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Solar Photocatalytic Degradation of Organic Contaminants in Landfill Leachate Using TiO_2 Nanoparticles by RSM and ANN

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ABSTRACT

In the present study, artificial neural network (ANN) and response surface methodology (RSM) models were used to investigate the heterogeneous photocatalysis performance in removal of chemical oxygen demand (COD) from landfill leachate using compound parabolic collector. Effect of the three parameters, i.e. pH, catalyst dosage and irradiation time were studied for COD removal efficiency and these parameters are optimized by the RSM. The optimum values of pH 5, the dosage of 0.75 g/L and irradiation time of 100 minutes is capable to remove 32.19% of COD from the leachate. A good agreement is shown by the analysis of variance for the regression coefficient R^2 for predicted value (0.92268) and adjusted value (0.9776). The proposed RSM and ANN model R^2 values were found to be 0.9882 and 0.9974 respectively, which confirms the ideality of RSM and ANN. The results also confirm that the input and output data from RSM could be appropriate to build the ANN model. Further BOD_5/COD ratio is studied for the biodegradability of leachate and it was found that increase of biodegradability value from 0.17 to 0.47 was at pH 3, catalyst dosage of 1 g/L and irradiation time of 150 minutes.

INTRODUCTION

It is observed that the countries having high Gross Domestic Product (GDP) are generating more MSW compared to the developing and underdeveloped countries (Shekdar 2009). Municipal Solid Waste Management (MSWM) is now becoming an important segment, because of increased population, environmental degradation caused by pollution, emerging newer technologies, rapid urbanization and public importance towards hygiene and sanitation (Joshi & Ahmed 2016). Most of the developing countries including India have adopted landfilling as the final disposal method for their MSW, because of proven technology, cost-effectiveness, easy to implement and operate. Unavoidable pollutants produced from the landfill are methane gas and leachate.

Leachate is highly hazardous, consisting of high organic pollutants, salts, ammonia and toxic heavy metals. The organic pollutants studied for leachate globally are for Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), five-day Biochemical Oxygen Demand (BOD_5), and Dissolve Organic Carbon (DOC). Other two indicator ratios are BOD_5/COD and COD/TOC (Deng 2009, Renou et al. 2008, Abu-Daabes et al. 2013). Available conventional treatment methods, for treating these parameters are not feasible in the present days, because of continuous hardening of the discharge standards in many countries and new pollutants emerging from the industrial processes where conventional methods fail to treat these pollutants (Gehrke & Somborn-schulz 2015, Renou et al. 2008). The treatment using nanotechnology is gaining importance due to its efficiency, significant reduction in treatment time and combining this technology with conventional treatment will offer new technology opportunity in liquid waste treatment (Saleh & Gupta 2012, Gehrke & Somborn-schulz 2015).

Nanotechnology is found useful in wastewater treatment by adsorption, membrane process, advanced oxidation process and disinfection (Qu et al. 2013, Gehrke & Somborn-schulz 2015). The last 10 years of research papers (2001 to 2011) show that the researchers are more interested in the field of biological process and Advanced Oxidation Process (AOP) for treating the leachate (Silva et al. 2013). Heterogeneous photocatalysis is an AOP over the surface of a semiconductor-based photocatalyst. Semiconductor metal oxides are used as a photocatalyst, because of light-absorbing capacity, the favourable combination of electronic structure, charge transport characteristics and excited state lifestyles (Thiruvenkatachari et al. 2008). Semiconductor nanomaterials such as TiO_2, α-Fe_2O_3, ZnO, WO_3, CdS, SnO_2 etc.

are used in the process of heterogeneous photocatalysis. Titanium dioxide (TiO_2) is a widely used semiconductor nanomaterial, because of its nontoxicity, cost-effectiveness, high chemical stability during the reaction with acidic and basic compounds, and has high oxidizing power (Spasiano et al. 2015).

Photocatalysis process depends upon different factors such as catalyst dosage, pH, contact time, temperature and light intensity (Julkapli & Bagheri 2018). The Central Composite Design (CCD) and Response Surface Methodology (RSM) are systematic tools, which provide an optimum number of experiments, mathematical and statistical techniques for understanding the effects of different factors and their interactions at the response and helps in optimizing the process (Varank et al. 2016, Ghaedi et al. 2015, Garba & Rahim 2014).

ANN is a technique used for solving nonlinear systems when there is more than one parameter interaction involved in the process. One of the advantages of ANN is that, it does not require previous information on the interactions of process variables for handling simulation of the complicated systems. ANN has achieved more popularity in water and wastewater treatment studies (Garg et al. 2017, Sabonian & Behnajady 2015, Aghaeinejad-Meybodi et al. 2015).

Photocatalysis is carried out in photoreactors to absorb maximum solar radiation which helps in performing the photochemical reaction. Compound Parabolic Collectors (CPC) are more efficient than that of the parabolic and non-concentrating collectors, because of the high amount of sunlight absorption, no solar trackers required, small place to install and can be used in cloudy days also. (Thiruvenkatachari et al. 2008, Spasiano et al. 2015).

In recent days, many researchers have studied the removal of organic contaminants such as COD, BOD_5, TOC and DOC from the leachate and wastewater using TiO_2, with UV lamps as the light source and few studies show using natural sunlight. Jia et al. (2011) used UV mercury-vapour lamp and TiO_2 nanomaterial for the removal of COD, DOC and colour from the landfill leachate. Their study shows that, at pH 4 and dosage of 2 g/L, the removal efficiency of COD, DOC and colour was 60, 72 and 97% respectively. El-mekkawi et al. (2016) investigated the percentage of COD removal in six different substrates by ten different synthesized and commercial TiO_2 samples. They have considered the initial COD concentration as 30 mg/L and volume taken was 100 mL for their study. They have carried out their experimental procedure at pH 3 and TiO_2 dosage of 0.5 g/L. Results of the study revealed that, TiO_2 of Degussa P25 found to be more efficient in removal of COD from all the substrates in exposure dose of $\leq$ 9.36 mWH/cm^2.

With the best of our knowledge, the study based on RSM and ANN is not reported for the COD removal from landfill leachate using photoreactor in natural sunlight. Therefore, in the present study TiO_2/H_2O_2/sunlight are used for the treatment of COD, BOD_5 and BOD_5/COD using CPC (photoreactor). The RSM, CCD and ANN techniques are used for modelling and optimizing the influencing parameters on COD. The BOD_5 and BOD_5/COD ratio are studied for the improvement in biodegradability of the leachate.

