

**MATERIALS AND METHODS**

Wastewater from Mother Dairy, Raichur (Karnataka) was collected and estimated the characterization using standard methods. Chemical reagents required for the synthesis of nano-adsorbents were purchased from M/s. Sigma Aldrich Chemicals, Bengaluru, India. The pH was measured using a pH meter. BOD and COD were estimated by following the method described by AOAC (1990). Synthesized nano-adsorbents were characterized by using a scanning electron microscope with elemental detection sensor (SEM-EDS) and atomic force microscope (AFM).

**Synthesis of nano-adsorbents**

CZnO nano-adsorbent was synthesized by using co-precipitation method as described by Thirugnanasambandham & Sivakumar (2015). ZnO (3.75 g) was dissolved in 500 mL of 1% acetic acid, and 50 mL of 60% nitric acid. Chitosan (5 g) was added to this solution and stirred for 3 h at 500 rpm by using magnetic stirrer. Sonication was performed by using ultrasonicator for 15 min and the pH of the solution was increased up to 10 by adding 4M sodium hydroxide solution. After reaching pH 10, precipitate of CZnO was formed and this precipitate was kept in a water bath at 60 °C for 3 h. The precipitate was filtered and washed with distilled water and dried in a hot air oven at 50 °C for 24 h. Synthesized CZnO particle size was reduced to nano-size using a high-speed cryo ball mill and preserved in an airtight glass container for further use.

CTiO2 nano-adsorbent was synthesized by co-precipitation method as described by Haldorai & Shim (2014). One gram of TiO2 was dissolved in 100 mL of 1% (v/v) acetic acid and 10 mL of 60% nitric acid. To this solution, chitosan (1 g) was added and stirred at 500 rpm using a magnetic stirrer for 3 h continuously to get a clear solution. After that, sonication was performed by using ultrasonicator for 15 min. Sodium hydroxide solution (1M) was added in a dropwise manner until the solution attained pH 10. The precipitate formed was heated at 80 °C for 5 h. It was then filtered, washed with distilled water and dried in a
hot air oven at 60 °C for 12 h. Synthesized CTiO₂ particle size was reduced to nano-size using a high-speed cryo ball mill.

**Batch adsorption experiment**

Batch adsorption study for \%R\textsubscript{BOD} and \%R\textsubscript{COD} by using CZnO and CTiO₂ nano-adsorbent particles was performed according to the method described by Thirugnanasambandham et al. (2014a). Synthetic BOD solution was prepared by dissolving 150 mg/L of glucose and glutamic acid (i.e. 1,000 mg/L stock solution). Synthetic COD solution was prepared by dissolving 0.085 g of potassium hydrogen phthalate in 1 L distilled water (i.e. 1,000 mg/L stock solution) (AOAC 1990). The prepared synthetic BOD and COD stock solutions were used for initial BOD and COD concentrations in batch adsorption study.

Initial BOD (100–300 mg/L) and COD (200–600 mg/L) concentrations, CZnO and CTiO₂ (0.50–2.00 mg/L) nano-adsorbent dosages were prepared in 100 mL distilled water in a 250 mL conical flask. The pH (2–12) of prepared BOD and COD solutions were adjusted with 0.1 M concentrated sulfuric acid or sodium hydroxide solution. The conical flask containing solutions were agitated at different time intervals (20–100 min) at 200 rpm by using orbital shaker incubator at 30 °C temperature. Samples obtained from the batch adsorption experiment were taken by using 10 mL syringe and filtered through 0.22 μm membrane filter prior to BOD and COD analysis (Thirugnanasambandham et al. 2014a). Triplicate experiments were conducted, and results were tabulated. The value of \%R\textsubscript{BOD} and \%R\textsubscript{COD} were calculated using the Equation (1):

\[
\text{Per cent reduction} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)
\]

where \(C_0\) and \(C_e\) are the initial and final concentration of model pollutants (BOD or COD).

**Response surface methodology**

The input factors were varied at different levels to observe their effect on \%R\textsubscript{BOD} and \%R\textsubscript{COD} by using CZnO and CTiO₂ nano-adsorbents. The obtained results of the experimental design matrix were performed by using RSM. The quadratic model of RSM and experimental data obtained by using Box- Behnken Design (BBD) was used to train the ANN model by using feed-forward back propagation neural network (Yadav et al. 2018).

In this study, the effect of initial concentration, pH, dosage and contact time of CZnO and CTiO₂ nano-adsorbents were investigated. The number of experimental runs of BBD was calculated by using Equation (2):

\[
N = 2(X - 1) + C_0 \quad (2)
\]

where \(X\) is the number of variables and \(C_0\) is the number of center points in the design.

