Optimisation and Modeling Approaches for the Textile Industry Water Treatment Plants

M. Magesh Kumar

Abstract The textile industry is considered a major pollutant source among all the industrial units because this industry intensively uses a variety of chemicals for the pre-treatment and processing of fibres, wool etc. The wastewater generated from textile processing plants has a complex chemical composition and abnormally elevated physical characteristics. Various chemicals such as organic dyes, bleaching agents, fixing agents etc., are used to upgrade the characteristics of the finished textile materials. A number of methods such as adsorption, coagulation, electro-Fenton oxidation, membrane separation and biological degradation are followed to eliminate the undesirable components from the outlet stream. The success of the treatment process depends on understanding the underlying mechanism of mass transfer by diffusion, the kinetics of pollutant removal and hydrodynamics of mixing. Modeling represents a process by mathematical equations, which comprises the variables affecting the process performance. The model equation shows the relationship between the input and response variables in a process. Model of a process helps to simulate the conditions and understand the robust behavior of systems. The optimisation is a mathematical approach to identify the best condition for a process. The objective of optimisation is to minimise the operating cost or maximise process efficiency. In the wastewater treatment domain, modelling and optimisation are helpful to understand the pollutant removal rate, demarcate the major variables affecting the process efficiency and identify the range of operating conditions. Textile wastes have high salinity, prohibitive total dissolved solids and residual organic dye compounds. The important models developed for a treatment plant are the mass transfer, kinetic, adsorption, and process models. The mass transfer model gives an insight into the rate of diffusion of pollutants in an aqueous medium. A kinetic model explains the rate at which undesirable compounds are removed from wastewater and elucidates the effects of temperature on the process. The process models are used to realise the important variables affecting the process efficacy. The process model explains the interactive effect and linear effect of variables on the response variable. The modelling

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tools used in textile treatment plants are response surface method (RSM) and Artificial Neural Networking (ANN). RSM is the most widely used method to develop the model equations and optimise the process. The second order quadratic models developed by the RSM method interpret the effects of parameters on the response variables. RSM utilises the experimental design method to develop the complete model expression for the operation with the least number of experiments. Irrespective of treatment strategies for textile wastewater such as coagulation, adsorption, electrochemical oxidation, bio-degradation, ozonation, photolytic degradation and membrane filtration, the RSM is used as a versatile method for building the model and process analysis. The quality of the model equations is tested by statistical tools such as ANOVA table, fit statistics table, 2-D contour graph and 3-D response surface plot.

Keywords Response surface methodology · Kinetic model · Mass transfer model · Quadratic model · Wastewater treatment

1 Introduction

Textile industries are responsible for generating a large volume of wastewater because a sizeable quantity of fresh water is used for the dyeing of processed fibres and finished goods. Textile wastewater is characterised by high pH value, excessive suspended solids concentration, and prohibitive concentration of chlorides, nitrates, copper, chromium, and outrageous biochemical oxygen demand (BOD) and chemical oxygen demand (COD) value. The point of source for the wastewater decides the concentration level of contaminants. This industry is considered one of the highest polluting industrial units because of the volume of waste generated and its hazardous constituents. Textile wastewater shows utmost COD, BOD, pH, colour, and salinity variations. The properties of chemicals, dye compounds and organic compounds determine the characteristics of the effluent stream from the textile industry. Almost 10–50% of unfixed dye molecules are lost to the environment as pollutants in the dyeing process. The dye chemicals are less susceptible to biodegradation, and hence they persist in the effluent stream for a long period. The textile industry is associated with spinning natural and synthetic fibres into yarn, and the fabrics are produced from yarn. Various unit operations and unit processes such as carding, weaving, bleaching, drying, sizing, dyeing finishing etc., take place in processing raw fibre into useful textile products. The process of adding dye compounds to textile products is called dyeing. The bleaching process removes natural colour and odour from textile raw materials. Around 140–200 l/d of water is consumed for producing 1 kg of fabric material in a textile dyeing unit (Report on assessment of pollution 2014). Different chemicals such as strong acids, bases, colouring agents, bleaching agents, finishing chemicals, thickening agents, surfactants and dispersing agents are used in each stage of the textile industry. The aesthetic appearance of the finished goods is improved by using multi-colour dyeing compounds. A typical textile processing unit is composed of the steps elucidated in Fig. 1.