MATERIALS AND METHODS

Collection and Characterisation of Leachate

Leachate sample is collected from the "Turmuri sanitary landfill" Belgaum, Karnataka. The existing capacity of Integrated Municipal Solid Waste (IMSW) facility is 100 tonnes per day (TPD) and it is proposed to expand up to 450 TPD. The total landfill area is of 26.7 hectares, which includes compost processing facility, material recovery, refuse-derived fuel and sanitary landfill. The aerobic composting method was adopted at the site (Windrow Compost Method) (Ramky Enviro Engineers Ltd. n.d.). Leachate sample was collected from the leachate collection tank of landfill site in a plastic container and stored at below 4°C until use. The initial physicochemical characteristics are analysed and summarised in Table 1.

Experimental Study

In the present study the raw leachate is diluted to 1:25 dilution with tap water. Photocatalytic TiO_2 is procured from Sisco Research Laboratories Pvt. Ltd (SRL)-India, which is Anatase and has a specific surface area of 326 m^2/g with an average particle size of 7 nm. Hydrogen peroxide (H_2O_2) reagent (30% w/v) is used to trap the photo-induced electron and further it acts as an oxygen source to improve the mineralisation. 1 M nitric acid and sodium hydroxide were used for pH adjustment in the process.

All the photocatalysis experiments were conducted during the summer, the solar irradiance found during April and May months are 2212 kWh/m^2 and 2303 kWh/m^2 respectively. Photocatalysis process is carried out in CPC, wherein CPC profile is prepared in AutoCAD software by taking two halves of the parabola with closely located focal points and their axes inclined to each other (Tanveer & Tezcanli 2013, Strauss et al. 2018). The half acceptance angle (θ_c) is 15.8° for the constructed CPC. The CPC height, width of receiver and width of the absorber are 417.5, 360 and 100 mm respectively. The aluminium foil is used on the reflective surface to collect maximum photons from the sun.

Table 1: Physicochemical characteristics of raw leachate.

Parameters	Range value
Temperature (°C)	31
pH	8.06
Electrical Conductivity (µS/cm)	15880
Total Dissolved Solids (mg/L)	8099
Total Suspended Solids (mg/L)	400
COD (mg/L)	6418
BOD_5 (mg/L)	1106
BOD_5/COD	0.17
Chloride (mg/L)	2345
Sulphates (mg/L)	350
Nitrate (mg/L)	1496
Sodium (mg/L)	80
Potassium (mg/L)	1720
Alkalinity (mg/L as $CaCO_3$)	1800
Lead (mg/L)	0.0091
Cadmium (mg/L)	0.0014
Chromium (mg/L)	0.0777
Copper (mg/L)	0.0267
Zinc (mg/L)	0.0528
Iron (mg/L)	3.0290

The transparent borosilicate glass tube of capacity one litre is mounted on CPC as shown in Fig. 1. The glass tube is having an internal diameter of 6 cm and a length of 38 cm. The end of the glass tube is fitted with rubber bush and pipes are connected to it. The collection tank of capacity 1.5 litres is built with glass. The connectors, motor parts and recirculating pipes in contact with the leachate were of PVC material. The diluted leachate, 2 mL of hydrogen peroxide and TiO_2 are added in suspension, which is then magnetically stirred for 30 minutes in dark to attain adsorption and desorption equilibrium between the leachate and TiO_2. After the dark adsorption whole solution was taken into the CPC reactor for the photocatalysis experiment and recirculated through the glass cylinder with the aid of a low rpm water pump. During all the runs a uniform flow rate of 1000 mL/minute was maintained.

After the treatment, the solution was filtered through 0.45 µm membrane filter paper. The COD (Open reflux method) and BOD_5 tests were conducted as per the standard methods (APHA 1999). The pH was measured with a Systronics Make 361.

Central Composite Design (CCD)

The DESIGN EXPERT 11 (Stat-Ease Inc., Minneapolis, MN, USA) software was used to study the individual and synergetic effects of three factors: pH, dosage and irradiation time on the reduction of COD and biodegradability of the leachate. CCD is performed with 2^n factorial runs (n=3), the number of runs is obtained by the equation $2^n + 2n + n_c$, which provides 2^n factorial points are in 8 numbers and axial (2n) and centre (n_c) points as 6 each in numbers with a total of 20 runs. The factors are coded as +1 and -1 for high and low values. The range of high and low variables was decided based on the literature and are provided in Table 2. The response values obtained from the CCD and percentage removal of COD against each experiment is shown in Table 3. Rotatability value of α=1.687 is obtained by Eq. (1). The value of α depends on the number of factors in the factorial portion of the design (Garba & Rahim 2014, Ghaedi et al. 2015, Amini et al. 2008).

$$\alpha = N_p^{1/4} \qquad \ldots(1)$$

Where $N_p = 2^n$ is the number of points, n is the number of factors.

The quadratic equation model is used to optimize and predict the response Y against the three independent factors, which can be expressed according to Eq. (2) (Ghafari et al. 2009, Varank et al. 2016).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i \le j}^{k} \sum_{j}^{k} \beta_{ij} X_i X_j + \cdots + \varepsilon \qquad \ldots(2)$$

Where Y is the predicted response; X_i and X_j are the variables (independent factors), and β_0 is the constant coefficient, β_i, β_{ii} and β_{ij} are the coefficients for the linear, quadratic, and interaction effect respectively, k signifies the number of independent variables and ε is the random error.

Artificial Neural Network (ANN)

In the present study sigmoid transfer function with a back propagation structure is used in the ANN modelling, which consists of a total of three layers of input, hidden and output layers as shown in Fig. 2. All calculations were done with MATLAB®2013 to develop the ANN model. Input variables examined for the neural network are pH, dosage and irradiation time. The output value is the percentage of COD removal from the leachate. The sigmoid transfer function is commonly used transfer function for the input and hidden layers because of its differentiability. ANN will provide input-output mapping with nonparametric statistical inference, adaptive and fault-tolerant. The ANN output is expressed by Eq. (3).

$$P(w) = f[x_1, x_2, \ldots x_n, w] \qquad \ldots(3)$$

Where, $P(w)$ is the expected output of the multilayer neural network. The hyperbolic tangent function is given by

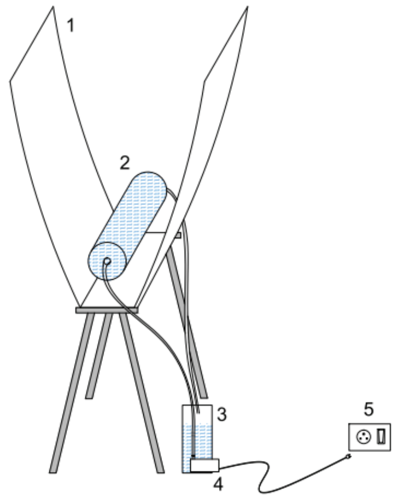

Fig. 1: Compound parabolic collector (CPC) schematic diagram.

