DOI : <http://doi.org/10.22438/jeb/42/6/MRN-1724>

Adsorptive removal of dairy industrial pollutants by chitosan zinc –oxide nanoadsorbent- A comparative study of artificial neural network and quadratic Box-Behnken design

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Received: 13.10.2020

Revised: 24.03.2021

Accepted: 08.06.2021

Abstract

Aim: To investigate the effect of operational parameters on the adsorption of biological oxygen demand (BOD) and chemical oxygen demand (COD) on Chitosan zinc oxide (CZnO) nanoadsorbent using cost-effective and eco-friendly nanoadsorbent based effluent treatment processes.

Methodology: CZnO nanoadsorbent particle was synthesized using chemical precipitation method. The nano size <100 nm was achieved using high-speed cryo all mill, followed by the characterization using high-end instruments such as scanning electron microscope with elemental detection sensor (SEM-EDS), atomic force microscope (AFM), X-ray diffractometer (XRD) and Fourier transform infrared spectroscopy (FT-IR). Modeling and optimization of operational parameters were done with the artificial neural network (ANN) and Box-BehnkenDesign (BBD) statistical tools.

Results: Optimized treatment combination for adsorption of BOD and COD were found at initial BOD and COD concentration of 100 and 200 mg l⁻¹, pH of 7.0 and 2.0, adsorbent dosage of 1.25 mg l⁻¹, contact time of 100 and 60 min. In these condition the desirability values of 0.988 and 0.950 were found for BOD and COD adsorption. The maximum per cent reduction of BOD and COD by using CZnO nanoadsorbent was found to be 96.71 and 87.56. Two models such as Quadratic Box-Behnken and ANN were compared in term of sum of square errors (SSE), root mean square error (RMSE) and correlation coefficient (R²) values.

Interpretation: The results obtained reveal the well trained ANN model found to be more accurate in prediction of BOD and COD adsorption process parameters compared to BBD model.

Key words: Biological oxygen demand, Chemical oxygen demand, Dairy industry, Nanotechnology, Wastewater treatment

How to cite : Dinesha, B.L., S. Hiregoudar, U. Nidoni, K.T. Ramappa, A.T. Dandekar, M.V. Ravi and K.B. Sankalpa: Adsorptive removal of dairy industrial pollutants by chitosan zinc –oxide nanoadsorbent- A comparative study of artificial neural network and quadratic Box-Behnken design. *J. Environ. Biol.*, **42**, 1442-1451 (2021).

Introduction

Ever increasing industrialization and rapid urbanization have considerably increased the rate of water pollution worldwide. Among various kinds of industries in India, dairy industry (DI) is of crucial importance and contributes 35 % of the total Asian milk (Thirugnanasambandham and Ganesamoorthy, 2019). Wastewater released from the DI contain high amount of total dissolved solids, total suspended solids, pH, electrical conductivity, turbidity, biological oxygen demand, chemical oxygen demand, phosphate, sulphate, nitrate-nitrogen, ammoniacal-nitrogen, chloride, oil and grease (Dinesha et al., 2021a).

To defend the non-toxic global water inventory, the various environmental regulations and emission standards have been represented to address pollution issues. To meet the wastewater discharge limits set by the state as well as central pollution control boards, the DI are following various treatment methods (biological and physicochemical) before discharging in to the environment (Qasim and Mane, 2013).

Biological treatment methods can be generally classified as aerobic and anaerobic treatments. A common aerobic method such as activated sludge process is performed by allowing wastewater flow into the aerated tank and agitating the sludge. Trickling filters, rotating biological contactor process, and biotowers have also been employed for the treatment of wastewater. Anaerobic treatment composes processes that occur in an environment devoid of air or elemental oxygen (Thirugnanasambandham et al., 2014). However, the performance of the biological treatment process is low due to the high organic load and the toxic nature of the dairy industry wastewater (DIWW). The traditional physicochemical treatment processes have accomplished to some extent. Hence, secondary pollution occurs due to low BOD and COD reduction in existing dairy industrial effluent treatment plants (Thirugnanasambandham and Sivakumar, 2015).