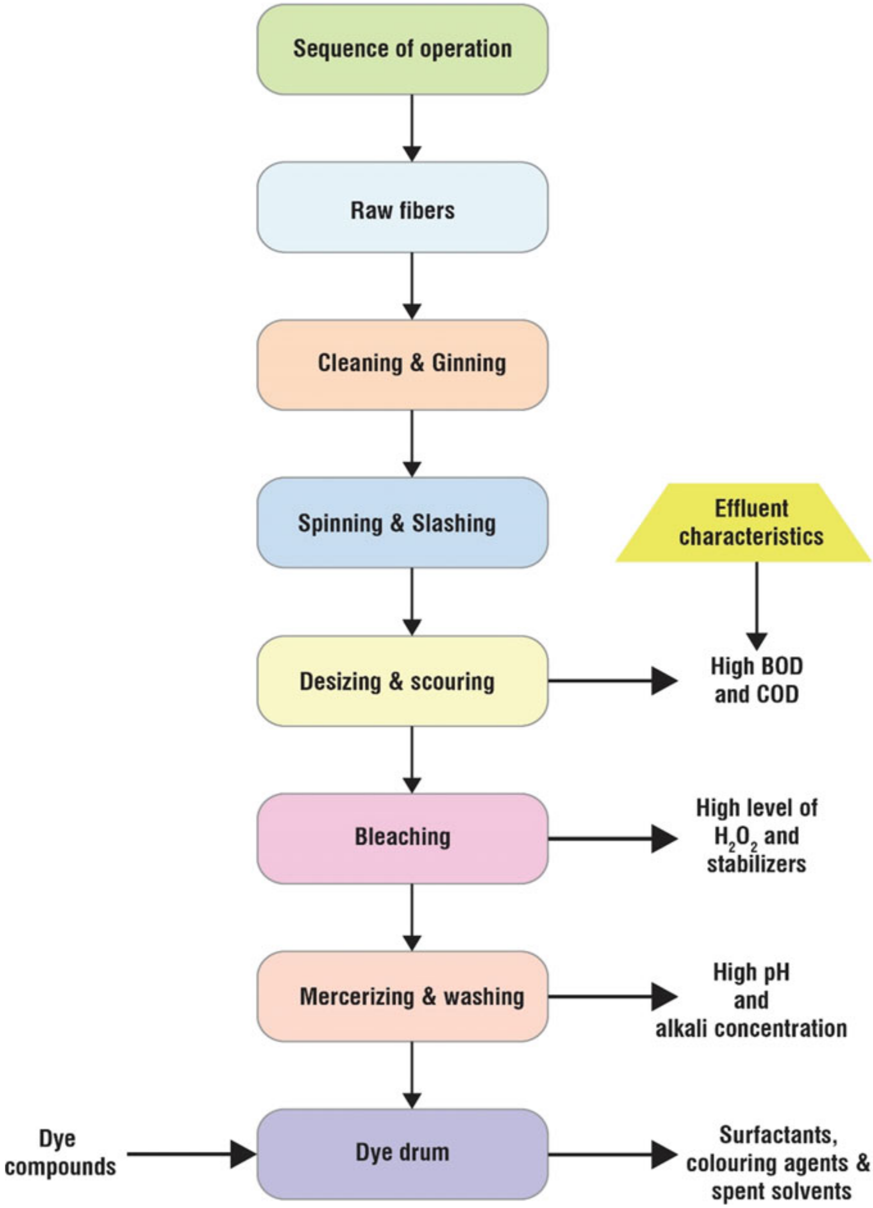

Fig. 1 Sequence of steps in a textile processing unit and characteristics of effluent generated from each process

Table 1 Physico-chemical properties of effluent streams produced from different unit operation and unit process in tannery industry

Unit operation/unit process involved	Physico-chemical characteristics of wastewater
Sizing	Outrageous values of BOD and COD
De-sizing	Outrageous values of BOD and COD; elevated dissolved solids concentration
Bleaching	High alkalinity, excessive suspended solids
Mercerizing	High pH, high dissolved solids
Dyeing	Strong colour, high BOD, dissolved solids

The effluent stream from each step has the Physico-chemical properties defined in Table 1.

Process modeling is the representation of a physical system by variables and equations. Modeling a process requires a sound knowledge of major process variables, operating conditions used and constraints applicable. The model equation explains the variation of the dependent variable as a function of independent variables. The three major components in a general model equation are the input, response, and parameter. Process models are used to calculate and interpolate the responses as well as calibrate and optimise the process variables. The average magnitude of the output variable is calculated for a specific amalgamation of the input variables. The interpolation is done to determine the new values of the response variable without conducting the experiments. Mathematical modeling has suffused all branches of engineering and science and assisted in better understanding of processes mechanism. Process industries provide the analytical basis for the design and control of equipment and process optimisation with limited effort and time. The purpose of the mathematical model is to understand the system's robustness and predict the system's future behaviour (Bravo et al. 2011). The modeling of the process can be broadly categorised into a series of activities, namely, building, studying, testing and use. The developed model equations are useful in all stages of operation in the industry. It helps screen the important process parameters and analyse the influence of various process parameters on selecting control strategies and optimisation methodology to follow. Analysis of simulated results from a model equation gives an idea about the best arrangement of process equipment to improve the yield from a process. In the wastewater treatment domain, the ordering of units determines the treatment potential of the wastewater treatment plant.

2 Textile Industry Wastewater: Source, Characteristics and Environmental Impacts

Textile industry discharges effluent stream with pollutants such as colouring agents, sizing agents, fixing salts, bleaching agents etc. The wastewater discharged from the textile industry is a complex mixture of organic and inorganic chemicals with poor biodegradability and a high concentration of dissolved salts. Even though textile industries generate all kinds of waste, liquid effluent is a major concern because of its bulk volume and antagonistic environmental impacts. The physicochemical nature of liquid effluent generated depends on the nature of fiber being processed, type of chemical reagents used, technology adapted, operating variables etc. The pollutants from the textile industry are due to the processes such as desizing, scouring, mercerising, bleaching, neutralising, dyeing, printing and finishing. Apart from these sources, gaseous pollutants such as suspended particulate matter, sulphur oxides and nitrogen gases are produced from boilers, thermo-pack utilities and generators.

Textile industry liquid waste is characterised by high pH value, and excessive concentration suspended particles, outrageous chloride and nitrate ions. Severe environmental damages are caused by the contaminants present in wastewater emanating from the textile industry. The composition of textile wastewater changes dynamically because of the process diversity and varieties of chemicals used in each unit process (Correia et al. 1994). The different categories of chemicals used in the textile industry are detrimental to the environment and health. The stain remover can cause ozone depletion; oxalic acid is toxic to aquatic organisms, printing gums is responsible for dermatitis, liver malfunction and kidney damage, bleaching agent chlorine causes skin irritation, and azo dyes are well-known carcinogens. The organic waste present in the effluent stream consumes dissolved oxygen from receiving water bodies and destroys the aquatic biosphere. The liquid wastes have high BOD and COD concentrations because the concentration of dissolved oxygen is too low in the effluent stream. The high colour intensity of effluent reduces the sunlight penetration into receiving water bodies and decreases the oxygen solubility. Apart from other chemicals used in various processing stages, the effluents contain inflated dye concentrations. The effluent has excessive dye concentration apart from having varieties of spent chemicals used in different processing units. Various health hazards such as haemorrhage, skin dermatitis, severe ulcer of skin etc., are caused by remnant metals, namely Cr, As, Cu and Zn.

The major environmental concern associated with textile dyeing units is removing colour and dissolved salts from wastewater. Along with these pollutants, the effluents do contain trace elements such as chromium, arsenic, copper, zinc, which has the potential of causing health ailments including haemorrhage, skin rashes and cancer, dermatitis etc. Azo dyes are mainly used as a colouring agent for cotton fibers. The azo dyes are electron deficient because they have a nitrogen-nitrogen bond in the chemical structure. The waste stream containing these dye compounds can cause damage to flora and fauna in receiving water bodies. The hazardous effect of azo dye depends mainly on the duration of exposure time and exit dye concentration (Hassaan and Nemr 2017). The textile wastewater is of potential environmental concern because it substantially decreases the dissolved oxygen concentration in the receiving water body due to hydrosulfides. Textile industry wastewater is one of the reasons for rapid environmental degradation and human illnesses. The quantum of degradation caused is very high compared with other process industries. The carcinogenic nature of colourants used in the textile industry is due to the presence of organic chlorine.