The total number of experiments found by Equation (2) was 29, in which five experiments were found at centre points. The interaction relationship of the variables was determined by fitting the second-order quadratic polynomial model (Equation (3)) to the obtained data (Reddy et al. 2014). The quality of the model was evaluated using Analysis of Variance (ANOVA) and a test of significance (Bhanarkar et al. 2014). For four factors \((n = 4)\) and three levels (low (-), medium (0), and high (+)), the total number of experiments were found to be 29 (Yadav et al. 2018).

\[
Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + e \quad (3)
\]

where, \(Y\) as predicted value of response (\%R\textsubscript{BOD} and \%R\textsubscript{COD}); \(b_1, b_2, b_3\) and \(b_4\) are linear coefficients; \(b_{11}, b_{22}, b_{33}\) and \(b_{44}\) are quadratic coefficients; \(X_1, X_2, X_3\) and \(X_4\) are initial concentration of model pollutants (mg/L), pH, dosage of nanoadsorbents (mg/L) and contact time (min); \(b_{12}, b_{13}\) and \(b_{14}\) are cross-products coefficients, and \(e\) is the error term.

All experiments were performed in replication and average values have been reported. BBD matrix of experimental data sets and their observed responses were tabulated. Design Expert software (8.0.7.1 version) was used for RSM modelling (Jha et al. 2017). Independent variables and their levels selected for \%R\textsubscript{BOD} and \%R\textsubscript{COD} by using CZnO and CTiO₂ nano-adsorbents are depicted in Table 1.

**Artificial neural network**

Feed-forward artificial neural network model was applied for the simulation of the experimental data of batch adsorption study by using MATLAB Subroutine Prepca-007 software. Twenty-nine patterns were used for ANN modelling. Two components viz., BOD (Y₁) and COD (Y₂) were used for training, cross-validation and testing the neural networks. Four components viz., initial concentration (X₁), dosage (X₂), pH (X₃) and contact time (X₄) were used for
input variables (Figure 1). Before the training, the principal component analysis was performed to test the correlation between the input and output datasets (Youssefi et al. 2019).

The training process was run until the sum of square errors (SSE) reached minimum values in the validation process (Karimi et al. 2012). The performance of the trained network was estimated based on the accuracy of the network with the test data. A feed-forward MLP was used for network training. Back-Propagation algorithm was selected to develop the predicted model because of its reported ability to model any function. ANN parameters were adjusted by using the number of hidden layers, neurons, type of transfer function, learning rate, momentum and number of patterns. A hyperbolic tangent sigmoid transfer function was used to activate neurons (Youssefi et al. 2019).

Comparison of RSM and ANN models

Both well trained RSM and ANN models were compared in terms of SSE, root mean square error (RMSE), correlation coefficient ($R^2$) and adjusted $R^2$ (Adj. $R^2$) values (Yadav et al. 2018). The experimental and predicted data were analyzed and plotted against the corresponding experimental values to study their modelling abilities (Sarve et al. 2013). The value of correlation coefficient ($R^2$) measures the scattering of predicted data around the straight line (1:1) and the value closed to 1.0 indicates the model is good fit (Yadav et al. 2018). The model parameters were calculated by using the Equations (4)–(6):

\[
SSE = \frac{1}{n} \sum_{i=1}^{n} (Y_{ie} - Y_{ip})^2 \\
RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (Y_{ie} - Y_{ip})^2} \\
R^2 = 1 - \frac{\sum_{i=1}^{n} (Y_{ip} - Y_{ie})^2}{\sum_{i=1}^{n} (Y_{ip} - Y_{e})^2}
\]

where $n$ is the number of experiments, $Y_{ie}$ is experimental value of $i$th experiment, $Y_{ip}$ is the predicted value of $i$th experiment by model and $Y_{e}$ is experimentally determined average value.

RESULTS AND DISCUSSION

The various characteristics of DIWW (Mother Dairy, Raichur, Karnataka, India) were determined, and were found in the range of 2,400.25–2,626.77 mg/L for TDS, 1,538.96–1,778.28 mg/L for TSS, 5.18–5.33 for pH, 2.38–2.71 $\mu$S/cm for EC, 918.00–1,077.50 mg/L for BOD, 9,931.28–11,538.33 mg/L for COD, 200.37–234.91 mg/L for sulphate, 32.93–40.62 mg/L for phosphate, 116.20–141.87 mg/L for ammoniacal-nitrogen, 379.90–356.50 mg/L for nitrate-nitrogen and 860.18–867.95 mg/L for chloride (Table 2).