Some of the major important traditional methods of wastewater treatment process are preliminary treatment, which is used for removal of large solids such as rags, sticks, grit and grease (Arora et al., 2005). Primary treatments are used for the removal of floating and settleable materials such as, suspended solids and organic matter (Bora and Dutta, 2014). Secondary treatment includes both biological (aerobic and anaerobic treatments) and chemical methods (Ferric chloride, Aluminum chloride, Aluminum sulfate and Ferric chloride) to remove biodegradable organic matter and suspended solids (Stoller et al., 2016). Tertiary or advanced treatments methods are used for the removal of residual suspended solids or dissolved solids by using membrane techniques (micro and ultrafiltration) (Routh et al., 2016), reverse osmosis, ozone technology (Pandiselvam et al., 2020), electro-coagulation (Qasim and Mane, 2013) and activated sludge treatment (Teh et al., 2014). Some of the promising wastewater treatment techniques or tools introduced

by nanotechnology are photocatalysis (Oladipo et al., 2017), nanomembranes (Dinesha et al., 2017) and nanoadsorbents (Thirugnanasambandham and Ganesamoorthy, 2019).

Generally, BOD and COD adsorption approaches include the traditional and novel adsorption methods. Among these methods, novel physico-chemical methods (adsorption, photocatalysis, ozone technology and ion exchange) are generally in usage due to eco-friendly, highest reduction capacity of the pollutants, low cost and operators friendly (Pathak et al., 2016). In this contest, to meet the global environmental sustainability the synthesis and characterization of novel adsorbents with high adsorption capacity and high rate gives more commercial importance (Dinesha et al., 2021a). Previous studies reported that, metal oxide based materials were highly efficient adsorbents for adsorption of organic pollutants (Raut et al., 2016). Recently, metal oxide based nanoparticles gained demand in environmental and biological engineering due to their charming intrinsic properties (Thirumavalavan et al., 2013). The development of an eco-friendly and energy-efficient approach at larger scale is still a challenge (Maran et al., 2013).

Performance of the adsorption process at an insignificant state could be more reagent consumption and it may take more time. Hence, process optimization for adsorption of BOD and COD is very much important (Dinesha et al., 2021a). One factor at a time (OFAT), response surface methodology (RSM) and the artificial neural network (ANN) modeling approaches are generally used for optimization (Dinesha et al., 2021b). Generally ANN and RSM were used for adsorption process optimization and standardization in the field of wastewater treatment. There are several disadvantages in the OFAT method, such as operational parameters between interaction effects were not considered for optimization and not used for validation (Pandiselvam et al., 2020). In views of this, present study mainly aimed to optimize the process technology for per cent reduction of BOD and COD from DIWW using CZnO nanoadsorbent with BBD and ANN models.

Materials and Methods

Chemical reagents required for the synthesis of nanoadsorbents were purchased from M/s. Sigma Aldrich Chemicals, Bengaluru, India. BOD and COD were estimated according to the method described by AOAC (2006) (Method 973.44 and 973.46). Synthesized nanoparticles were characterized by using Scanning electron microscope with Elemental detection sensor (SEM-EDS), Atomic force microscope (AFM), X-ray diffractometer (XRD) and Fourier transform infrared spectroscopy (FT-IR).

Synthesis of CZnO nanoadsorbent: CZnO nanoadsorbent was synthesized as per the method described by Thirugnanasambandham and Sivakumar (2015).

Batch adsorption experiment: Batch adsorption study for per

cent reduction of BOD (%R_{BOD}) and percent reduction of COD (%R_{COD}) by using CZnO nanoadsorbent was performed according to the method described by Thirugnanasambandham *et al.* (2014). The value of per cent reduction of BOD and COD were calculated by the following equation:

$$\text{Per cent reduction} = \left[\frac{C_0 - C_e}{C_0} \right] \times 100$$

Where, C_0 and C_e are initial and final concentration of BOD

Box-Behnken Design: The input variables varied at different levels to observe their effect on per cent reduction of BOD and COD by using CZnO nanoadsorbent. The obtained results of the experimental design matrix were performed by using BBD. The quadratic model of RSM and experimental data obtained by using BBD were used to train ANN by using feed forward back propagation neural network (Yadav *et al.*, 2018). BBD matrix of experimental data sets and their observed responses were tabulated. Design Expert software (8.0.7.1 trial version) was used for BBD modeling. Independent variables and their levels were selected for %R_{BOD} and %R_{COD} by using CZnO nanoadsorbent (Table 1).