Eq. (4) and it is used as the activation function for the hidden layer. Whereas, linear activation function specified in Eq. (5) will be employed for the output layer.

$$\phi(v)\ tanh(v)_{tanh} \qquad \ldots(4)$$

$$\phi_{lin}(v) = v \qquad \ldots(5)$$

Where, v is the net input of the neuron, further, w is the weight factor vector which need to recognize throughout the course of action of training and $x_1, x_2, \ldots x_n$ characterize the system inputs. The weights w are estimated by minimizing the cost function $\xi(w)$ which is given in Eq. (6)

$$\xi(w) = \frac{1}{2N}\sum \varepsilon(w)^2 + \frac{1}{N} w^T Dw \qquad \ldots(6)$$

Where, $\varepsilon(w) = y - \hat{y}(w)$ and D is the weight decay matrix and calculation of D is given by Eq. (7).

$$D = \beta[I]_{m\times m} \qquad \ldots(7)$$

Where, β is the weight decay term and I is the identity matrix. To get a better overview, data on network points are separated arbitrarily into three subsets consisting of 70%, 15% and 15% of data. The first subsets are employed for training while the other two subsets are employed for validation and cross-validation (Simon 2014, Liang et al. 2002).

RESULTS AND DISCUSSION

Statistical Analysis

A quadratic polynomial RSM was used to analyse the experimental results found by CCD. Based on the experimental design results, the regression equations with coded variables established for the photocatalysis processes is presented in Eq. (8). The coded equation will help in finding the relative effect of the factors by comparing the factor coefficients.

% COD removal by photocatalysis process =

$$30.77 - 11.14X_1 + 8.43X_2 + 3.87X_3 - 0.45X_1X_2 - 1.95X_1X_3 - 3.26X_2X_3 + 2.78X_1^2 - 2.70X_2^2 - 1.52X_3^2 \qquad \ldots(8)$$

The positive and negative signs before the expressions indicate the synergistic and antagonistic influence of the respective variables. The presence of a single variable in a term shows a unifactor influence; two variables indicate a double factor influence and a second-order term of variable occurrence indicate the quadratic influence.

In mandate to evaluate the individual interface and quadratic effects of the variables influencing on the percentage removal of COD, analysis of variance (ANOVA) is carried out. ANOVA validated the importance and adequacy of the models. The superiority of polynomial model suitability

Table 2: Experimental factors and levels in the central composite design.

Factors	Levels			Star Point α=2	
	Low	Central	High	-α	+α
(X_1) pH	3	5	7	1.634	8.363
(X_2) Dosage (g/L)	0.5	0.75	1	0.329	1.170
(X_3) Irradiation time (min)	50	100	150	15.910	184.09

Table 3: Data statistics of model variable.

Std	Run	X_1: pH	X_2: Dosage g/L	X_3: Irradiation time Minutes	COD % Removal
6	1	7.00	0.50	150.00	15.88
19	2	5.00	0.75	100.00	32.19
9	3	2.00	0.75	100.00	57.97
5	4	3.00	0.50	150.00	39.92
4	5	7.00	1.00	50.00	26.82
16	6	5.00	0.75	100.00	29.89
20	7	5.00	0.75	100.00	28.75
7	8	3.00	1.00	150.00	53.16
14	9	5.00	0.75	184.00	32.12
3	10	3.00	1.00	50.00	44.86
15	11	5.00	0.75	100.00	32.19
17	12	5.00	0.75	100.00	29.89
12	13	5.00	1.17	100.00	37.85
18	14	5.00	0.75	100.00	31.34
13	15	5.00	0.75	16	22.86
10	16	8.00	0.75	100.00	21.35
11	17	5.00	0.33	100.00	10.45
8	18	7.00	1.00	150.00	24.13
2	19	7.00	0.50	50.00	2.35
1	20	3.00	0.50	50.00	21.78

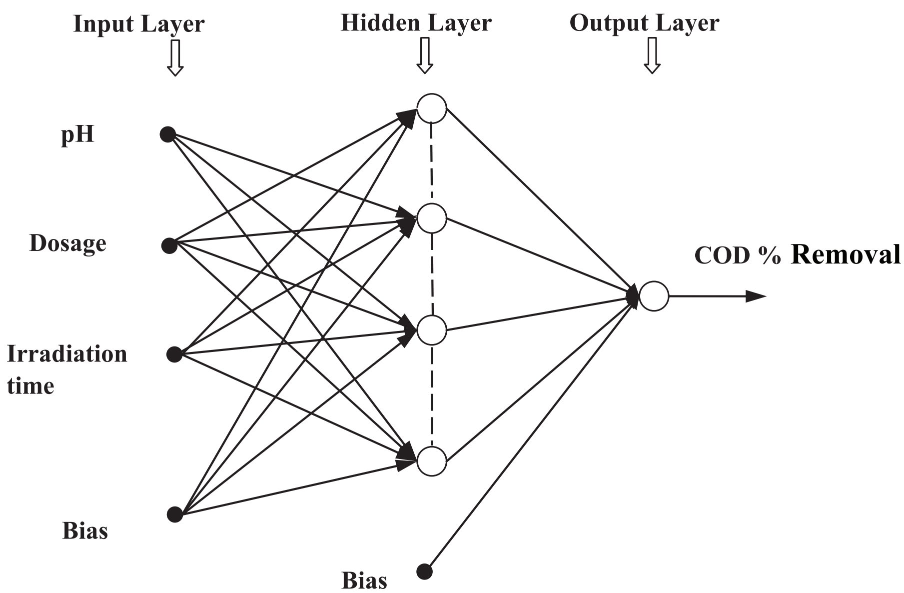

Fig. 2: Artificial neural network.

is studied in terms of coefficient of determination R^2 and model terms are assessed by p-value and F-value (Varank et al. 2016).

For the COD removal, whether the model is significant or insignificant is studied by the relationship between predicted and actual data as shown in Fig 3. The R^2 value predicted for the COD is 0.9268 and is in reasonable agreement with the adjusted R^2 value of 0.9776; the difference is less than 0.2. To check the model significance, further, it is verified in terms of F-value, P-value and adequate precision.

Therefore, the sum of squares and mean square of each factor, F-values as well as P-values are shown in Table 4 for the percentage of COD removal. In Table 4, dividing the sum of the squares of each of the various sources, the model and the error variance by the respective degrees of freedom gives the mean square values. The model terms with values of P less than 0.05 are considered significant. With respect to COD percentage removal, the Model F-value of 2.90 suggests that the Lack of Fit is not significant compared to the pure error. There is a 13.35% chance for a lack of Fit F-value, this could happen due to noise. Non-significant lack of fit is suggested to be good.