Particle size and zeta potential of synthesized nano-adsorbents were measured by using particle size analyzer (Zetasizer). The average particle size of CZnO and CTiO$_2$ nano-adsorbents were found to be 88.35 and 87.43 d. nm, respectively. The surface area of the synthesized nano-adsorbents was depicted in terms of Zeta potential (-23.70 and -28.20 mV).

Characterization of nano-adsorbents

SEM image (Figure 2(a)) of synthesized CZnO nano-adsorbent showed rough surface and rod-like formations. This might be
due to increased NaOH concentration during the synthesis of CZnO, that increased the interaction between chitosan and ZnO (Vaseeharan et al. 2013). The surface morphological variations were observed among standard chitosan, standard ZnO and synthesized CZnO nano-adsorbent. EDS spectra (Figure 2(b)) of CZnO as shown the characteristic peaks of zinc (59.98%), chlorine (0.43%) and carbon (39.60%). Similarly, SEM images (Figure 2(c)) of synthesized CTiO$_2$ nano-adsorbent was found to be rod shape, rough surface and aggregated particle structures. This might be due to higher sodium hydroxide concentration and stirring time during the synthesis of CTiO$_2$ (Zhong & Yun 2015). The EDS spectral (Figure 2(d)) results depicted a negligible amount of carbon (1.72%) in CTiO$_2$ nano-adsorbent. This might be due to solvent evaporation and sintering of chitosan and TiO$_2$ during the synthesis process (Ali et al. 2018).

Topography and profile image (Figure 3(a)) obtained by AFM for CZnO nano-adsorbent was indicated by the height (Y-axis) and width (X-axis) of the particles. Surface roughness value of 6.75 nm was obtained due to the rough surface area of the CZnO nano-adsorbent. Thin grooves on the 3D image were due to the presence of the ZnO as confirmed by the results of Abdelhady (2012). Three-dimensional surface profiles obtained from AFM for CTiO$_2$ nano-adsorbent is shown in Figure 3(b). Lateral dimensions are influenced by the shape of the probe. The height measurements can provide the height of particles with a high degree of accuracy and precision. Average height and surface roughness of CTiO$_2$ nano-adsorbent were found to be 65.49 nm and 0.99 nm,

| Sl. No. | Characteristics | Range values |
|--------|----------------|-------------|
| 1      | TDS (mg/L)     | 2,400.25–2,626.77 |
| 2      | TSS (mg/L)     | 1,538.96–1,778.28 |
| 3      | pH             | 5.18–5.33    |
| 4      | EC (μS/cm)     | 2.38–2.71    |
| 5      | BOD (mg/L)     | 918.00–1,077.50 |
| 6      | COD (mg/L)     | 9,931.28–11,538.33 |
| 7      | Sulphate (mg/L)| 200.37–234.91 |
| 8      | Phosphate (mg/L)| 32.93–40.62 |
| 9      | Ammoniacal-nitrogen (mg/L) | 116.20–141.87 |
| 10     | Nitrate-nitrogen (mg/L) | 379.90–356.50 |
| 11     | Chloride (mg/L)| 860.18–867.95 |

Figure 2 | SEM images and EDS spectrum of C2nO (a & b) and CTiO2 (c & d) nano-adsorbents.
respectively. Larger roughness value was obtained due to the rough surface area of the CTiO₂ nano-adsorbent. The particles of CTiO₂ were agglomerated, this might be due to the deposition of the TiO₂ on the surface tends to form cluster during AFM analysis (Yusof et al. 2019).

RSM analysis

Lack of fit test and model summary statistics for linear, two factorial interaction (2FI), quadratic and cubic models for the adsorption of BOD and COD into CZnO and CTiO₂ nano-adsorbent was performed. According to the significant lack of fit test, R², Adj. R², SSE and RMSE values of the quadratic model was performed for two responses (%RBOD and %RCOD). A quadratic model was selected for the analysis of responses (Reddy et al. 2014). ANOVA (Table 3) for the quadratic model was used to test the statistical significance of the factors. ANOVA for adsorption of BOD and COD into CZnO nano-adsorbent was shown good model F-values of 80.55 and 17.25, respectively. Similarly, for adsorption of BOD and COD into CTiO₂ nano-adsorbent was resulted good model F-values of 45.68 and 19.36, respectively. Lower p-values (<0.0001) of the quadratic model confirmed the prototype applicability for correlating the adsorption of BOD and COD into CZnO and CTiO₂ nano-adsorbents. Similarly, the lack of fit F-values for adsorption BOD and COD into CZnO nano-adsorbents were obtained to be 11,039.84 and 125,833.00, respectively. Values of 4,466.40 and 66,019.90 were obtained for adsorption BOD and COD into CTiO₂ nano-adsorbent, respectively. The p-values were not significantly related to the pure error values (Bhanarkar et al. 2014). Therefore, insignificant lack of fit is good and model is a fit for all the responses. Finally, based on these results, an empirical relationship between the responses and independent variables were obtained and expressed in the form of second-order polynomial equation (Jha et al. 2017). The final equations obtained in terms of actual factors are given in Equations (7)–(10).