Artificial Neural Network: ANN was applied for the simulation of

experimental data of batch adsorption study by using MATLAB Subroutine Prepcas-007 software (Karimi *et al.*, 2012). Twenty-nine patterns were used for ANN modeling. Two components viz., BOD (Y_1) and COD (Y_2) were used for training, cross-validation and testing the neural networks. Four components viz., initial concentration (X_1), dosage (X_2), pH (X_3) and contact time (X_4) were used for input variables. The training process was run until the Sum of Square Errors (SSE) reached minimum values in the validation process. The performance of the trained network was estimated based on the accuracy of network with the test data. A feed-forward multilayered perceptron (MLP) was used for network training. Back-propagation (BP) 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.*, 2013).

Comparison of RSM and ANN models: Both well trained RSM and ANN models were compared in terms of sums of square error (SSE), root mean square error (RMSE), correlation coefficient (R^2) and adjusted R^2 values. These were

Table 1: Independent variables and their levels for per cent reduction of BOD and COD by CZnO nanoadsorbent

Variables	Unit	Factors	Levels		
			Low (-1)	Middle (0)	High (+1)
Initial concentration	mg l ⁻¹	$X_{1(BOD)}$	100	200	300
		$X_{1(COD)}$	200	400	600
pH		X_2	2	7	12
Dosage	mg ⁻¹	X_3	0.5	1.25	2
Contact time	min	X_4	20	60	100

Table 2: Results of ANOVA for the Response Surface Quadratic model

Source of variation	CZnO nanoadsorbent					
	R% _{BOD}			R% _{COD}		
	Sum of squares	F value	p-value Prob > F	Sum of squares	F value	p-value Prob > F
Model	6047.46	80.55	< 0.0001	8246.62	17.25	< 0.0001
X_1	5955	1110.51	< 0.0001	2824.71	82.7	< 0.0001
X_2	5.94	1.11	0.003	41.66	1.22	0.002
X_3	6.24	1.16	0.002	3.21	0.09	0.007
X_4	47.01	8.77	0.001	237.1	6.94	0.001
X_1X_2	0.42	0.08	0.007	0.23	0.01	0.009
X_1X_3	3.5	0.65	0.004	4.54	0.13	0.007
X_1X_4	4.58	0.85	0.003	106.81	3.13	0.009
X_2X_3	0.47	0.09	0.007	1.16	0.03	0.008
X_2X_4	0.09	0.02	0.008	0.65	0.02	0.008
X_3X_4	0.96	0.18	0.006	15.29	0.45	0.005
Residual	75.07			478.17		
Lack of Fit	75.07	11039.8	< 0.0001	478.17	125833	< 0.0001

carried out between experimental and predicted data as depicted in Eqn. (4) to (6). To study the modeling abilities of RSM and ANN, the values predicted by RSM and ANN models were plotted against the corresponding experimental values

(Srikanth *et al.*, 2020). Value of correlation coefficient measures the scattering predicted data around the straight line (1:1). R^2 value closed to 1.0 indicates that the model is good fit (Jha *et al.*, 2017).

Table 3: Verification of predicted and actual responses of per cent reduction of BOD and COD by using CZnO nanoadsorbent

	Pollutants	Nano adsorbents	Initial concentration (mg l ⁻¹)	pH	Dosage (mg l ⁻¹)	Contact time (min)	% 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		
% Relative deviation (%RD)			-	-	-	-	-0.004		
Predicted	COD	CZnO	200	2	1.25	60	87.55	0.986	0.950
Experimental			200	2	1.25	60	87.56		
% Relative deviation (%RD)			-	-	-	-	0.0003		

Table 4: Coded and un-coded Box-Behnken design of independent variables and their corresponding experimental and predicted values