P-values less than 0.05 indicate model terms are significant. In this case X_1, X_2, X_3, X_1X_3, X_2X_3, X_1^2, X_2^2 , X_3^2 are significant model terms. X_1X_2 are not significant as values greater than 0.05 indicate the model terms are not significant.

The adequate precision ratio should be more than 4 for a significant model. In the present study, COD has an adequate precision ratio of 37.53. From the statistical results attained, it was observed that the COD model (Eq. 8) was adequate to predict the COD removal within the applied range of variables.

ANN Modelling

To develop a suitable model for ANN requires large data. However, if the data of input and output are statistically significant by the ANOVA in RSM it could be appropriate to build the ANN model (Sarve et al. 2015). Different topologies of ANN with the number of hidden neurons varying from 2 to 10 are trained in the present study. The topology which provides minimum mean square error (MSE) is chosen as the best topology to predict the parameter of COD reduction. The MSE corresponding to the best architecture (number of

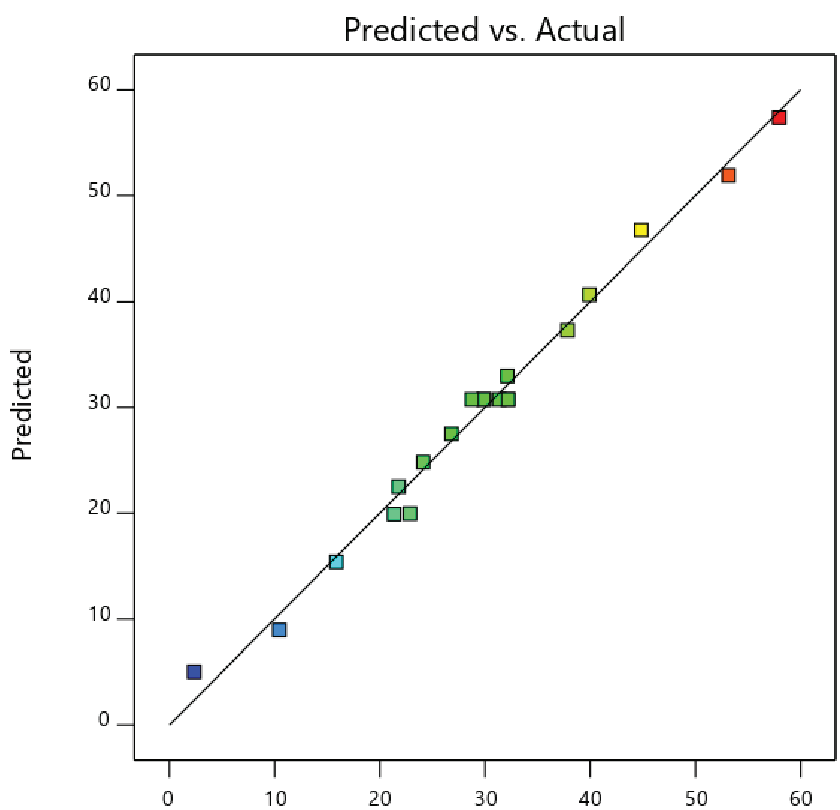

Fig. 3: Relationship between predicted and experimental data for COD removal.

Table 4: The ANOVA for response surface quadratic model of COD removal by photocatalysis.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	p-value	Remarks
COD Model	3261.27	9	362.36	93.18	< 0.0001	significant
X_1-pH	1694.59	1	1694.59	435.76	< 0.0001	significant
X_2-Dosage	970.42	1	970.42	249.54	< 0.0001	significant
X_3-Irrdiation time	204.55	1	204.55	52.60	< 0.0001	significant
$X_1 X_2$	1.62	1	1.62	0.4166	0.5332	Not significant
$X_1 X_3$	30.42	1	30.42	7.82	0.0189	significant
$X_2 X_3$	84.89	1	84.89	21.83	0.0009	significant
X_1^2	111.71	1	111.71	28.73	0.0003	significant
X_2^2	105.01	1	105.01	27.00	0.0004	significant
X_3^2	33.23	1	33.23	8.55	0.0152	significant
Residual	38.89	10	3.89			
Lack of Fit	28.92	5	5.78	2.90	0.1335	Not significant

hidden neurons) for parameter prediction is given in Table 5 and also shown in Fig. 4. The best architectures found (Table 5) is 3_8H_1 with MSE validation of 0.0235 which is used for predicting of COD removal.

The accuracy of the developed model is evaluated by regression analysis. The criterion used for measuring the model accuracy in regression analysis is correlation coefficient R^2. The correlation coefficient measures the strength of the relationship between estimated and measured variables and it can be expressed by Eq. (9).

$$R^2 = \left(\frac{N\sum X_{meas} X_{est} - \sum X_{meas} \sum X_{est}}{\sqrt{\left[N\sum X_{meas}{}^2 - \left(\sum X_{meas}\right)^2\right]\left[N\sum X_{est}{}^2 - \left(\sum X_{est}\right)^2\right]}} \right) \quad \ldots(9)$$

Where, N, X_{mesa}, and X_{est} are the number of operating points in a data set, measured variable and estimated variable respectively. The value of R^2 represents the correlation coefficient of determination. The R^2 ranges between -1 and +1. R^2 value close to +1 indicates a stronger positive linear relationship, while R^2 value close to -1 indicates a stronger negative linear relationship. Further, the comparison of measured and estimated COD is done for all the data sets of points.

The coefficient of determination (R^2) for COD is depicted in Fig. 5 and it is concluded that the developed model allows the accurate prediction of COD as it is having a coefficient of determination of 0.9974.

Effect of Independent Factors on COD Removal and Optimisation of Process

Effect of pH on COD removal: The percentage removal of COD is studied with the independent factors by the RSM in the form of 3-dimensional charts as shown in Fig. 6. It is observed from Fig. 6(a), that the set of optimum values of pH 5, a dosage of 0.75 g/L and irradiation time of 100 minutes are capable to remove 32.19% of COD from the leachate. To study the effect of various individual parameters on COD removal, the ramp diagrams are used. In ramp diagrams, two optimized parameters are kept as constant and the other one is varied to obtain maximum and minimum values.

To understand the effect of pH on COD reduction, the value of pH is fixed at 3 and 7 as shown in ramp diagrams in

Table 5: Results of the ANN model to predict COD reduction.