\[
R_{\%\text{BOD}} \text{ in presence of CZnO} = 69.85 - 22.28X_1 - 0.70X_2 + 0.72X_3 + 1.98X_4 + 0.33X_1X_2 - 0.93X_1X_3 - 1.07X_1X_4 + 0.34X_2X_3 + 0.15X_2X_4 - 0.49X_3X_4 + 1.34X_1^2 - 0.65X_2^2 - 0.63X_3^2 + 0.59X_4^2 \tag{7}
\]

\[
R_{\%\text{BOD}} \text{ in presence of CTiO₂} = 58.11 - 29.97X_1 - 0.73X_2 + 3.53X_3 + 2.96X_4 - 0.10X_1X_2 + 0.80X_1X_3 - 3.01X_1X_4 - 0.033X_2X_3 - 0.093X_2X_4 - 0.93X_3X_4 - 2.12X_1^2 + 0.80X_2^2 - 0.24C^2 - 3.26D^2 \tag{8}
\]

\[
R_{\%\text{COD}} \text{ in presence of CZnO} = 37.53 - 15.34X_1 - 1.86X_2 + 0.52X_3 + 4.45X_4 - 0.24X_1X_2 + 1.07X_1X_3 + 5.17X_1X_4 + 0.54X_2X_3 + 0.40X_2X_4 - 1.96X_3X_4 + 27.16X_1^2 + 0.40X_2^2 + 1.08X_3^2 + 3.82X_4^2 \tag{9}
\]

\[
R_{\%\text{COD}} \text{ in presence of CTiO₂} = 39.53 - 13.65X_1 - 1.85X_2 + 0.84X_3 + 2.60X_4 - 2.54X_1X_2 + 1.41X_1X_3 + 1.63X_1X_4 + 1.07X_2X_3 + 0.81X_2X_4 + 0.28X_3X_4 + 24.90X_1^2 - 0.26X_2^2 - 1.00X_3^2 + 3.00X_4^2 \tag{10}
\]

Optimization

The responses are maximized to obtain the best condition in the adsorption process (Sarve et al. 2015). Therefore, the desirability function approach under BBD was used as goal by choice of value from 0.0 (unacceptable) to 1.0 (acceptable) (Youssefi et al. 2009). Verification of predicted and actual responses are depicted in Table 4. The optimized treatment combination for %RBOD using CZnO and CTiO₂ nano-adsorbents were found at initial concentration of 100 mg/L, pH of 7, dosage of 1.25 mg/L and contact time of 100 min. At this optimized condition, percent relative deviation (%RD) of −0.004 and −0.001; desirability of 0.981 and 0.952; and R² of 0.988 and 0.979, respectively, were found. Similarly, the optimized treatment combination for %RCOD using CZnO and CTiO₂ nano-adsorbents were found at an initial concentration of 200 mg/L, pH of 2, the dosage of 1.25 mg/L and contact time of 60 min. This optimized treatment condition resulted the %RD of 0.0003 and 0.04; desirability of 0.986 and 0.965; and R² of 0.950 and 0.945, respectively.
## Table 3
The results of ANOVA for the response surface quadratic model

