A Study on removal of Methylene Blue dye by photo catalysis integrated with nanofiltration using statistical and experimental approaches

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Abstract

In this work, the removal of Methylene Blue dye from the synthetic textile effluent has been investigated using a hybrid system (photocatalysis and nanofiltration). The Commercial ZnO powder was used as a catalyst in the photocatalytic operation. Response surface methodology (RSM) was employed to optimize the various operating parameters such as pH, catalyst loading and time duration and this optimization has enhanced the decolorization efficiencies. The results were compared and contrasted with the individual as well as the combined systems at optimized conditions. The results indicate that the photocatalysis process alone has resulted in 33% of dye decolorization and 26.5% of total organic carbon (TOC) removal, while the individual ceramic nanofiltration system has yielded 43% of decolorization and 35.03% TOC removal. About 94% of the dye were decolorized, and 70% of TOC was removed in 94.23 minutes of operation by the hybrid system at optimized initial operating conditions.

Keywords:

Photocatalysis, Nanofiltration, Wastewater treatment, TOC removal, Decolorization, Hybrid system.

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1. Introduction

Photocatalytic oxidation has been being studied well for many decades as it is an advanced oxidation technology for reducing water pollution. Photocatalysis oxidizes and degrades various recalcitrant organic and inorganic pollutants present in the aqueous media, and it was investigated over a wide range of non-biodegradable organic pollutants for degradation and converting into less harmful intermediates. Due to its various advantages, photocatalytic reactors are in utilization on pilot or commercial scale for purification of recalcitrant industrial wastewaters [1–4]. Photocatalysis is classified into two distinct ways namely; homogenous and heterogeneous. In homogeneous photocatalysis, the catalyst will be in homogenous state and hence it is difficult to retrieve the catalyst after the water treatment. Whereas, it is easy to separate and reuse the catalyst in case of heterogeneous photocatalysis due to suspended or immobilized form. Saikia et al.[5] synthesized different morphologies of ZnO nanomaterials by distinct methods. The activity of the synthesized catalysts like flower-shaped homocentric pencil-like ZnO nanorod bundles and ZnO nanoparticles were investigated under solar light. They found that these nanomaterials exhibit excellent photocatalytic degradation of malachite green dye. El-Kemary et al. [6] have synthesized nanostructured ZnO semiconductor with 2.1 nm diameter by employing chemical precipitation process. The synthesized ZnO nanoparticles have been used for the ciprofloxacin drug degradation in aqueous solutions at distinct pH values under UV light irradiation. They found that pH 7.0 and 10.0 had shown effective photocatalytic property for the degradation of ciprofloxacin, whereas ineffective at pH 4.0. After 60 min of operation, maximum degradation efficiency (50%) of the drug was noticed at pH 10.0. Photo degradation in combination with membrane methods may have a better pollutant removal efficiency due to its retaining capacity towards the pollutants.

The larger size of organic pollutants in wastewater can reinstate by microspores that are present in the membrane. Generally, the membrane-based separation has compact in footprint, consumes lower energy for separation and easy operation [5]. The concentration polarization of retentate organic pollutants onto the membrane surface due to adsorption and precipitation generally results in fouling and reduces the efficiency of membrane separation [7-8]. This is the very common phenomenon observed in the case of both polymeric and ceramic membranes. Few researchers have confirmed that fouling issue results in the reduction in the membrane processes by combining advanced oxidation process with

membrane separation [9][10]. The ceramic membrane rejects the degraded pollutants through partial oxidation along with the photocatalyst.

Cui et al.[11] studied the hybrid system (Photocatalysis and membrane separation) for the treatment of wastewater. In this work, the authors have reported that the combination of photocatalysis with the membrane-based filtration on a single set of unit shows many advantages in terms of lower footprint, maintenance, investment etc.[12]. TiO_2 deposited on the surface of the membrane, and its membrane pores lead to the membrane fouling. It was observed that in combined technique of photocatalysis and membrane filtration system developed by Yang et al and Rajeswari et al.[13], the TiO_2 photocatalyst has been in the suspended form, and they have studied the removal of carbaryl, a carbamate pesticide using ozonation (O_3), photolytic ozonation (O_3/UV), and photocatalysis (TiO_2/UV). They observed that Photocatalysis combined with ozonation process ($\text{TiO}_2/\text{UV}/\text{O}_3$) resulted 92% of chemical oxygen demand (COD) reduction at pH 6.0 with 0.28 g/h of ozone and 1 g/L of TiO_2 in 180 min.