The normal functioning of cells is disturbed in living organisms due to this chemical pollutant which ultimately affects the physical appearance and biological mechanisms. The heavy metals are non-biodegradable and accumulate in vital organs in the body. The partially treated or untreated effluent from the textile industry is very harmful to all life forms, including aquatic and terrestrials. Many methods such as oxidation methods (cavitation, photocatalytic oxidation, ozone, hydrogen peroxide oxidation, Fenton oxidation process), physical methods (adsorption and filtration) and biological methods (fungi, algae, bacteria, microbial fuel cell) are followed to minimise the pollutant concentration in textile wastewater (Holkar et al. 2016).

3 Treatment Methods and Strategies

The textile processing unit is a water-intensive industry because it utilises a large quantum of water for washing, dyeing, and finishing operations. Hence this industry releases a huge volume of wastewater characterised by its immense colour, high level of suspended solids and dissolved solids concentration. The methods, namely biological treatment, coagulation and flocculation, adsorption, oxidation, is widely used to treat textile wastewater. The activated sludge process can reduce the COD concentration to a significant level. The treated water from this process has high ammonia content and residual colouring agents. Coagulation-flocculation is suitable to remove dissolved colour completely from wastewater, but this method suffers from the drawbacks such as unreliable performance of the plant and secondary sludge disposal problems. The physical adsorption method is most suited for the elimination of suspended as well as dissolved solids. The efficiency of this method depends on the way of regenerating the spent adsorbent and methods of handling the secondary pollutants generated. Membrane filtration is used for the post-treatment process to remove the pollutants present at the microscopic level. Membrane techniques are efficient than conventional methods, and it is very specific to handling dissolved pollutants. The processes based on membranes are used to improve the quality of wastewater which is already treated by conventional methods. This method is used to fine tune the characteristics of wastewater by removing the micro level pollutants even when they are present in very small quantities. The only problem associated with the membrane technique is the efficient management of concentrate because the concentrated stream from the membrane treatment unit is a complex mixture of varieties of contaminants.

Ozonation is employed for wastewater having oxidisable pollutants. The decomposition of ozone produces hydroxyl radicals which are highly reactive and deteriorate the pollutants present in wastewater. This method focuses mainly on colour removal and the disinfection process. This method is expensive because the operating cost is high. Photocatalysis is the acceleration of the reaction rate of a photochemical reaction in the presence of a catalyst. The pollutant reduction using the electrolysis method is a feasible approach to remove the hazardous pollutants, which is not eliminated by conventional treatment techniques. The efficacy of the electrolysis method depends primarily on the rate of energy consumption, the lifetime of electrodes and the foaming tendency of wastewater during the treatment process.

4 Process Modeling

4.1 Mass Transfer Modeling and Kinetic Modeling

Mass transfer modeling in an aqueous effluent treatment plant is essential to understand the rate of pollutant movement, energy cost involved, and equipment design. These modeling aspects include the adsorption of pollutants, diffusion process and oxygen transfer in the oxidation process. The mechanism of the adsorption process for pollutant removal is understood by a mass balance equation of the adsorbate, rate of pollutant movement from the bulk solution to the surface of adsorbent and adsorption isotherm. An unsteady state solute balance equation in a fixed bed adsorber for an elemental section is written as,

$$\varepsilon\frac{\partial c}{\partial t} + (1-\varepsilon)\rho_p\frac{\partial q}{\partial t} = -v\frac{\partial c}{\partial z} + \frac{\partial^2 c}{\partial z^2} \tag{1}$$

where ε is the fraction of void volume in bed, v is the superficial velocity (m/s) in vacant bed, ρ_p is particle density (kg/m^3), and D is axial dispersion coefficient (m^2/s). The leading term indicates the accumulated solute concentration in the liquid, and the second term represents the quantity of solute adsorbed in the adsorbent. The third term gives the amount of solute movement by convective (bulk) movement. The rearmost variable measures the extent of solute dispersion in the axial direction and measures the degree of mixing between the solute and solvent. The second model equation explains the kinetics of the adsorption process

$$\rho_b\frac{\partial a}{\partial t} = k_i\,(c - c^*) \tag{2}$$

where k_i is the mass transfer coefficient (s^{-1}), q is adsorption capacity (gm adsorbed/gm adsorbate), and C* is the equilibrium concentration of adsorbed species. The third equation is the equilibrium isotherm which is generalized as

$$a = f(c^*) \tag{3}$$

The equilibrium concentration of solute between the liquid phase and solid phase adsorbent is defined by the Freundlich equation and Langmuir equation.

The gas–liquid mass transfer models are very important to understand the mechanism of the advanced oxidation process and ozone treatment of wastewater. Aeration is a key process for achieving the best treatment efficiency in a water treatment unit.

Various theories such as two-film theory, penetration theory and surface-renewal theory are developed to elucidate the rate and mechanism of oxygen transfer. The governing model equation for the absorption of oxygen in the liquid is defined as

$$\frac{dC}{dt} = Q_{O2} = k_{liq}\, a'(C^{*} - C) \tag{4}$$

where Q_{O2} is the oxygen transfer rate, a' is the gas–liquid interfacial area per unit liquid volume and k_{liq} is liquid phase mass transfer coefficient.

The two film theory defines the rate equation for direct mass transfer as

$$-\frac{dC}{dt} = \left[\frac{1}{\frac{1}{k_{Ag}\, a} + \frac{H_A}{k_{Al}\, a}}\right]\left(p_A - H_A\, C_A\right) \tag{5}$$

where H_A is the Henry law constant and C_A is the moles of oxygen dissolved per unit volume in the liquid phase.