Run	X ₁ (mg l ⁻¹)		X ₂	X ₃	X ₄ (min)	R% _{BOD} in CZnO nanoadsorbent			R% _{COD} in CZnO nanoadsorbent		
	BOD	COD				Y _{EXP}	Y _{RSM}	Y _{ANN}	Y _{EXP}	Y _{RSM}	Y _{ANN}
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)	51.4	48.64	51.72	60.08	51.85	60.04
3	100(-1)	200(-1)	12(+1)	1.25(0)	60(0)	92.5	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)	0.5(-1)	20(-1)	70.06	66.62	69.75	39.75	35.51	39.76
6	200(0)	400(0)	7(0)	2(+1)	20(-1)	72.51	69.04	71.98	43.64	40.45	43.64
7	200(0)	400(0)	7(0)	0.5(-1)	100(+1)	71.56	71.56	72	56.89	48.31	56.91
8	200(0)	400(0)	7(0)	2(+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	90.36	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	97.1	96.38	80.3	83.12	80.26
12	300(+1)	600(+1)	7(0)	1.25(0)	100(+1)	49.54	50.41	49.53	59.1	62.78	59.11
13	200(0)	400(0)	2(-1)	0.5(-1)	60(0)	69.42	68.89	69.04	35.84	40.89	35.82
14	200(0)	400(0)	12(+1)	0.5(-1)	60(0)	67.29	66.8	67.89	32.58	36.09	32.59
15	200(0)	400(0)	2(-1)	2(+1)	60(0)	67.86	69.65	67.91	38.16	40.85	38.19
16	200(0)	400(0)	12(+1)	2(+1)	60(0)	67.1	68.93	67.63	37.05	38.2	37.05
17	100(-1)	200(-1)	7(0)	0.5(-1)	60(0)	89.45	91.18	89.41	80.45	81.65	80.44
18	300(+1)	600(+1)	7(0)	0.5(-1)	60(0)	45.76	48.49	45.27	45.76	48.85	45.74
19	100(-1)	200(-1)	7(0)	2(+1)	60(0)	95.05	94.49	95.15	78.05	80.56	78.04
20	300(+1)	600(+1)	7(0)	2(+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	42.6
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	69.82	37.51	37.53	37.5
28	200(0)	400(0)	7(0)	1.25(0)	60(0)	69.82	69.85	69.83	37.52	37.53	37.53
29	200(0)	400(0)	7(0)	1.25(0)	60(0)	69.85	69.85	69.85	37.52	37.53	37.5

X₁– Initial BOD concentration (mg l⁻¹); X₂– pH; X₃– CZnO dosage (mg l⁻¹); X₄– Contact time (min); Y_{EXP}– Experimental value; Y_{RSM}– Predicted by RSM model; Y_{ANN}– Predicted by ANN model.

Fig. 1: SEM image (a) and EDS spectrum; (b) of CZnO nanoadsorbent (88.35 d.nm).

Fig. 2: Profile image obtained by using AFM for CZnO nanoadsorbent.

Results and Discussion

Average particle size and Zeta potential of synthesized CZnO nanoadsorbent was found to be 88.35 d. nm and -23.70 mV. SEM image (Fig. 1a) of synthesized CZnO nanoadsorbent showed rough surface and rod-like formations, which might be due to increased NaOH concentration during CZnO synthesis and increased the interaction between chitosan and ZnO (Preethi *et al.*, 2020). EDS spectra (Fig. 1b) of CZnO showed the characteristic peaks of zinc (59.98%), chlorine (0.43%) and carbon (39.60%). Topography image (Fig. 2) obtained by AFM for CZnO nanoadsorbent indicated 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 CZnO nanoadsorbent. Thin grooves on 3D image were due to the presence of ZnO as confirmed by the results of Wardana *et al.* (2020). A definite line broadening XRD peaks indicated that the material consisted of particles in nanoscale. Diffraction peaks (Fig. 3) of CZnO indicated the nanocrystalline nature, identical to the hexagonal phase with Wurtzite structure (Hamedani and Farzaneh, 2006). CZnO peaks at angle (2θ) were found to have 19.80° , 33.18° , 34.47° , 36.29° , 47.53° , 48.38° , 56.57° , 62.86° , 66.42° , 67.95° and 69.08° corresponding to the reflection from 4.48° , 2.81° , 2.69° , 2.59° , 2.47° , 1.91° , 1.87° , 1.62° , 1.47° , 1.40° , 1.37° and 1.35° crystal planes, respectively.

All these diffraction peaks are in good agreement with those of hexagonal wurtzite structure of ZnO (Preethi *et al.*, 2020). FT-IR spectrum of CZnO nanoadsorbent (Fig. 4) showed bands at 3365.78 and 2881.65 cm^{-1} due to the stretching vibration mode of NH_2 and OH groups. The peaks at 2428.38 and 1788.01 cm^{-1} were typically carboxylic acid O-H stretching vibration, while the bands at 1647.21 and 1560.41 cm^{-1} were due to amide I group (N-H bend). The transmission peak at 1340.53 cm^{-1} was attributed to C-H deformation. The special broad peaks at 1151.50 and 1026.13 cm^{-1} were attributed to the vibration mode of alkoxy C-O (Oladipo *et al.*, 2017). Lack of fit test and model summary statistics for linear, 2FI, quadratic and cubic models for the adsorption of BOD and COD into CZnO nanoadsorbent was performed.