Few studies are available on fouling in membrane filtration as well as the possible measures for the prevention of fouling. Zahrim et al.[14] have published a review on the wastewater treatment using combination of coagulation and nanofiltration. In this work, the authors had observed minimal membrane fouling, drastic reduction in COD and color when the flocculent aid was added before the operation. Damodar et al.[15] have investigated purging of reactive black 5 (RB5) dye from aqueous media using microfiltration membrane [polytetrafluoroethylene (PTFE) MF membrane module] with a lab-scale photocatalytic slurry reactor. Their studies have shown that with combined approach 82–100% decolorization, 45–93% TOC removal, and 50–85% of COD removal was achieved. Damszel et al.[16] have studied Photocatalysis with immobilized catalyst bed/Nanofiltration and photocatalysis in suspension/UF/MD for the separation of azo dyes such as acid red 18, direct green 99 and acid yellow 36 from aqueous stream. Berberidou et al.[17] used combined system of photocatalysis and reverse osmosis filtration/nanofiltration to achieve a complete decolorization of reactive black 5 from synthetic dye effluent. They concluded that the organic content was reduced to more than 95% and the salinity can be obtained using the proposed hybrid system. Mozia et al.[18] have studied decolorization of acid red 18 dyes from aqueous media using two-hybrid approaches such as photocatalysis, ultrafiltration and photocatalytic membrane distillation. Among different photocatalysts, zinc oxide (ZnO) is widely used as an excellent photocatalytic material for the purification of various wastewater since it exhibits high photocatalytic performance [19–23] in comparison to other metal oxides

including TiO_2 [24][25]. Hence, in this work ZnO was used as a photocatalyst for the decolorization and degradation of MB dye.

Experimental design methods are very much convenient and can be used to optimize the initial operating parameters. One such important experimental design method is the Response Surface Methodology (RSM). The RSM's major purpose is to optimize the response surface of the initial inputs. It investigates the connection between various input variables and output variables. Several steps are involved in RSM's design mechanism. It includes a) Conducting set of experiments for a good response of interest. b) Development of second-order mathematical model c) Estimation of favorable initial parameters with the least and the most output value of the conducted experimental data and d) Representation of operating conditions in two and three-dimensional graphs. RSM can be used to determine the interaction, quadratic and the linear effects of the parameters and also for the response of a predictive model [26][27].

The present work explores the efficiency of the combined operation of photocatalytic oxidation and nanofiltration for the decolorization and degradation of MB dye. As many of the works have dealt with the use of polymeric MF membranes in conjunction with photocatalysis, this work made an important contribution towards the combined operation of photocatalysis and ceramic nanofiltration membranes. The individual and the combined effect of photocatalysis and nanofiltration processes were assessed for different ZnO and MB dye concentrations. To the best of our awareness, no such research is investigated so far in the literature for the decolorization and degradation of the MB dye from aqueous media.

2. Materials and Method

2.1 Materials

Methylene Blue dye ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) and Zinc oxide (ZnO) photocatalyst were procured from M/s Sisco Research Laboratories Pvt. Ltd. Maharashtra, India. Sulfuric acid (98%) and NaOH pellets were purchased from M/s SD Fine Chemicals Ltd., Mumbai, India. All the chemicals used in this research work are analytical grade. Except for NaOH and H_2SO_4 all other chemicals were utilized as collected from the provisioner.

2.2 Experimental set-up and Methodology

The schematics of the integrated system exercised in this work for decolorization and degradation of MB dye from aqueous media is shown in Fig. 1. A feed tank of 10 L volume was mounted with a 250 W UV light from the top.