The kinetics of the coagulation process is concerned with establishing the rate equation for the formation of flocs and also investigates the influence of pollutant concentration and temperature on the process mechanism. The rate at which the pollutant concentration decreases with time is expressed by n^{th} order general rate equation defined as (Marichamy and Ramasamy 2015)

$$-\left(\frac{dC}{dt}\right) = k\,.\,C^{n} \tag{6}$$

where the variable C represents residual pollutant concentration in mg/L at the instantaneous time, k stands for the rate constant (min^{-1}. $(mg/L)^{(1-n)}$), n is the order of the process, and t (min) is operating time. The value of rate constant and process order is calculated using the kinetic data obtained from experiments. There are two approaches to estimate the kinetic parameters in the rate equation: the integral method of analysis and the differential method of analysis. The process order is assumed in the integral method, and after appropriate mathematical manipulations and integrations, a final equation between concentration term and time is obtained. The residual pollutant concentration versus time data obtained from the experiment is fitted with the final rate equation obtained. If the data satisfies the rate equation, the assumed order is correct. In the differential analysis method, the kinetic data are fitted directly to the rate equation without any integration. The rate equation defined by Eq. (6) is linearised by taking logarithm on both sides, and a plot is prepared between $\log_{10}\left(\frac{-dC}{dt}\right)$ variables along the ordinate axis and $\log_{10}(C)$ along the abscissa axis. The straight line slope gives the magnitude of process order (n), and the vertical axis intercept made by the trend line gives the magnitude of the rate constant. For most of the wastewater treatment methods, it was observed that the process obeyed the second order kinetic model. This means that the rate of decrease in pollutant load per unit volume varies directly proportional to residual concentration square. The proportionality constant is called the rate constant, which indicates the speed of floc aggregation and pollutant depletion from the waste stream.

4.2 Development of Process Model

Modeling a process is useful in all engineering disciplines, basic sciences, process economics and biological sciences. The models are developed based on physical, chemical and mathematical laws. The dynamic characteristic of a system is understood by developing a process model relating the changes in one variable with respect to time. The standard of the proposed model is based on assumptions made, creativity and innovativeness of the engineers and scientists. The invalid assumptions impose restrictions on the model and significantly affect the predicted results. The solvability of the models is tested with the “degrees of freedom (DF)” of the system. If the number of variables equals the number of equations, then the DF value is zero, making the model easily solvable. If the number of variables is greater than or less than the number of equations, then it is concluded that the system is either over specified or under specified. The model developers shall think about the possible solution methodologies to simulate the model equations. The simulated results from the model equation should match with the real time process output. The worth of the equation depends on how far the model results match with the real world output.

4.3 Basics of RSM Modeling and ANN Modeling

In the early 1950’s Response Surface Methodology (RSM), based on statistics and mathematics, was introduced as an analysis tool by Box and Wilson. This method is useful for optimising process variables to obtain the maximum or minimum response value. It is based on the design of the experiment’s approach and helpful to study the effects of major independent variables on process outcome. The number of experiments to be conducted can be minimised with the design of the experiment concept. RSM is also used to develop and solve the model equations to obtain optimised process variables. RSM is used to find optimal process conditions, trouble shoot problems, identify weak points in the process and develop a process model having more robustness against external influences.

RSM investigate the effective correlations between the independent variables and response variables. The simplest model considered is the first order model defined by the expression

$$y = \alpha_o + \alpha_1 x_1 + \alpha_2 x_2 + \varepsilon \tag{7}$$

where α_o is the constant term, α_1 α_2 the linear terms, and the error term.

A second order response surface model would be appropriate to represent the process if significant interactions between the process variables and curvature are obtained. It is expressed by the equation as

$$y = \alpha_o + \alpha_1 x_1 + \alpha_2 x_2 + \alpha_{11} x_1^2 + \alpha_{22} x_2^2 + \alpha_{12} x_1 x_2 + \varepsilon \tag{8}$$

where α_o is the constant term, α_1 α_2 are the linear terms, α_{11} α_{22} are the quadratic terms and α_{12} is the interaction term. RSM approach is a sequential procedure because identifying the optimum point is done in sequences to move from the current point, which is far away from the exact stationary point. The positive sign for the coefficients indicates an increase in response value, whereas the negative sign indicates a decrease in the response value. The change in response variable value as a function of two independent variables is represented by 3-D response surface plots. Contour curves are the 2-D representation of response surface and are considered iso-response curves. The fitness quality of proposed models is tested with statistical parameters such as p-value, coefficient of determination (R^2) and F-value. The magnitude of the p-value is a measure of the effect of the independent variable on process response. It is based on testing the null hypothesis "coefficient term is zero," which means zero effect on process output. A lower p-value ($p < 0.05$) indicates that the variable profoundly affects the response variable. The R^2 square value explains the variation of predicted data from actual data. The response curve fits the real data when the R^2 value is high, and the ideal value is one. The predictive capability of the complete model is determined statistically with the help of the F-value. The larger the F-value, the better is the model forecasting ability. The null hypothesis is rejected if the F-value is large.

The most widely used experimental design for response optimisation is Central composite design (CCD) and Box-Behnken design. The CCD procedure gives a response surface curve that adequately fits the second order quadratic model. The curvature of the response surface is estimated by combining centre points with a group of star points. In CCD, the distance between each axial point (start point) and center is designated by the symbol alpha (α). This alpha value determines whether a design is rotatable and orthogonally blocked. The alpha value depends on the properties of response surface design and a number of factors describing the process. The equation defines the value of α

$$\alpha = (\text{number of factorial runs})^{0.25} \tag{9}$$

When full factorial is used then value of α is defined by the expression

$$\alpha = \left(2^{\mathrm{k}}\right)^{0.25} \tag{10}$$

There are three types of central composite designs: Circumscribed, Inscribed, and Face Centered.

The second widely used procedure for process optimisation is the Box-Behnken design. The fractional factorial design is not available in this configuration, and hence it is considered as an independent quadratic design. The treatment combinations are located at the midpoint of each cube's edge and one at the center of the cube body. The number of runs required by the Box-Behnken design is 15 and 54 when the number of factors involved is 3 and 6, respectively. The equation calculates the number of experiments to be conducted according to this design

$$N = 2f^2 - 2f + Co \tag{11}$$

where f is the number of factors and Co is the center point of design space. The levels of the process variables are usually represented as coded variables such as -1, 0, $+$ 1, which indicates lower, middle and higher level values, respectively.