S. No.	Input Parameters	Output Parameter	Architecture	MSE (Validation)
	pH, Dosage, Irradiation time	COD	3_2H_1	0.1372
	pH, Dosage, Irradiation time	COD	3_4H_1	0.1263
	pH, Dosage, Irradiation time	COD	3_6H_1	0.0362
	pH, Dosage, Irradiation time	COD	3_8H_1	0.0235
	pH, Dosage, Irradiation time	COD	3_10H_1	0.0471

Figs. 7(a) and 7(b) respectively. The results obtained from the ramp diagrams indicate that at pH 3 (COD removal 44.69%) the removal efficiency of COD is higher than at pH 7 (COD removal 22.41%) for the dosage of 0.75 g/L and irradiation time of 100 minutes. Many researchers have reported that the maximum COD removal can be achieved in acidic pH (Pekakis et al. 2006, Iqbal et al. 2017), and pH plays a very important role in photocatalysis solution, which provides greater influence on the mechanism of OH radicals production and point of zero charge (pH_{zpc}) of TiO_2 nanomaterial. The pH_{zpc} for TiO_2 is 6.5 when pH value is lower than pH_{zpc} the TiO_2 surface becomes positively charged and attracts anionic pollutants. If pH is greater than 6.5 then surface gets charged negatively and attracts cationic pollutants. It is assumed that the pollutants whose exact composition is not known are negatively charged species, therefore their photodegradation process would be favoured at acidic condition rather than of neutral or alkaline conditions (Fotiadis et al. 2007, Pekakis et al. 2006, Julkapli & Bagheri 2018).

Effect of catalyst dosage on COD removal: Figs. 6(b), 8(a) and 8(b) show the effect of catalyst dosage on COD removal. Which indicate that, as the dosage increases, the percentage removal of COD also increases. In the ramp diagram 8(a) and 8(b) the highest dosage of 1 g/L and minimum dosage of 0.5 g/L is fixed at the pH 5 and irradiation time 100 minutes. The ramp diagram clearly shows that, at 1 g/L (COD removal 36.49%) catalyst dosage is efficient compared to 0.5 g/L (COD removal 19.63%). The dosage plays an important role in the photocatalysis process as an increase in the concentration of nanoparticles in the area of illumination helps in improved availability of catalyst sites for the adsorption. Further, it helps in generation of reactive free radicals and their interaction. It is also reported that the application of excessive dosage above the saturation level can reduce the light absorption coefficient due to the shielding effect, which in turn reduce the efficiency of the pollutant reduction. It is also necessary to note that, the dosage of catalyst depends on the initial concentration of the pollutant and operating conditions of the reactor (Julkapli & Bagheri 2018, Manassah 2011).

Effect of irradiation time on COD removal: Fig. 6(c), 9(a) and 9(b) demonstrate the change in the percentage of COD removal with respect to the graph and ramp diagram. These indicate that, as the time increases, the removal efficiency of COD increases. In Fig. 9(a) and 9(b) maximum (150 minutes) and minimum (50 minutes) irradiation time were considered, and COD removal efficiency is calculated as 33.11% and 25.37% respectively for the pH 5 and dosage of 0.75 g/L. Extended irradiation time helps in speeding up mixing and dispersion of adsorbent into the solution, COD from the leachate will biodegrade faster in initial stages and further increase of time may not help in removal of COD, because COD removal amount is fixed by the refractory compounds and by-products produced during the longer reaction time of photocatalyst (Sahar et al. 2018, Mokhtarani et al. 2016).

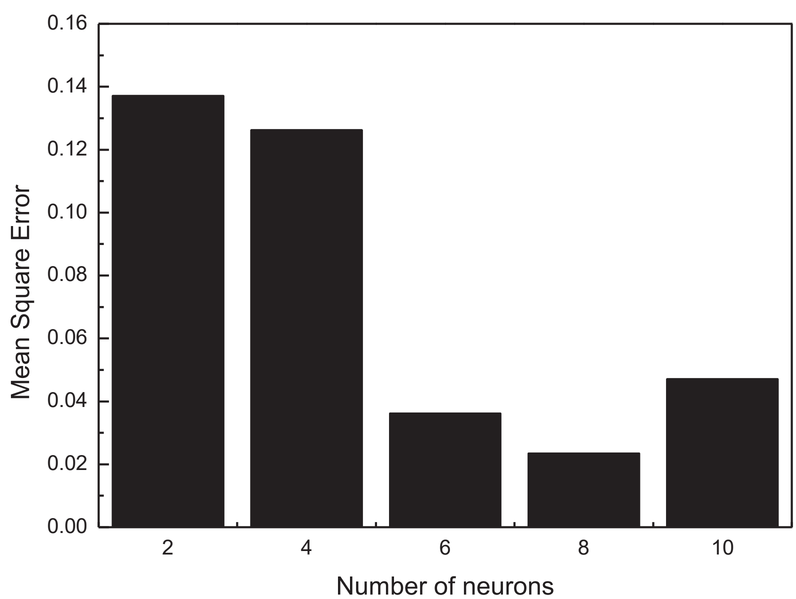

Fig. 4: Effect of the number of hidden neurons on the performance of the neural network.

Biodegradability Study of Leachate

BOD_5/COD ratio has been commonly used to indicate the biodegradability of the waste. This ratio helps in coupling biological treatment with chemical treatment. It is suggested that the BOD_5/COD ratio should be more than 0.4 for biological treatment. If it is in the range of 0.3 to 0.4, it indicates the partial biodegradability of waste (Jia et al. 2011, Khattab et al. 2012). The biodegradability study was carried out for each run and is shown in Fig. 10 with respect to pH, catalyst dosage and irradiation time. The results indicate that there will be a considerable increase of BOD_5 fraction with initial and final irradiation time. At the initial stage of 0-100 minutes, BOD_5 fraction was increased due to the active changes in structures and chemical properties of the refractory materials and due to the presence of original organic matter. The catalyst dosage plays a crucial role in the increase of BOD_5 fraction, because of reduction in organic by-products residual in the treated medium and to the upswing of decarboxylation rate. The pH of the medium was studied with biodegradability and it is seen that at acidic pH the BOD_5/COD is more. The results of Wiszniowski et al. (2006) indicated that at pH 7.2 BOD_5/COD, percentage removal is less compared to the pH 4. In the present study, the BOD_5/COD ratio was 0.17 and it was found to be increased up to 0.47 at pH 3, catalyst dosage of 1 g/L and irradiation time of 150 minutes. The optimum BOD_5/COD ratio of 0.35 can be attained by a pH of 5, dosage 0.75 g/L and irradiation time of 100 minutes.