Fig.1 Experimental setup of the hybrid system

The stainless steel (SS-316) was used for the construction of photocatalytic reactor, and it was provided with a cooling jacket to keep the temperature constant inside the reactor. Centrifugal pumps of 0.87 HP were connected at the rear side of the setup to pump wastewater through the nanofiltration unit. The commercial tubular ceramic membrane module procured from M/s TAMI Industries was used for the typical experiments. The tubular ceramic membrane consists of single or multi-channels with a titanium oxide active layer on the tube side surface.

Table 1: Technical Parameters

Parameter	Semi pilot installation
Configuration	Tubular
Membrane material	Titanium oxide
Effective surface area (m ²)	0.3
Number of Channels	3
Internal channel diameter (mm)	3.5
External membrane diameter (mm)	10
Membrane length(mm)	600

The typical specifications of the commercial ceramic membrane module used in this study are given in Table 1. Control valves, Rota meter and Pressure gauges were arranged at desired locations between the reactor and nanofiltration unit to adjust and support the required flow rates and pressures. For the higher efficiency and enhancement in the degradation and

decolorization of dye, the retentate from the nanofiltration unit was reprocessed to the feed tank. The permeate was fetched in test tubes at every 15 minutes of time interval.

In the course of filtration, the permeate and retentate samples were regularly collected for every 15 min and analyzed for dye concentration in both permeate and Retentate. The permeate volume flux (J) is determined using the following equation (1):

$$J = \frac{V}{t.A} \text{ m}^3/\text{m}^2 \text{ day} \quad (1)$$

Where,

V = Permeate volume (m³)

t = time (day)

A = effective membrane area (m²)

The percentage rejection of dye by nanofiltration unit was determined using equation (2).

$$\text{Dye rejection (\%)} = \frac{C_r - C_p}{C_r} * 100 \quad (2)$$

Where,

C_r = concentration of dye (g/m³) in retentate

C_p = concentration of dye (g/m³) in permeate

2.3 Optimization of process parameters

RSM is a convenient experimental design method which benefits in systematic resource utilization. RSM has enormous advantages, and this design technique can be used to develop, improve and optimize experimental parameters. RSM design models used in the evaluation of integrated system of Photocatalysis with nanofiltration resulted in fewer resources utilization and better outputs.

Table 2: CCD matrix with low and high values

Factor	Range	Response (R1)
Catalyst loading (A)	0.1 g/L – 0.3 g/L	% MB Dye Decolourization
pH (B)	3 - 7	
Time (C)	80 - 100	

In this study, the central composite design (CCD) technique of RSM has been adapted for the optimization of operating parameters of photocatalysis combined with nanofiltration. Several experiments were conducted in different combinations that are generated by CCD matrix. The

operating parameters optimized are; Catalyst loading - A (g/L), pH –B and Time - C (Min) [28][29]. The initial factors, their ranges and the response are mentioned in Table 2.

2.4 Characterization and Analysis

The commercial ZnO powder was characterized using X-Ray Diffraction (XPRT-PRO) and particle size distribution analyzer (Malvern zeta sizer Instrument) to confirm the crystalline nature and particle size of photocatalyst. For identifying the decolorization of MB dye in aqueous media, UV-Vis Spectrophotometer (Evolution 300 supplied by Thermo scientific, UK) was utilized. The maximum absorbance ($\lambda_{\max}$) of MB dye is 663 nm. The standard calibration chart was prepared and used for the identification of concentration of permeate collected at different time intervals. TOC analyzer (TOC LCPN analyzer, Shimadzu, Japan) was employed to determine mineralization of organic carbon in aqueous media.

3. Results and discussion

3.1 Inlet operating pressure and its effect on permeate flux

Fig.2 Inlet pressure and its effect on permeate flux in the hybrid system

Due to the diffusion model, the flux through the membrane is likely to increase with an increase in inlet pressure. An appropriate driving force is necessary to overcome the membrane surface fouling and membrane resistance. With the increase in feed pressure, the appropriate driving force can be obtained. The impact of inlet pressure on nanofiltration for the dye eviction demonstrates proportional relationship to flux and pressure. The impact of distinct inlet pressures to the nanofiltration for dye removal is shown in Fig.2.