4.4 *Objectives and Uses of RSM*

RSM is useful for solving different types of optimisation problems in industries. The objective is to develop the process model equations, optimise the process conditions and enhance the process output. This objective is achieved by following the three steps: screening, improvement, and predicting the optimum. Screening refers to identifying the important factor influencing the process, whereas improvement cites the procedure to reach out the optimum by continuously changing the factor settings. The response surface methodology (RSM) is a mathematical strategy to elucidate the interrelationship between the independent variables with the dependent variables and explain the influence of these parameters on responses. There are six different general steps involved in the RSM technique: (1) identifying the major process factors and response under study (2) endorsing appropriate experimental design plan (3) performing regression analysis with the multivariable model of the process (4) pointing out the parameters significantly affecting process responses using analysis of variance (ANOVA) method (5) guessing whether screening of variables is necessary or not (6) conducting experiments at optimal conditions to verify the characteristics of the response.

4.5 *Analysis and Transformation of Models*

Analysis of variance (ANOVA) is a statistical approach used to test the quality of the model as a whole and also the nature of individual terms. To check whether the correct model is chosen or not, the descriptive statistics are tested along with other statistical tests and the significance of the parameters, variables and coefficients are judged. The ideal starting point for the model is chosen based on the results of the fit summary table. The key parameters to look in fit summary table is:

- Mean which represents the sum of squares for the consequence of mean
- Linear measures the sequential sum of squares for the linear term. The addition of linear terms to the intercept and block effect and significance of this addition is tested with the aid of F-value magnitude
- The quadratic term indicates the sequential sum of squares for quadratic (A-squared, B-squared, etc.) terms. The importance of adding the quadratic terms in the model is verified with F-value. It is observed that the model prediction ability is improved when a small p-value (prob > F) is obtained from statistical tests.

5 Response Surface Design and Analysis of Variance (ANOVA)

The following parameters and plots are used to analyse and interpret the fitted models: Normal plots are used to highlight significant active factors. Residual plots are used to check the validity of normality and constant variance assumption. The fit of the proposed models could be improved by evaluating the response on a log scale and reported in the Box-Cox plot for power transformation. The linear term in a model explains the average effect of varying a control, whereas the interaction term studies the influence of altering a variable with the setting of another independent process variable. The quadratic terms (x^2) explain the effects of process factors on the curvature of the response curve. The purpose of ANOVA is to check if there is any deviation among the group of variables. The elementary proposition of ANOVA is to assess the magnitude of variation within the samples relative to the quantity of variation between the samples. There are two different approaches for ANOVA.

First is One-way (or single factor) ANOVA, in which only one factor is considered, and it is to be observed that varieties of samples can materialise inside that factor. The subsequent steps involved with this technique are: mean of each sample is obtained, the sum of squares for variance between the samples (SS) is then calculated, diving SS obtains the mean square (MS) among the samples by degrees of freedom connecting the samples. In one way ANOVA, the F-statistic ratio is defined by the expression:

$$\boldsymbol{F} = \frac{\textbf{variation between the sample means}}{\textbf{variation with in the samples}} \tag{12}$$

F–test could be used to assess the equality of variance. ANOVA compares the known variance (caused by input variables) to the unknown source of variance (mainly due to disturbance errors).

The two-way ANOVA test calculates an F value. It is used to test whether the means are significantly different or not. Two independent variables are used as input instead of one input variable, as in one-way ANOVA. The means and sum of squares statistics are calculated for each combination of independent variables. The predictive stability of the model is gauged using Adjusted R^2. For a good model, the predictive strength should be more than 10% if the significance level is set at 5%. The definitive relationship response value and input variable are confirmed if the model has a 10% relative improvement over the predictive strength. The ANOVA can be calculated using one of three types of sums of squares (SS). Type I or sequential SS calculations are done based on the order of adding the factors to the design. The process starts with the main effects, followed by the interactive effects. Type II or classical SS is followed when at least one multilevel categoric factor. The main effect SS calculation of factor is done by assuming that the factor is not a part of interactive effects. Type III or Partial SS corresponds to nil multilevel categoric factors and check for all other terms in the model before the SS is calculated for an individual term. ANOVA table for experimental design consists of the following terms:

- The residual, which shows the strange disparity in the response, lack of fit refers to missed observations by the model predictions
- sum of squares (SS) measures the squared differences between the accumulated average and the quantity of difference explained by the source
- degree of freedom used to calculate source's sum of squares using the number of estimated variables
- p-value (Prob > F) explains the probability of getting the observed F-value if the null hypothesis is not false. The model equation and terms are significant if the Prob > F value is very small (should be less than 0.05)
- coefficient of variation is defined as the standard deviation expressed as mean% and estimated by dividing standard deviation with the mean and multiplying the result with 100
- PRESS stands for Predicted Residual Error Sum of Squares which measures the fitting capacity of the model to each point in the design. It is calculated by initially predicting the likelihood of other points except for the point under study.
- R squared is defined by the expression and appraises the quantity of discrepancy about the mean explained by the model

$$\mathrm{R}^2 = 1 - \left[\frac{SS\,\text{residual}}{SS\,\text{residual} + SS\,\text{model}}\right] \tag{13}$$

- Adjusted R^2 squared assesses the disparity around the mean, which is delineated by the model and adjusted for the number of terms present in the model. As the quota of model terms increases, there is a decrease in the adjusted R^2 square value. The expression defines it:

$$\text{Adjusted}\,\mathrm{R}^2 = 1 - \left[\left(\frac{SS\,\text{residual}}{df\,\text{residual}}\right)\Big/\frac{SS\,\text{residual} + SS\,\text{model}}{df\,\text{residual} + df\,\text{model}}\right] \tag{14}$$

- Predicted R^2 measures the quantity of deviation in new data elucidated by the model. It is defined as

$$\text{Predicted}\,\mathrm{R}^2 = 1 - \left[\frac{\text{PRESS}}{SS\,\text{residual} + SS\,\text{model}}\right] \tag{15}$$

Either the data or the model may have problems if the predicted R^2 and adjusted R^2 is exceeding 0.2.

6 Types of Model Equations and Graphs in Response Surface Design

Model equations are used to predict the response values at a set of experimental conditions, and graphs are used to analyse the variation of output variables as a function of input variables. The most widely used models in process optimisation are the first order and second order models. The order of a model shows a trend followed by the experimental data. This factor explains how effective the model equation is to describe the data and predict an output. A linear model can explain the steady rate of change in the data. A quadratic model represented as a parabolic shaped curve can explain data's curvature. A polynomial model can describe a "peak-and-valley" trend in the data.