| Source of variation | C\textsubscript{ZnO} nano-adsorbent | C\textsubscript{TiO\textsubscript{2}} nano-adsorbent |
|---------------------|-----------------------------------|-----------------------------------------------|
|                     | \textit{R}\textsubscript{\%BOD} | F-value | p-value | \textit{R}\textsubscript{\%COD} | F-value | p-value |
| Model               | Sum of squares | 6,047.46 | 80.55 | <0.0001 | 8,246.62 | 17.25 | <0.0001 |
|                     | F-value | 8,246.62 | 17.25 | <0.0001 | 11,181 | 45.68 | <0.0001 |
| \textit{X}\textsubscript{1} | 5,955 | 1,110.51 | <0.0001 | 2,824.71 | 82.7 | <0.0001 |
| \textit{X}\textsubscript{2} | 5.94 | 1.11 | 0.003 | 41.66 | 1.22 | 0.002 |
| \textit{X}\textsubscript{3} | 6.24 | 1.16 | 0.002 | 3.21 | 0.09 | 0.007 |
| \textit{X}\textsubscript{4} | 47.01 | 8.77 | 0.001 | 237.10 | 6.94 | 0.001 |
| \textit{X}\textsubscript{1}\textit{X}\textsubscript{2} | 0.42 | 0.08 | 0.007 | 0.23 | 0.01 | 0.009 |
| \textit{X}\textsubscript{1}\textit{X}\textsubscript{3} | 3.50 | 0.65 | 0.004 | 4.54 | 0.13 | 0.007 |
| \textit{X}\textsubscript{1}\textit{X}\textsubscript{4} | 4.58 | 0.85 | 0.003 | 106.81 | 3.13 | 0.009 |
| \textit{X}\textsubscript{2}\textit{X}\textsubscript{3} | 0.47 | 0.09 | 0.007 | 1.16 | 0.03 | 0.008 |
| \textit{X}\textsubscript{2}\textit{X}\textsubscript{4} | 0.09 | 0.02 | 0.008 | 0.65 | 0.02 | 0.008 |
| \textit{X}\textsubscript{3}\textit{X}\textsubscript{4} | 0.96 | 0.18 | 0.006 | 15.29 | 0.45 | 0.005 |
| Residual           | Sum of squares | 75.07 | 478.17 | 244.78 | 349.91 |
|                     | F-value | 75.07 | 11,039.80 | <0.0001 | 75.07 | 11,039.80 | <0.0001 |

\(X\textsubscript{i}\) – Initial BOD concentration (mg/L); \(X\textsubscript{2}\) – pH; \(X\textsubscript{3}\) – Dosage of nano-adsorbents (mg/L); \(X\textsubscript{4}\) – Contact time (min); \(\textit{R}\textsubscript{\%BOD}\) – Percent reduction of BOD; \(\textit{R}\textsubscript{\%COD}\) – Percent reduction of COD.
Effect of process variables on %RBOD and %RCOD

Response surface plots as a function of two variables at a time and holding all other variables at centre levels were a more powerful tool for understanding the main and interaction effects (Karimi et al. 2012). Therefore, the response surface and contour curves (Figures 4 and 5) were plotted to understand the interaction of the variables and to determine the optimum level of each variable. The pH of the solution was increased from 2 to 12, the %RBOD and %RCOD increased (Figures 4(a) and 5(a)). This might be due to higher pH, the functional groups of chitosan and, therefore, it could take part in the surface complexation (Dehaghi et al. 2014). If initial concentration of BOD increased, the %RBOD and %RCOD showed decreasing trend. This might be due to more organic substances were adsorbed on the surface of the adsorbent. Thus, distribution coefficients were decreased and limited the number of absorption sites available for adsorption at a higher initial concentration of the BOD and COD (Nassar et al. 2014).

%RBOD and %RCOD increased with the increasing CZnO dosage (Figures 4(b) and 5(b)). This might be presumed that the availability of active sites on the CZnO and CTiO2 nano-adsorbents were increased at higher dosages (Thirugnanasambandham et al. 2014a). On the other hand, the %RBOD and %RCOD decreased with increasing pH. This might be due to reduction in potential binding sites of chitosan containing the amine and hydroxyl groups at higher pH (Thirugnanasambandham & Sivakumar 2015).

The effect of contact time increased from 20 to 100 min, the %RBOD and %RCOD increased significantly (Figures 4(c) and 5(c)). This might be due to the abundant availability of binding sites on the surface of the CZnO and CTiO2 nano-adsorbent at a prolonged time (Thirumavalavan et al. 2013). On the other hand, as the CZnO and CTiO2 dosage increased from 0.50 to 2 mg/L, the %RBOD and %RCOD increased.

Results obtained from batch adsorption study of CZnO and CTiO2 nano-adsorbents were compared with non-nano-adsorbents (CZnO (868 d. nm) and CTiO2 (987 d. nm)). The %RBOD by using CZnO and CTiO2 non-nano-adsorbents were found to be 42.80 and 19.70%. Similarly, %RCOD by using CZnO and CTiO2 non-nano-adsorbents were found to be 30.12 and 32.46%. These values were lower compared to the nano-adsorbents. Nassar et al. (2014) reported for the COD adsorption by using magnetic iron oxide nano-adsorbent, results were found from 962 to 460 (mg O2/L) for synthetic and real Olivemill wastewater.