From the results, it was observed that the permeate flux of membrane increases with respect to the increase in the inlet pressure from 2 to 4 bars. However, with the progress of operation, the flux through the nanofiltration was reduced from 1.66 to 1.43, 1.86 to 1.54, and 2.08 to 1.7 l/m².min at 2, 3, and 4 bars respectively over 90 min of operation. The reduction in flux across the membrane could be due to concentration polarization or fouling of organic pollutants on the membrane surface. From the obtained results, it was identified that 4 bar inlet pressure had shown higher permeate flux across the membrane among different inlet pressures.

The polarization of organic contaminants on the membrane surface might be the reason for the decline of flux. In this study, at 4 bar greater flux values were observed [30–38].

3.2 Catalyst loading and its effect on dye decolorization and degradation

The effect of catalyst loading on the dismissal of MB dye was studied by varying the dosage of ZnO catalyst in the photocatalytic reactor. In the typical experiments, the photocatalytic reactor was charged with 5 L of MB dye wastewater containing 500 mg/L of concentration. Dye removal studies were carried out using hybrid system at 4 bar inlet pressure and various catalyst dosages such as 0.1, 0.2, 0.5 and 1.0 g/L.

Fig.3(a). Effect of catalyst loading on dye removal in hybrid system [Initial concentration = 500 mg/L, 4 bar inlet pressure]. 3(b). Percentage decolorization of MB dye in hybrid system at different catalyst loadings [Initial concentration=500 mg/L, 4 bar inlet pressure]

The operating temperature of the hybrid system was kept constant at 25 °C. From the results, it was identified that the 0.2 g/L of ZnO catalyst possesses the maximum photocatalytic activity towards mineralization and decolorization of MB dye in aqueous media. Around 80% of

decolorization of MB dye was achieved by integrating the process of photocatalysis with nanofiltration. The effect of dosage of ZnO catalyst for decolorization and the percentage reduction of MB dye is shown in Fig.3a and Fig.3b, respectively.

From the achieved results, it was observed that 0.1, 0.2, 0.5, and 1.0 g/L of the catalyst dosage had resulted in 76, 80, 28, and 14% of dye decolorization respectively in the combined system. Catalyst dosage beyond 0.2 g/L has shown lower dye decolorization. This effect might be due to aggregation of catalyst particles at excess loading which shows that the adsorption of dye molecules decreases due to the depletion of total available active sites on the catalyst surface. Moreover, the higher loading of catalyst resulted in high turbidity of wastewater that minimizes the transmittance of light across wastewater during irradiation. This ultimately deactivates the active catalyst molecules by smashing with ground-state molecules [32]. This study concludes that 0.2 g/L ZnO dosage is sufficient to attain better decolorization of MB dye using hybrid system. Therefore, 0.2 g/L of ZnO catalyst was observed as optimal catalyst dosage for MB dye removal and further studies were carried out at this optimized catalyst dosage.

Pair of holes and electrons will be generated in the valence and conduction band when the electrons present in the ZnO valence band exhilarates upon irradiation of ZnO surface by the UV light. A positive hole (h^+) and negative electron (e^-) pair were generated because of the elevation of electron to the ZnO conduction band by the surplus energy of the exhilarated electron. The neighbouring water molecules get absorbed by the h^+ and split them to form the H_2 radicals and gas. A superoxide anion (O_2^-) will be formed when the O_2 molecules react with the e^- and h^+ of ZnO. Sequence of reactions are commenced on the ZnO surface because of the periodic production of hydroxyl radicals [39]. The adsorbed H_2O and OH reacts with the holes to form the hydroxyl radicals.

The OH radicals production will be lowered if the dye ions substitute the adsorbed OH radicals. The catalyst required for the degradation increases with the increase in initial dye concentration. In this study, on increasing the concentration of the dye, the O_2^- and OH radicals were decreased because of the constant quantity of the catalyst and the illumination time. This proves the decrease in efficiency of the photocatalytic degradation [39].

3.3 Effect of initial pH

Different initial pH ranging from pH 1.0 to pH 10.0 was studied for decolorization of MB dye and removal of TOC using hybrid system. The pH of wastewater was adjusted by using

diluted NaOH and H₂SO₄. The primary dye concentration and ZnO catalyst dosage were fixed as 500 mg/L and 0.2 g/L discretely for all the pH experiments.