In the first order model, the cross product terms, which is an indication of response surface curvature, is ignored and consist only linear effect of the process variables. It is defined by

$$y = \alpha_o + \alpha_1 x_1 + \alpha_2 x_2 + \varepsilon \tag{16}$$

where α_1 and α_2 are the linear terms, α_o is the constant coefficient, and ε is the error or deviation variable. The variability between the model predicted value and the real time experimental value is called an error. This error should be less for the best model, and zero is the value for the ideal fitting model. The process is modeled as a first-order equation when the response changes linearly according to independent variable changes. The first order model is used to understand the orientation of flat planar surfaces with reference axis and is not suitable for finding maximum, minimum or saddle points for a function. For a small interval of x axis variable lying between $a \leq x \leq b$, the first order is suitable because the variation in function value is almost linear. The first order model is inadequate for response surfaces having curvature. A second order model is used to fit the response surface with curved shapes for such response surface designs.

Some of the widely used diagnostics plots are:

- Residuals versus Predicted plot: The persistent variance assumption is tested with this plot. A randomly scattered plot indicates that the residuals are spread across a constant range in the graph. A transformation is needed if the plot is showing an expanding variance pattern. The predicted values are taken along the horizontal X axis, and residuals are taken along the vertical Y axis. This plot helps us to

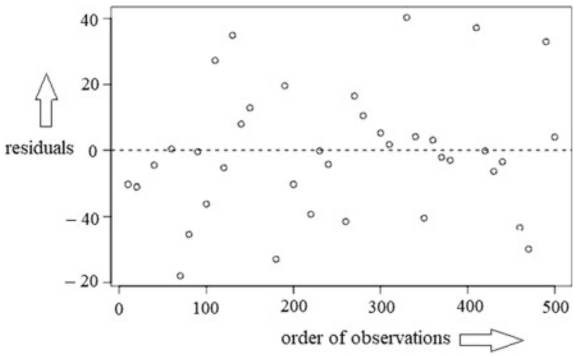

Fig. 2 Experimental run order affecting model residuals

determine whether a multiple regression model should be used or not. A well behaved plot should give a horizontal band around the residual = 0 line.

- Residuals versus Run order plot: This is a graph between residuals and experimental run order. The influence of lurking variables on output variables is checked using this plot. A random scatter plot should be obtained for a good model. If the data points are scattered above and below the reference line (residual = 0), the developed model equations are the best. A sample plot is shown in Fig. 2, which shows the random scattering of data points around the reference line.
- Predicted versus Actual plot: This plot of forecasted output values versus the real response values. It is used to check the presence of a value or group of values that the model cannot predict easily. The points should reside near the fitted line with narrow confidence interval width. Points located vertically, very far away from the line, represent the possibility of outliers.
- Contour plots: A graphical technique used to represent a 3-D surface on a 2-D graph format is called a contour curve. Contour curves are also called iso-response curve because it is obtained by plotting for constant response values. This plot is used to find the change in function value (Z) as a function of two independent variables, x and y. Let the contour function be Z = f(x, y). The value of response variable 'Z' changes with respect to 'x' and 'y' variables (see Fig. 3).

  The contour plot is plotted by taking independent variable 2 along the vertical axis and independent variable 1 along the horizontal axis. The response variable curves are represented by concentric circles, elliptical or linear shapes. The shape of contour curves gives a rough indication of the effects between the process variables. Circular shaped contour curves represent nil interaction between the independent variables, whereas elliptical contour curves indicate the best interactive effect between the input variables. Elliptical shaped contours are produced by a second order model containing interaction terms.
- 3D Response surface plots: This plot explains the relationship between a dependent variable and the two independent variables. It is useful to identify the desired operating conditions for the process in order to achieve optimised results. It has two components: predictor variable on the x- and y-axes and an output variable on the z-axis. A particular combination of x and y variables will give the peaks or

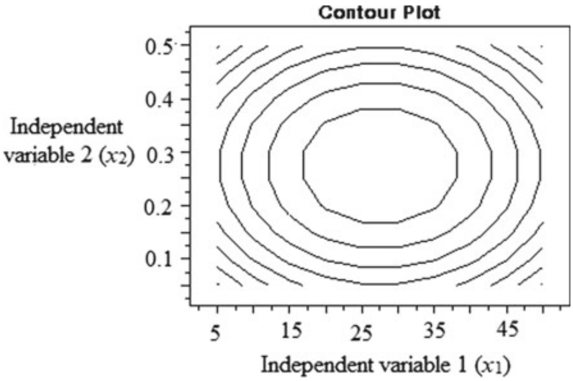

Fig. 3 Contour plot expressing the interactive effects between the two independent variables on process response

valleys, thus producing local maxima or minima. Different types of patterns occur in contour plots and 3D response surface plots. The point at which the maxima are obtained is called the critical point or stationary point, where the slope of the tangent plane is zero. In the minimax pattern, a decrease in the output is observed when the variables are either increased or decreased at the same time near the design center (see Fig. 4).

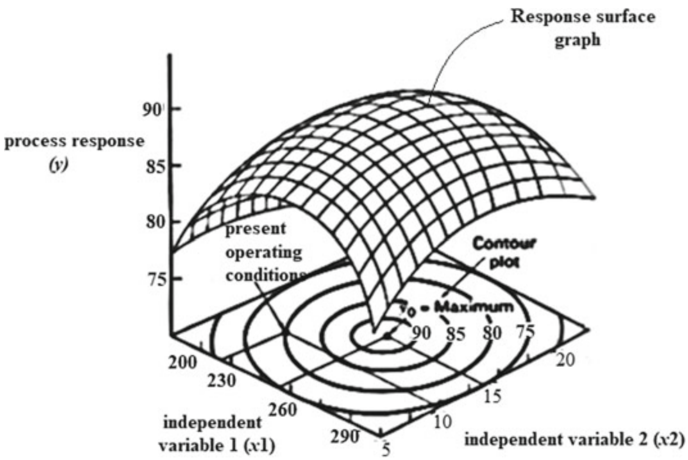

Fig. 4 Response surface graph illustrating the interaction effects between the two input variables on process response

6.1 Applications of RSM in Wastewater Treatment Domain

The optimisation is a mathematical technique which plays a major role in optimising waste handling treatment systems. Using RSM in the waste treatment realm is highly advantageous because it is flexible, can provide reliable results and is less time consuming. Apart from optimising the process conditions, this technique is used to analyse the effects of system variables on process output. Varieties of the industrial wastewater treatment process are optimised using the RSM technique. This chapter gives a brief overview of the usability, efficiency and drawbacks of RSM for process optimisation in waste handling treatment plants. A literature review has shown the widespread applications of RSM in the wastewater treatment unit. Modeling is the mathematical formulation of a system that relates dependent variables, independent variables and parameters in a process. The process model equations are used to understand the mechanism of the process, devise control strategies for automated systems, optimise the design and process variables, troubleshoot the process and in the economic analysis. In the textile wastewater treatment process, modeling and optimisation play a significant role in process synthesis and analysis. The model equations developed for the textile wastewater treatment process and the plant is used to analyse the effects of important process variables on treatment efficiency. The simulated results from the model equations are used to analyse the suitability of the treatment system for treating wastewater with specific characteristics.