According to the significant lack of fit test, R-squared, adjusted R-squared and the predicted R-squared values of quadratic model was performed for two responses ($\%R_{\text{BOD}}$ and $\%R_{\text{COD}}$). A quadratic model was selected for the analysis of responses. ANOVA (Table 2) for the quadratic model was applied to test the statistical significant factors. ANOVA for adsorption of BOD and COD into CZnO nanoadsorbent was shown good model F-values of 80.55 and 17.25, respectively. Lower P-values of (<0.0001) quadratic model conformed well applicability for

Fig. 3: Diffractogram of standard ZnO, chitosan and synthesized CZnO nanoadsorbent.

Fig. 4: FT-IR spectrum of standard ZnO, chitosan and synthesized CZnO nanoadsorbent.

Fig. 5: Response surface plots for per cent reduction of BOD using CZnO nanoadsorbent as a function of (a) pH and initial concentration; (b) Dosage and pH and (c) Contact time and dosage.

correlating the adsorption of BOD and COD into CZnO nanoadsorbent. Similarly, the Lack of Fit F-values for adsorption BOD and COD into CZnO were obtained to be 11039.84 and 125833, respectively. The final equations obtained in terms of actual factors are given as following equations (Eqn. 2-3):

$$R\%_{\text{BOD}} \text{ in presence of CZnO} = 69.85 - 22.28 \cdot X_1 - 0.70 \cdot X_2 + 0.72 \cdot X_3 + 1.98 \cdot X_4 + 0.33 \cdot X_1 \cdot X_2 - 0.93 \cdot X_1 \cdot X_3 - 1.07 \cdot X_1 \cdot X_4 + 0.34 \cdot X_2 \cdot X_3 + 0.15 \cdot X_2 \cdot X_4 - 0.49 \cdot X_3 \cdot X_4 + 1.34 \cdot X_1^2 - 0.65 \cdot X_2^2 - 0.63 \cdot X_3^2 + 0.59 \cdot X_4^2 \quad \dots (2)$$

$$R\%_{\text{COD}} \text{ in presence of CZnO} = 37.53 - 15.34 \cdot X_1 - 1.86 \cdot X_2 + 0.52 \cdot X_3 + 4.45 \cdot X_4 - 0.24 \cdot X_1 \cdot X_2 + 1.07 \cdot X_1 \cdot X_3 + 5.17 \cdot X_1 \cdot X_4 + 0.54 \cdot X_2 \cdot X_3 + 0.40 \cdot X_2 \cdot X_4 - 1.96 \cdot X_3 \cdot X_4 + 27.16 \cdot X_1^2 + 0.40 \cdot X_2^2 + 1.08 \cdot X_3^2 + 3.82 \cdot X_4^2 \quad \dots (3)$$

In the adsorption process, to obtain the best condition the responses are maximized. Therefore, the desirability function approach under BBD was used as goal by choice of value from 0.0 (unacceptable) to 1.0 (acceptable). Verification of predicted and

Fig. 6: Comparison of experimental with predicted values of RSM and ANN models plot (a) %R_{BOD} in presence of CZnO nanoadsorbent and (b) %R_{COD} in presence of CZnO nanoadsorbent.

actual responses is depicted in Table 3. The optimized treatment combination for %R_{BOD} using CZnO nanoadsorbent was found at initial concentration of 100 mg l⁻¹, pH 7, dosage of 1.25 mg l⁻¹ and contact time of 100 min. This optimized treatment combination resulted, the per cent relative deviation (%RD) values of -0.004, desirability values of 0.981 and R-squared values of 0.988.

Similarly, the optimized treatment combination for %R_{COD} using CZnO nanoadsorbent was found at an initial concentration of 200 mg l⁻¹, pH 2, dosage of 1.25 mg l⁻¹ and contact time of 60 min. This optimized treatment combination resulted, the per cent relative deviation (%RD) values of 0.0003, desirability values of 0.986 and R-squared values of 0.950.

Response surface plot as a function of two variables at a time and holding all other variables at centre levels were more powerful tool for understanding the main and interaction effects. Therefore, the response surface and contour curves were plotted to understand the interaction of variables and to determine the optimum level of each variable for maximum response. The pH of the solution increased from 2 to 12 while the per cent reduction of BOD and COD increased (Fig. 5a). This might be due to the fact that at higher pH, the functional groups of chitosan gets dissociated as their dissociation constants, thereby taking part in the surface complexation (Da-Silva-Alves *et al.*, 2021). On the other side, the initial BOD concentration increased the per cent reduction of BOD and COD showed a decreasing trend due to adsorption of more organic substances on the surface of the adsorbent. Thus distribution coefficient decreased limiting the number of absorption sites available for adsorption at a higher initial concentration of BOD and COD (Anjum *et al.*, 2019).