CONCLUSION

Performance of TiO_2 was studied with CCD based on RSM and ANN models for the COD removal from the landfill leachate using photoreactor in natural sunlight. The constructed photoreactor was found to be efficient in capturing solar photons from sunlight, and maximum removal of COD at pH 2 and pH 3 was found to be 57.97% and 53.16% respectively with dosage of 1.0g/L and irradiation time of 150 min. The favourable condition for COD removal from leachate is an acidic phase and the same is reported by other authors also. Further results indicate that the other two parameters, catalyst dosage and irradiation time, also influence the COD removal. In the present study, optimum parameters were obtained as pH 5, the dosage of 0.75 g/L and irradiation time of 100 minutes for COD removal of 32.19%. The ANOVA results of p values less than 0.05 indicate that the models are significant, F-value of 2.90 and the adequate precision ratio of 37.53 from statistical results confirm that the COD model is adequate to predict the COD removal within the applied range of variables. The ramp diagrams are shown to help in varying weights or importance of the parameters to check the percentage removal of COD. The ANN model R^2 value, found to be 0.9974, indicates that the model has been trained perfectly for the input and output data of CCD based RSM. In ANN, best architecture found is 3_8H_1 with MSE validation of 0.0235 which is used for predicting of COD removal.

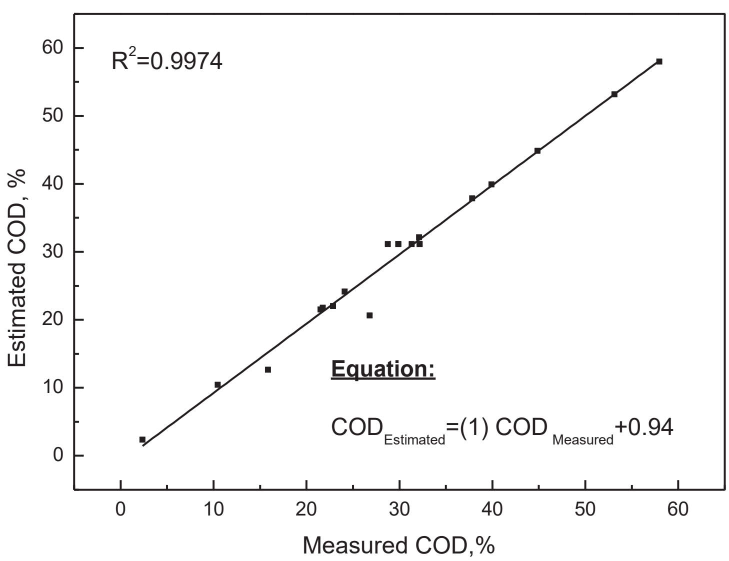

Fig. 5: Measured and estimated COD.

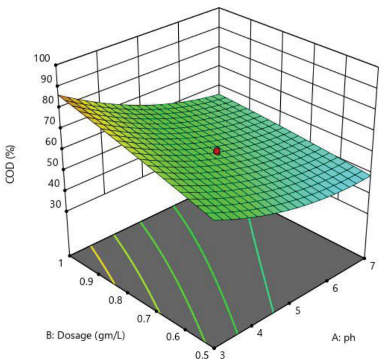

Fig. 6(a): Effect of pH and Dosage on removal of COD.

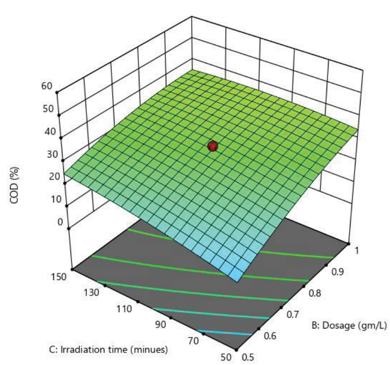

Fig. 6(b): Effect of Dosage and Irradiation time on removal of COD.

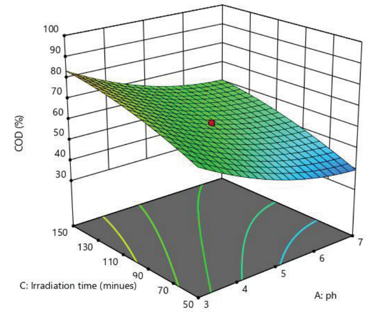

Fig. 6(c): Effect of pH and Irradiation time on removal of COD.

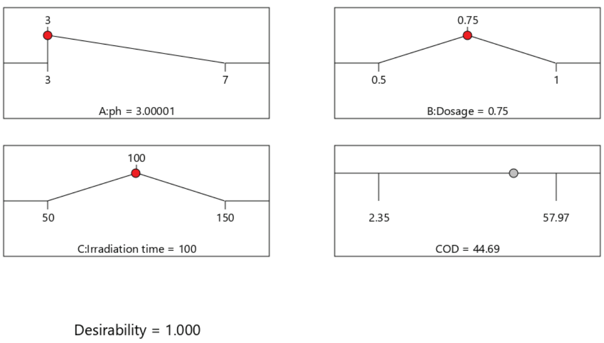

Fig. 7(a): Effect of 3 pH on removal of COD.

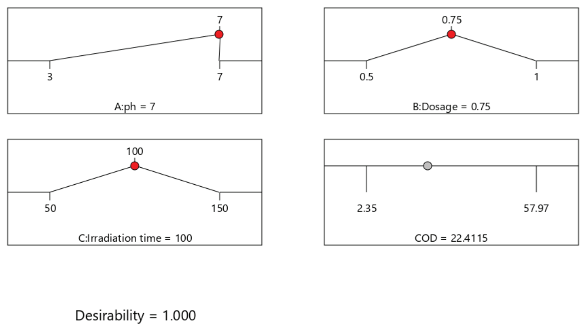

Fig. 7(b): Effect of 7 pH on removal of COD.

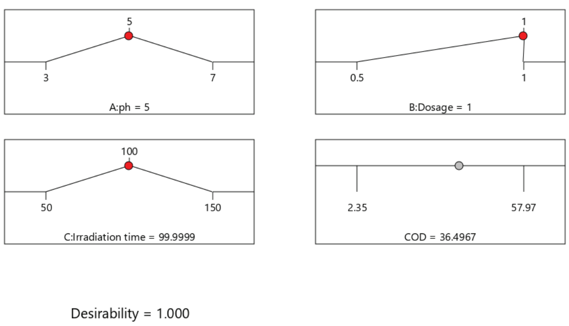

Fig. 8(a): Effect of 1 g/L catalyst dosage on removal of COD.