Milk processing wastewater was successfully treated using a four compartmented multistage flexible fibre biofilm reactor (Abdulgader et al. 2020). The performance of this novel reactor is maximised at optimum operating conditions, which is obtained using RSM. Two important variables considered in this study is COD_{in} and HRT and 9 dependent response variables such as soluble and total COD (SCOD and TCOD), soluble and total BOD5 (SBOD5 and TBOD5), TSS, effluent pH, effluent turbidity, the retention time of sludge and substrate utilisation rate per unit mass were found from the experiments. The ANOVA results indicate that a quadratic regression model with lesser terms was better to elucidate the response surface for effluent pH of MS-FFBR.

In another study (Jadhav and Mahajan 2014), RSM was used as a tool to optimise the coagulation-flocculation process for turbid effluent treatment using a plant based coagulant prepared from *Coccinia indica*. The effects of coagulant dose, initial turbidity concentration, and pH of solution were studied using the central composite design method. A quadratic model having second order was developed to explain the progress of the coagulation process and analyse the interactive and non-interactive effects between the process variables. The worthiness of the proposed models was validated with the immensity of coefficient of determination (R^2) and adjusted R^2, which had values of 0.941 and 0.926, respectively. This study concludes that RSM is an appropriate and ideal tool for optimising a process whose response depends on more than one stimulus variable.

Another author studied the applications of RSM for treating poultry slaughterhouse wastewater (PSW) which consists of organic matters, suspended solids, dissolved nitrogen and detrimental nutrients (Williams et al. 2019). This study has utilised an Expanded Granular Sludge Bed (EGSB) to remove COD from PSW using hydraulic retention time (HRT) and organic loading rate (OLR). RSM augmented with a central composite design matrix was applied to identify the maximum achievement range of this reactor.

The applications of RSM is extended to slaughterhouse wastewater treatment because it contains varieties of pollutants, including organic matter (chemical oxygen demand (COD), biochemical oxygen demand (BOD)), total nitrogen, total suspended solids, total phosphorus, grease, and oil (Gökçek and Özdemir 2020). The process parameters such as initial pH, coagulants concentration, rate of rapid mixing and settling time were optimised using RSM to calculate the maximum removal % of process responses like COD, turbidity and suspended solids of the raw wastewater. Based on the response surface graph, the removal efficiency attained for COD, SS and turbidity removal was observed to be 75.25, 90.16, and 91.18%, respectively.

RSM was used to optimise the process variables for treating abattoir wastewater using Chito-protein coagulant extracted using crab shell (Okey-Onyesolua et al. 2020). To study the effects of pH, settling time, temperature and adsorbent storage on the removal of BOD, COD, turbidity and color from wastewater, RSM was used as an interlinking tool. The model predicted and experimental values had good correlations, indicating that the model equation developed using RSM is most suitable for understanding the underlying mechanism of process influencing factors.

The applications of RSM are also extended to the treatment of aqueous effluent from petroleum refinery plants (Singh and Kumar 2020). A central composite design matrix was applied to identify the best combination of the independent variables such as pH and coagulants to optimise the process output responses, including final pH, % of COD, turbidity, TDS and color removal from the targeted wastewater. ANOVA was employed to examine the statistical significance of the proposed models and their prediction ability. Second order quadratic model explained the relationship between the input and output variables.

The wastewater from the sunflower oil refinery industry was conditioned to achieve desired characteristics, and optimisation of the process variables was studied using the Box Behnken design (Sharma et al. 2020). This study highlighted the effects of current density, pH/H_2O_2 dosage and process time in removing COD, total organic carbon and dissolved organic carbon. The optimised condition for the electrocoagulation process was found to occur at 6.07 pH, and a current density of 5.69 mA/cm^{-2} was applied for 18 min.

Modeling the process behavior and optimising the conditions were studied to treat petroleum industry aqueous effluent by Fe/Zn nanoparticles using RSM tools (Moghadam and Qaderi 2019). In this research, the critical point for the parameters phenol initial concentration, light source power, retention time, pH and the nanocatalysts concentration was estimated using RSM. The maximum removal of phenol 89% was found to occur at 5.23 pH, power of light equal to 43.53 W, feed phenol concentration of 50 ppm, 1.57 gm/lit nano concentration and process time of 58.6 min.

RSM was used to model and analyse the process for the treatment of cutting oil wastewater (Popović et al. 2019). The independent variables optimised were the twisted tape aspect ratio and cross flow rate. The effects of varying the input variables were analysed by following the change in numerical values of the variable flux and specific energy consumption. The developed model equation concludes that the linear influence of aspect ratio and cross flow rate had a synergistic effect on the response flux. It was observed from the variable analysis that the aspect ratio's squared effect has statistical significance in process optimisation. The process modeling concept is also used in the treatment of textile dye wastewater in the packed-bed reactor (Devi et al. 2015), in the treatment of textile dye by adsorbing on organoclay using an artificial neural network (Elemen et al. 2012) and for the kinetic analysis of textile wastewater treatment using hybrid column upflow anaerobic fixed bed reactor (Sandhya and Swaminathan 2006).

7 Optimisation of the Process

The optimisation is a mathematical tool to identify the most economical design for a process and predict the efficient solution to a problem. In industrial processes, this approach is one of the major quantitative tools for decision making. The optimisation problem consists of three essential categories: the objective function to be optimised, equality constraints, and inequality constraints. The set of variables that satisfy equality and inequality constraints are called feasible solutions, whereas an optimal solution is defined as a set of values of process variables that satisfy both constraints. The method of solving the objective function depends on characteristics of the objective function, nature of the constraints and the number of dependent and independent variables involved in the development of process model equations.