Environmental safety and regeneration of the nano-adsorbents

There is wide debate regarding the safety of nano-adsorbents and their potential impact on the environment. There is a fervent hope that nanotechnology can play a significant role in providing clean water to the developing countries in an efficient, cheap and sustainable way (Jamshidi et al. 2015). Recently, metal oxide-based nano-adsorbents have

| Pollutants | Nano adsorbents | Initial concentration | pH | Dosage | Contact time | % Reduction | Desirability | R-Squared |
|------------|------------------|----------------------|----|--------|--------------|-------------|--------------|-----------|
| Predicted  | BOD              | CZnO                 | 100| 7      | 1.25         | 100         | 96.84        | 0.981     | 0.988     |
| Experimental|                 |                      | 100| 7      | 1.25         | 100         | 96.71        |           |           |
| %RD        |                  |                      | 0.00| 0.00   | 0.00         | 0.00        | −0.004       |           |           |
| Predicted  | CS-TiO2          |                      | 100| 7      | 1.25         | 100         | 90.52        | 0.952     | 0.979     |
| Experimental|                 |                      | 100| 7      | 1.25         | 100         | 90.48        |           |           |
| %RD        |                  |                      | 0.00| 0.00   | 0.00         | 0.00        | −0.001       |           |           |
| Predicted  | COD              | CZnO                 | 200| 2      | 1.25         | 60          | 87.55        | 0.986     | 0.950     |
| Experimental|                 |                      | 200| 2      | 1.25         | 60          | 87.56        |           |           |
| % Relative deviation | |                      | 0.00| 0.00   | 0.00         | 0.00        | 0.0003       |           |           |
| Predicted  | CS-TiO2          |                      | 200| 2      | 1.25         | 60          | 81.10        | 0.965     | 0.945     |
| Experimental|                 |                      | 200| 2      | 1.25         | 60          | 82.10        |           |           |
| %RD        |                  |                      | 0.00| 0.00   | 0.00         | 0.00        | 0.04         |           |           |

%RD – Percent Relative Deviation.
gained popularity in treating industrial wastewater due to their fascinating adsorption principle. These materials adsorb the particular pollutant on the surface of the adsorbents and adsorbed particles do not leach into the environment until giving external assistance (Raut et al. 2016). Hence, commercial applications of CZnO and CTiO2 nano-adsorbents were found to be eco-friendly technologies for treating DIWW treatment.

Adsorption efficiency of the nano-adsorbents could be enhanced by regeneration process according to the procedure given by Oladipo et al. (2017). Nano-adsorbents were regenerated using 1N concentrated hydrochloric acid (HCL) and NaOH. After elution, the nano-adsorbent particles were washed with distilled water until the wash effluent pH stabilized to near neutral. Four cycles of sorption–desorption–regeneration were carried out. The spent-of adsorbents were washed with distilled water severally and dried at 60 °C for 24 h. More than 90% of loaded organics was found to be desorbed in the first cycle within 120 min. The desorption efficiency of nano-adsorbents was reduced to 78% in the subsequent cycles. Hence, synthesized nano-adsorbents showed excellent regeneration potential for their re-usage.

ANN analysis

The pH, initial concentration, contact time and adsorbent dosages were used as input variables, and the %R_BOD and %R_COD were used as response/target to predict the BOD and COD adsorption behavior on CZnO and CTiO2 nano-adsorbents. Coded and un-coded values of independent variables and their corresponding experimental and predicted values are given in Table 5. The MLP was trained, validated and tested with 70, 15 and 15% of experimental data, respectively. The possibility of overtraining was a problem in the ANN and was overcome by proper selection of the number of neurons in the hidden layer. The performance of the network in the training phase was increased with increasing the number of the

Figure 4 | Response surface plots for %R_BOD using CZnO nano-adsorbents as a function of (a) pH and initial concentration (b) Dosage and pH (c) Contact time and dosage.
neurons. At the same time, as the performance of the network in testing data phase lead to optimum value at an optimal number of hidden neurons (Youssefi et al. 2013; Karimi et al. 2015). In the present work, four-layer feed-forward back propagation neural network (4–3-1) was designed by changing the four process variables of batch adsorption experiments viz., initial concentration, pH, dosage and contact time. The results were evaluated based on %RBOD and %RCOD. The MLP consisting the one input layer associated with four nodes, one hidden layer associated with four hidden nodes and one output layer with one output node value. All these neurons and nodes were coupled with different weights and bias. A multilayer feed-forward back propagation neural network was used with a hyperbolic tangent sigmoid (tansig) as a transfer function at a learning rate of 0.1 and a momentum rate of 0.5 and 21 epochs. The ANN architecture was trained using a stopping criterion as 1,000 iterations (Sarve et al. 2015; Yadav et al. 2018).