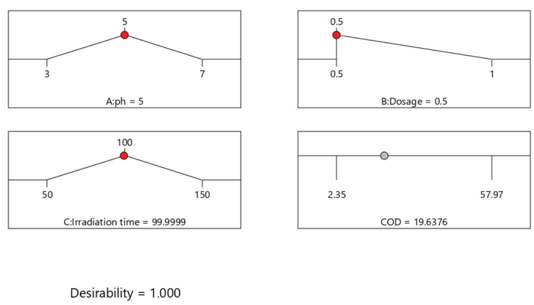

Fig. 8(b): Effect of 0.5 g/L catalyst dosage on removal of COD.

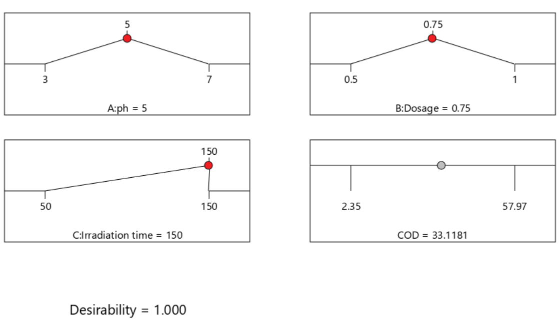

Fig. 9(a): Effect of 150 minutes irradiation time on removal of COD.

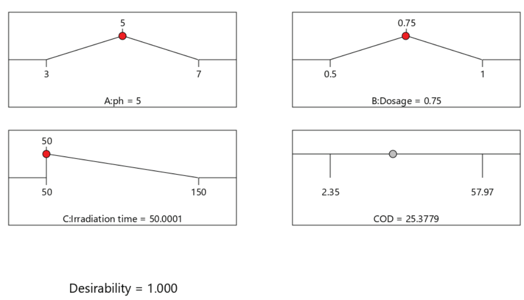

Fig. 9(b): Effect of 50 minutes irradiation time on removal of COD.

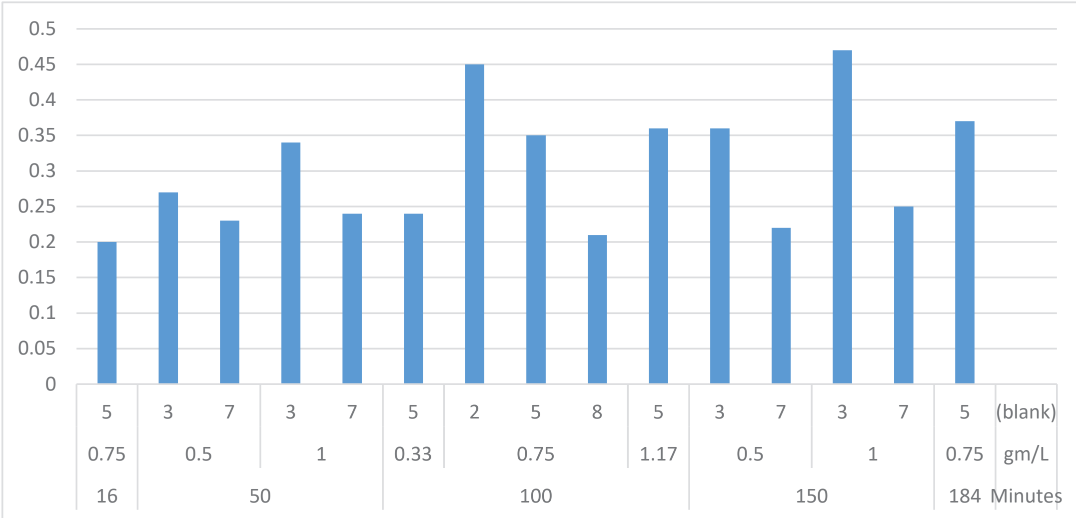

Fig. 10: BOD_5/COD ratio during the photocatalytic process.

REFERENCES

Abu-Daabes, Malyuba, Hani Abu, Qdais and Hatem, Alsyouri 2013. Assessment of heavy metals and organics in municipal solid waste leachates from landfills with different ages in Jordan. Journal of Environmental Protection, 4: 344-52.

Aghaeinejad-Meybodi, A., Ebadi, A., Shafiei S., Khataee, A.R. and Rostampour, M. 2015. Modeling and optimization of antidepressant drug fluoxetine removal in aqueous media by ozone/H_2O_2 process: comparison of central composite design and artificial neural network approaches. Journal of the Taiwan Institute of Chemical Engineers, 48: 40-48.

Amini, Malihe, Habibollah Younesi, Nader Bahramifar, Ali Akbar, Zinatizadeh Lorestani, Farshid Ghorbani, Ali Daneshi, and Mazyar Sharifzadeh 2008. Application of response surface methodology for optimization of lead biosorption in an aqueous solution by *Aspergillus niger*. Journal of Hazardous Materials, 154: 694-702.

APHA 1999. Standard Methods for the Examination of Water and Wastewater. Prepared and Published Jointly by the American Public Health Association, American Water Works Association, Water Pollution Control Federation, Joint Editorial Board, Michael J. Taras, Arnold, 2671.

Deng, Yang 2009. Advanced oxidation processes (AOPs) for reduction of organic pollutants in landfill leachate: a review. International Journal of Environment and Waste Management, 4(3-4): 366-384.

El-mekkawi, Doaa M., Norhan Nady, Nourelhoda A. Abdelwahab, and Walied A. A. Mohamed 2016. Flexible bench-scale recirculating flow CPC photoreactor for solar photocatalytic degradation of methylene blue using removable TiO_2 immobilized on PET sheets, International Journal of Photoenergy, 9270499 [CrossRef].

Fotiadis, Christos, Nikolaos, P. Xekoukoulotakis and Dionissios, Mantzavinos 2007. Photocatalytic treatment of wastewater from cottonseed processing: effect of operating conditions, aerobic biodegradability and ecotoxicity. Catalysis Today, 124(3-4): 247-53.

Garba, Zaharaddeen N. and Afidah Abdul Rahim 2014. Process optimization of $K_2C_2O_4$-activated carbon from *Prosopis africana* seed hulls using response surface methodology. Journal of Analytical and Applied Pyrolysis, 107: 306-12.

Garg, Alok, Vikas K. Sangal and Pramod, K. Bajpai 2017. Photocatalytic treatment of binary mixture of dyes using UV/TiO2 process: calibration, modeling, optimization and mineralization study. International Journal of Chemical Reactor Engineering, 15(2).

Gehrke, Ilka and Annette Somborn-schulz 2015. Innovations in nanotechnology for water treatment. Nanotechnology, Science and Applications, 8: 1-17.