8 Concept of Optimisation

The optimisation is the method of acquiring the supreme outcome for a given constraint. In the design, construction, operation and maintenance of any industrial process, engineers and scientists have to make crucial technical and managerial decisions at various stages. The utmost aim of all such decisions is to minimise the efforts, energy consumption, or maximise the desired output. Optimising a process or a system requires the following basic elements: An objective function is an indicator for quantitative performance measurer which should be either maximised or minimised. The system's behaviour is described by the predictive model, which is transformed to simultaneous equations and inequalities called constraints. The predictive model equations contain the variables that must be adjusted to satisfy the constraint equations. The optimisation algorithm is the major tool for process synthesis, process analysis, design and retrofit. It is also useful for real time optimisation, scheduling and planning a process and process integration and intensification.

9 Methods for Optimisation

The optimisation of model equations is done either by analytical method, numerical method, or graphical method. For the function of a single variable, a test based on the second derivative is used to find the maxima or minima values. The single variable function is differentiated with respect to the independent variable, and the first order derivative is equated to zero. The solution of this equation gives the critical point or stationary point of the function. At this point to the curve, the tangent line's slope is zero because the tangent would appear as a straight line parallel to the horizontal axis. The first derivative is differentiated again to give the second derivative. The magnitude of the second derivative is evaluated at a critical point. If the second derivative is negative, then the function is maximised at the critical point or otherwise, if the second derivative yields a positive quantity at a critical point, then the function attains the minimum at the stationary point. The other methods, namely scanning and bracketing procedure, Newton method and Quasi-Newton methods, are followed for optimising single variable functions.

Newton's method uses a quadratic model equation as equivalent to a given function for minimisation. If the objective function is quadratic in nature, then the minimum is obtained in one iteration. This method converges slowly when the value of the second derivative approaches zero. The quasi-Newton method finds the points that give the first derivative of the function f(x) are of opposite sign. This approach for predicting the functions with opposite signs is called the "regula falsi" method or false position. The quadratic interpolation method is a type of uni-dimensional minimisation technique using function values only. This method is based on equating the actual objective function to a quadratic equation and is more efficient than other methods if the first derivative is continuous. In the cubic interpolation method, the actual function is approximated as a third degree polynomial, and then the stationary point of the polynomial is calculated after differentiating it once and equating the resulting expression to zero. To estimate the maximum or minimum, either four values of the function or two function values and two derivative values are required.

The multivariable functions are frequently encountered in modeling a process by RSM. These functions are subjected to constraints or may not be constraint dependent. The methods that are used to optimise a multivariable function are the grid search method, Simplex search method, steepest descent method, conjugate gradient method etc. In the wastewater treatment domain, the proposed model equations are mostly quadratic. The Eigenvalues of the Hessian matrix are calculated to interpret the nature of function at a stationary point. The shape of the contour curve and Eigenvalue relations are used to examine the nature of the multivariable function. If the Eigenvalues of the Hessian matrix is equal, then the shape of contours are circles, whereas elliptical contours are formed for well-behaved functions. The necessary and sufficient conditions for optimising a multivariable second order quadratic function is that: the function is differentiable twice at a critical point, the gradient (slope) of the function is zero at the stationary point, and the Hessian matrix is positive-definite for a minimum to exist and becomes a negative-definite for a maximum to exist.

10 Recent Development and Future Scope

RSM is one of the conventional methods to develop the model equations and optimise the process variables in the textile wastewater treatment process. The scientific community has explored the applications of artificial neural networks and genetic algorithm to process modeling and parameter optimisation. The model equations are also developed using multiple linear regression techniques, and the variables are optimised using an imperialist competitive algorithm. The artificial neural network model based on utilising Levenberg–Marquardt algorithm composed of the linear transfer function is also used in the adsorption treatment of textile effluents. The wastewater treatment plants performance is also evaluated using a black-box modeling approach based on artificial neutral networking. The influent characteristics of the textile treatment plant are modeled with different meta-heuristic algorithms using a fuzzy interference system. The model prediction accuracy and sensitivity is improved by incorporating more terms and coefficients in the equation. In future, the development of advanced software modules, algorithm codes, artificial intelligence systems and machine learning tools would improve the quality of model equations and minimise the efforts to get the desired solution.

11 Conclusions

The textile industry utilised a large volume of water and is considered a water intensive unit. A large quantity of different waste characteristics is generated from the textile processing unit. Identifying a suitable treatment strategy is difficult because of the complicated nature of the wastewater produced. Dye compounds are considered the major pollutants in textile wastewater. The characteristics of effluents have detrimental effects on the environmental components because they decrease the oxygen solubility level in water bodies, prevent light penetration into the aquatic ecosystem and disturb the photochemical activity in water bodies. The volatile chemicals are easily evaporated and absorbed by cells, affecting normal biological activities such as respiration, osmoregulation, and reproduction. The partially treated effluent or the raw effluent without any treatment adversely affect the natural ecosystem and is responsible for chronic and acute health implications.

Various treatment techniques, namely adsorption, coagulation, ozonation, electrochemical degradation, membrane separation and ultra-filtration, are used to remove the pollutants from textile wastewater. The treatment techniques are broadly classified into biological, chemical and physical methods. Biological treatment is cheaper than chemical and physical methods because the microorganisms are easily available and are cost-effective. An integrated design approach is the need of the hour for the efficient operation of the wastewater treatment unit. The process equipment is designed using the Physico-chemical characteristics of raw textile wastewater. The kinetic study is essential because the rate equation elucidates the rate of pollutant degradation. Process modeling aims to represent the interrelationship between the process variables and parameters by means of mathematical expression. The response surface method is used to develop a process model and calculate the optimised process conditions. The optimisation conditions are evaluated using a contour plot, 3-D response surface plot. The quality of the models is adjudged by the statistical significance of the parameters in the ANOVA table and coefficient of determination. The optimisation is done to predict the best set of independent variables to produce the desired optimum response for the developed model equation. The efficiency of the treatment process depends on selecting the major process variables, developing the model equation that truly reflects the system characteristics, analysing the interactive effects between the variables and selecting the optimised conditions for the process. The modeling of the wastewater treatment plant is important to understand the process behaviour and modify the process equipment configuration.

Conflict of Interest The authors declare no conflict of interest.

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