**Comparison of RSM and ANN model**

The comparison of RSM and ANN model results showed that the RSM model was larger than the ANN model. This might be due to the ANN having a higher modelling ability rather than the RSM model for %RBOD and %RCOD. Linear regression analysis was carried out between the response values predicted by ANN and RSM models with their corresponding experimental values are shown in Figure 6(a)–6(d).

Goodness of fit values (SSE, R², Adj. R² and RMSE) for %RBOD using CZnO nano-adsorbent was found 45.81, 0.9925, 0.9922 and 1.303, respectively, by RSM; 0.007915, 1, 1 and 0.01712, respectively, by ANN. Similarly goodness of fit values for %RCOD using CZnO nano-adsorbent was resulted 50.62, 0.9965, 0.9964 and 1.065, respectively, with RSM; 0.01942, 1, 1 and 0.02682 with ANN. On the same way, goodness of fit values for %RBOD using CTiO2 nano-adsorbent was found 74.14, 0.9877, 0.9873 and 1.657, respectively, by RSM; 3.799, 0.9994, 0.9994 and 0.3751, respectively, by ANN. Similarly, goodness of fit values for %RCOD using CTiO2 nano-adsorbent was resulted 451.90, 0.9452, 0.9432 and 4.091, respectively, with RSM; 0.0156, 0.9999, 0.9999 and 0.0420 with ANN. Hence, from the results, it can be concluded that ANN model predictions lie much closer to the line of perfect prediction than the RSM model. Thus, the ANN model showed a significantly higher generalization capacity than the RSM model.

This higher predictive accuracy of the ANN model can be attributed to its universal ability to approximate the non-linearity of the system, whereas the RSM is restricted to a second-order polynomial. Generation of ANN model requires many iterative calculations, whereas RSM is only a single step calculation. ANN model requires high computational time and is more costly than an RSM model (Youssefi et al. 2009; Yadav et al. 2018).
Table 5 | Coded and un-coded values of independent variables and their corresponding experimental and predicted values