Ghaedi, M., Hajati, S., Zaree, M., Shajaripour, Y., Asfaram, A. and Purkait, M.K. 2015. Removal of methyl orange by multiwall carbon nanotube accelerated by ultrasound devise: optimized experimental design. Advanced Powder Technology, 26(4): 1087-93.

Ghafari, Shahin, Hamidi Abdul Aziz, Mohamed Hasnain Isa and Ali Akbar Zinatizadeh 2009. Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. Journal of Hazardous Materials, 163(2-3): 650-56.

Iqbal, Munawar, Jan Nisar, Muhammad Adil, Mazhar Abbas, Muhammad Riaz, M. Asif Tahir, Muhammad Younus and Muhammad Shahid 2017. Mutagenicity and cytotoxicity evaluation of photo-catalytically treated petroleum refinery wastewater using an array of bioassays. Chemosphere, 168: 590-98.

Jia, Chenzhong, Yanxin Wang, Caixiang Zhang and Qiaoyan Qin 2011. UV-TiO_2 photocatalytic degradation of landfill leachate. Water, Air & Soil Pollution, 217(1-4): 375-385.

Joshi, Rajkumar and Sirajuddin Ahmed 2016. Status and challenges of municipal solid waste management in India : A review. Cogent Environmental Science, 28(1): 1-18.

Julkapli, Nurhidayatullaili Muhd and Samira Bagheri 2018. Applications of titania as a heterogeneous catalyst for degradation of landfill leachates. In: Nanocatalysts in Environmental Applications, pp. 51-67, Springer, Cham.

Khattab, Ibrahim A., Montaser Y. Ghaly, Lars Österlund, Mohamed E.M. Ali, Joseph Y. Farah, Fatama M. Zaher and Mohamed I. Badawy 2012. Photocatalytic degradation of azo dye reactive red 15 over synthesized titanium and zinc oxides photocatalysts: a comparative study. Desalination and Water Treatment, 48(1-3): 120-29.

Liang, Jin, Nikiforuk, P.N. and Gupta, M.M. 2002. Neural networks for modelling and control of discrete-time nonlinear systems. In: Proceedings of IEEE International Conference on Systems, Man and Cybernetics, 2: 1122-1127.

Manassah, J. 2011. Treatment of highly polluted paper mill waste water by solar photocatalytic oxidation with synthesized nano TiO_2. Proceedings of the International Conference on Green Technology and Environmental Conservation, GTEC-2011, 168(1): 356-361.

Mokhtarani, Nader, Saeid Khodabakhshi and Bita Ayati 2016. Optimization of photocatalytic post-treatment of composting leachate using UV/TiO_2. Desalination and Water Treatment, 57(47): 22232-22243.

Pekakis, Pantelis A, Nikolaos, P. Xekoukoulotakis and Dionissios Mantzavinos Ã. 2006. Treatment of textile dyehouse wastewater by TiO_2 photocatalysis. Water Research, 40(6): 1276-1286.

Qu, Xiaolei, Pedro, J. J. Alvarez and Qilin, Li. 2013. Applications of nanotechnology in water and wastewater treatment. Water Research, 47(12): 3931-46.

Ramky Enviro Engineers Ltd. n.d. Prefeasibility Report For Expansion of Integrated Municipal Solid Waste Vengurla Road, Turmuri Village, Belgaum District, Karnataka, No. 19.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F. and Moulin, P. 2008. Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials, 150(3): 468-493.

Sabonian, Maryam and Mohammad, A. Behnajady 2015. Artificial neural network modeling of Cr(VI) photocatalytic reduction with TiO_2-P25 nanoparticles using the results obtained from response surface methodology optimization. Desalination and Water Treatment, 56(11): 2906-2016.

Sahar, A., Ali, S., Hussain, T., Jahan, N. and Zia, M.A. 2018. Efficient optimization and mineralization of UV absorbers: A comparative investigation with Fenton and UV/H_2O_2. Open Chemistry, 16(1): 702-708.

Saleh, T.A. and Gupta, V.K. 2012. Column with CNT/magnesium oxide composite for lead (II) removal from water. Environmental Science and Pollution Research, 19(4): 1224-1228.

Sarve, A., Sonawane, S.S. and Varma, M.N. 2015. Ultrasound assisted biodiesel production from sesame (*Sesamum indicum* L.) oil using barium hydroxide as a heterogeneous catalyst: Comparative assessment of prediction abilities between response surface methodology (RSM) and artificial neural network (ANN). Ultrasonics Sonochemistry, 26: 218-228.

Shekdar, Ashok V. 2009. Sustainable solid waste management : An integrated approach for Asian countries. Waste Management, 29(4): 1438-48.

Silva, T.F., Silva, M.E.F., Cunha-Queda, A.C., Fonseca, A., Saraiva, I., Sousa, M.A., Gonçalves, C., Alpendurada, M.F., Boaventura, R.A. and Vilar, V.J. 2013. Multistage treatment system for raw leachate from sanitary landfill combining biological nitrification–denitrification/solar photo-Fenton/biological processes, at a scale close to industrial-biodegradability enhancement and evolution profile of trace pollutants. Water Research, 47(16): 6167-6186.

Simon, Haykin 2014. Neural Networks and Learning Machines. Third Edition, ArXiv Preprint.

Spasiano, D., Marotta, R., Malato, S., Fernandez-Ibanez, P. and Di Somma, I. 2015. Solar photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach. Applied Catalysis B: Environmental, 170: 90-123.

Strauss, A., Reyneke, B., Waso, M. and Khan, W. 2018. Compound parabolic collector solar disinfection system for the treatment of harvested rainwater. Environmental Science: Water Research & Technology, 4(7): 976-991.

Tanveer, Muhammad and Gokce Tezcanli 2013. Solar assisted photo degradation of wastewater by compound parabolic collectors: Review of design and operational parameters. Renewable and Sustainable Energy Reviews, 24: 534-43.

Thiruvenkatachari, R., Vigneswaran, S. and Moon, I.S. 2008. A review on UV/TiO_2 photocatalytic oxidation process (Journal Review). Korean Journal of Chemical Engineering, 25(1): 64-72.

Varank, Gamze, Senem Yazici Guvenc, Gokhan Gurbuz and Guleda Onkal Engin 2016. Statistical optimization of process parameters for tannery wastewater treatment by electrocoagulation and electro-Fenton techniques. Desalination and Water Treatment, 57(53): 25460-25473.

Wiszniowski, J., Robert, D., Surmacz-Gorska, J., Miksch, K. and Weber, J.V. 2006. Leachate detoxification by combination of biological and TiO_2-photocatalytic processes. Water Science and Technology, 53(3): 181-190.