The per cent reduction of BOD and COD increased with the increasing CZnO dosage. It may be presumed that, the availability of active sites on the CZnO nanoadsorbent increased at higher dosages. On the other side, the per cent reduction of BOD and COD decreased with the increasing pH (Fig. 5b). This may be due to the potential binding sites of chitosan containing amine and hydroxyl groups decreased at higher pH (Thirugnanasambandham and Sivakumar, 2015). The effect of contact time increased from 20 to 100 min, the per cent reduction of BOD and COD increased significantly due to abundant availability of binding sites on the surface of CZnO at a prolonged time (Thirugnanasambandham and Ganesamoorthy, 2019). The perusal of data (Fig. 5c) revealed that as CZnO dosage increased from 0.50 to 2 mg l⁻¹, the per cent reduction of BOD and COD increased. To predict the BOD and COD adsorption behavior on CZnO nanoadsorbent, the pH, initial concentration, contact time and adsorbent dosages were used as input variables and the %R_{BOD} and %R_{COD} were used as a target. The ranges of input-output variables for each system are given in Table 4. The multilayer perceptron (MLP) was trained, validated and tested with 70%, 15% and 15% of experimental data, respectively.

The possibility of over-training was a problem in the ANN and can be overcome by proper selection of the number of neurons in the hidden layer. The performance of the network in training phase increased with increasing the number of neurons. At the same time, the performance of the network in testing data phase lead to optimum value at an optimal number of hidden neurons (Arismendy *et al.*, 2020). In the present study, 4-layer feed forward back propagation neural network (4-3-1) was designed by changing the four process variables of batch adsorption experiments. The results were evaluated on the basis of %R_{BOD} and %R_{COD}. MLP consisted of 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 momentum rate of 0.5 and 21 epochs. The ANN architecture was trained using a stopping criterion as 1000 iterations (Yadav *et al.*, 2018).

Comparative results of BBD and ANN models showed that, the BBD model was larger than the ANN model. Linear regression analysis was carried out between the response values predicted by ANN and BBD models with their corresponding experimental values as shown in Fig. 6 (a-b). ANN model predictions available is much closer to the line of perfect prediction than the BBD model. Thus, ANN model showed a significantly higher generalization capacity than the BBD model. This higher predictive accuracy of ANN model can be attributed to its universal ability to approximate the nonlinearity of the system whereas the BBD is restricted to a second-order polynomial. Generation of ANN model requires a large number of iterative calculations whereas BBD is only a single step calculation. ANN model may require a high computational time and it was more costly than an BBD model (Sen *et al.*, 2018).

In conclusion, the impact of operational parameters on the efficiency of adsorption process was carefully investigated by BBD and ANN models. The optimal conditions obtained from BBD in the presences of CZnO nanoadsorbent for %R_{BOD} and %R_{COD} was found at 100 and 200 mg l⁻¹ of initial BOD and COD concentration, 1.25 mg l⁻¹ of adsorbent dosage, 7.0 and 2.0 of pH, 100 and 60 min of contact time. The results of ANN model indicate that it is a highly robust statistical tool that accurately estimates dependent variables when compared with RSM.

Acknowledgment

The authors acknowledge their heartfelt gratitude to the Department of Science and Technology, Scheme for Young Scientist and Technologists (SYST) [SP/YO/2019/1583 (G)] New Delhi for the financial support extended for conducting this research work.

Add-on Information

Authors' contribution: B.L. Dinesha: Conceptualization, investigation, original draft preparation, conceived and designed the experiments; S. Hiregoudar: Project administration, funding acquisition, review and editing; U. Nodoni: Methodology, formal analysis, supervision, review and editing; K.T. Ramappa: Data analysis and discussion, revision of manuscript; A.T. Dandekar: Provided laboratory facility for analysis of BOD and COD; M.V. Ravi: Assisted in proof reading of manuscript; K.B. Sankalpa: Helped in BBD and ANN modeling, model validation, review and editing.

Research content: The research content of manuscript is original and has not been published elsewhere.

Ethical approval: NotApplicable

Conflict of interest: The authors declare that there is no conflict of interest.

Data from other sources: NotApplicable

Consent to publish: All authors agree to publish the paper *Journal of Environmental Biology*.

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