| Run | X1 (mg/L) | X2 | X3 (mg/L) | X4 (min) | R%R%BOD in CZnO | R%R%COD in CZnO |
|-----|-----------|-----|-----------|-----------|-----------------|-----------------|
|     | BOD       | COD |           |           | YEXP YRSM YANN | YEXP YRSM YANN |
| 1   | 100(−1)   | 200(−1) | 2(−1)     | 1.25(0)   | 60(0)          | 95.12 93.84 95.15 | 87.56 82.05 87.54 |
| 2   | 300(+1)   | 600(+1) | 2(−1)     | 1.25(0)   | 60(0)          | 51.40 48.64 51.72 | 60.08 51.85 60.04 |
| 3   | 100(−1)   | 200(−1) | 12(+1)    | 1.25(0)   | 60(0)          | 92.50 91.79 93.03 | 82.35 78.81 82.33 |
| 4   | 300(+1)   | 600(+1) | 12(+1)    | 1.25(0)   | 60(0)          | 50.08 47.88 50.67 | 53.91 47.65 53.87 |
| 5   | 200(0)    | 400(0)  | 7(0)      | 0.50(−1)  | 20(−1)         | 70.06 66.62 69.75 | 39.75 35.51 39.76 |
| 6   | 200(0)    | 400(0)  | 7(0)      | 2.00(+1)  | 20(−1)         | 72.51 69.04 71.98 | 43.64 40.45 43.64 |
| 7   | 200(0)    | 400(0)  | 7(0)      | 0.50(−1)  | 100(+1)        | 71.56 71.56 72.00 | 56.89 48.31 56.91 |
| 8   | 200(0)    | 400(0)  | 7(0)      | 2.00(+1)  | 100(+1)        | 72.05 72.02 71.85 | 52.96 45.43 52.95 |
| 9   | 100(−1)   | 200(−1) | 7(0)      | 1.25(0)   | 20(−1)         | 90.57 91.00 90.56 | 82.05 84.57 82.04 |
| 10  | 300(+1)   | 600(+1) | 7(0)      | 1.25(0)   | 20(−1)         | 47.68 48.59 47.08 | 40.18 43.56 40.12 |
| 11  | 100(−1)   | 200(−1) | 7(0)      | 1.25(0)   | 100(+1)        | 96.71 97.10 96.38 | 80.30 85.12 80.26 |
| 12  | 300(+1)   | 600(+1) | 7(0)      | 1.25(0)   | 100(+1)        | 49.54 50.41 49.53 | 59.10 62.78 59.11 |
| 13  | 200(0)    | 400(0)  | 2(−1)     | 0.50(−1)  | 60(0)          | 69.42 68.89 69.04 | 35.84 40.89 35.82 |
| 14  | 200(0)    | 400(0)  | 12(+1)    | 0.50(−1)  | 60(0)          | 67.29 66.80 67.89 | 32.58 36.09 32.59 |
| 15  | 200(0)    | 400(0)  | 2(−1)     | 2.00(+1)  | 60(0)          | 67.86 69.65 67.91 | 38.16 40.85 38.19 |
| 16  | 200(0)    | 400(0)  | 12(+1)    | 2.00(+1)  | 60(0)          | 67.10 68.93 67.63 | 37.05 38.20 37.05 |
| 17  | 100(−1)   | 200(−1) | 7(0)      | 0.50(−1)  | 60(0)          | 89.45 91.18 89.41 | 80.45 81.65 80.44 |
| 18  | 300(+1)   | 600(+1) | 7(0)      | 0.50(−1)  | 60(0)          | 45.76 48.49 45.27 | 45.76 48.85 45.74 |
| 19  | 100(−1)   | 200(−1) | 7(0)      | 2.00(+1)  | 60(0)          | 95.05 94.49 95.15 | 78.05 80.56 78.04 |
| 20  | 300(+1)   | 600(+1) | 7(0)      | 2.00(+1)  | 60(0)          | 47.62 48.07 47.49 | 47.62 52.01 47.54 |
| 21  | 200(0)    | 400(0)  | 2(−1)     | 1.25(0)   | 20(−1)         | 65.58 68.67 65.56 | 38.58 39.57 38.57 |
| 22  | 200(0)    | 400(0)  | 12(+1)    | 1.25(0)   | 20(−1)         | 64.47 66.95 64.51 | 34.47 35.04 34.45 |
| 23  | 200(0)    | 400(0)  | 2(−1)     | 1.25(0)   | 100(+1)        | 72.63 72.32 72.66 | 42.63 47.65 42.60 |
| 24  | 200(0)    | 400(0)  | 12(+1)    | 1.25(0)   | 100(+1)        | 72.13 71.22 71.17 | 40.13 44.73 40.15 |
| 25  | 200(0)    | 400(0)  | 7(0)      | 1.25(0)   | 60(0)          | 69.86 69.85 69.84 | 37.56 37.53 37.54 |
| 26  | 200(0)    | 400(0)  | 7(0)      | 1.25(0)   | 60(0)          | 69.88 69.85 69.87 | 37.52 37.53 37.51 |
| 27  | 200(0)    | 400(0)  | 7(0)      | 1.25(0)   | 60(0)          | 69.82 69.85 69.83 | 37.51 37.53 37.50 |
| 28  | 200(0)    | 400(0)  | 7(0)      | 1.25(0)   | 60(0)          | 69.85 69.85 69.85 | 37.52 37.53 37.50 |

X1 – Initial concentration of BOD or COD (mg/L); X2 – pH; X3 – Dosage of nano-adsorbents (mg/L); X4 – Contact time (min); YEXP – Experimental value; YRSM – Predicted by RSM model; YANN – Predicted by ANN model.

CONCLUSIONS

CZnO and CTiO2 nano-adsorbent particles were synthesized by co-precipitation method and characterized by using SEM-EDS and AFM. These nano-particles were successfully applied as adsorbents for simultaneous removal of BOD and COD in DIWW. The impact of operational parameters on the efficiency of the adsorption process was successfully investigated by RSM and ANN models. The maximum %R%BOD in the presence of CZnO and CTiO2 nano-adsorbents were found to be 96.71 and 87.56 at 0.981 desirability. The %R%COD in the presence of CZnO and CTiO2 nano-adsorbents were found to be 90.48 and 82.10 at 0.965 desirability. The performance of RSM and ANN models were evaluated based on modelling, prediction and generalization capabilities. The experimental and predicted data obtained by RSM and ANN models were compared based on the SSE, RMSE, R2 and Adj-R2 values. Capability of ANN model for %R%BOD and %R%COD in the presence of CZnO nano-adsorbent was found to be...
the within the range they trained than the RSM model. The results indicated that the ANN model is much more robust and accurate in estimating dependent variables when compared to RSM model.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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