Fig.4(a). Effect of initial pH of dye solution on the removal of MB dye in hybrid system [Initial concentration=500 mg/L, Catalyst loading = 0.2 g/L]. 4(b). Percentage decolorization of MB dye in hybrid system at various pH values [Initial concentration=500 mg/L, Catalyst loading = 0.2 g/L]

Fig. 4a depicts the effect of different solution pH on dye decolorization in the integrated process. It was observed that decolorization of MB dye was achieved up to 69, 85.98, 94, 87.5, and 75.6 % at pH 1, 3, 5, 7, and 10 respectively in the combined process of photocatalysis and nanofiltration. From Fig.4b, it was noticed that with an escalation in pH to 5, the decolorization of dye had been increased gradually, whereas decolorization and mineralization rate of organic carbon has been decreased after pH 5. From the obtained results, it has been found that pH 5.0 is an optimum value to achieve desired results. This could be due to adsorption of MB dye on the catalyst surface which is reliant on its surface charge. At pH 5, the ZnO surface might be negatively charged due to generation of massive hydroxyl radicals, which simplifies the adsorption of MB dye and also its self-sensitized breakdown [33].

Moreover, the solution pH>5 could have imparted negative charge to ZnO surface, consequently inhibiting dye degradation by lower adsorption of dye molecules onto ZnO surface. It was reported that production of hydroxyl radical was favored at high pH [25]. However, the hydroxyl ions can also be generated by lurking the photogenerated holes on the surface of ZnO particles. These hydroxyl ions compete with direct oxidative breakdown of dye by holes in the valence band of ZnO.

ZnO liquefies in basic as well as acidic medium because of its amphoteric nature. Mosaic like structures namely $[\text{Zn}(\text{OH})_4]^{2-}$ are formed by ZnO in alkaline pH and corresponding salts in acidic pH. Because of the photo dissolution and dissolution, ZnO exhibits less reactivity. The hydroxyl radical production is also considered as the pH function [35–38]. The development of hydroxyl radicals, dye molecule detachment and ZnO surface properties are affected by the pH [40]. Akyol et al. [41] has reported the ZnO's zero point charge (zpc) as 6 ± 0.3 . Because of the adsorbed OH^- ions, the ZnO surface is negatively charged above pH 6 and below this, it is positively charged. The $\text{OH}^\bullet$ radicals development is more supportive when huge amounts of OH^- ions are present in the reaction medium as well as on the surface of the particle. Under pH 6, the decolourization as well as the process efficiency increases.

Baslak et al. [42] by employing quantum dots (QDs) cellulose membrane and CdTeSe investigated the Rhodamine-B (RB) transportation mechanism. At high pH, the QDs and CdTeSe were expedited to transfer the RB in to stripping phase. The study has revealed that the feed phase pH should be more than the pH of the stripping phase and pH 12 is regarded as the optimum pH for the utmost RB transportation. RB–QDs complex were developed, RB subsisted as ionic form and CdTeSe QDs were deprotonated at these conditions. The dissimilarities between the pH of feeding and stripping phases is the reason for the driving force of diffusion of RB ions.

3.4 Effect of initial Dye concentration

The decolorization of MB dye in the hybrid system was investigated by altering initial dye concentration between 250 and 1000 mg/L, and the catalyst loading was kept constant as 0.2 g/L. The samples collected at regular time intervals from the permeate were tested under UV absorbance to calculate the percentage decolorization. From the results, it was identified that rise in dye concentration led to minimal decolorization. Fig.5a and 5b depict the effect of primary concentration of MB dye on the performance of hybrid system. The decrease in the dye decolorization at higher initial concentrations is due to lower reactivity of hydroxyl radicals. The other rationale might be enhancing the filter impact of dye in the blend [24]. It was perceived that the efficiency of the process was increased at higher initial concentrations with regard to complete amount of dye eviction. The initial dye concentrations used in this work are 250, 500, 750, and 1000 mg/L and these concentrations have shown decolorization about 95.68, 93.12, 88, and 83.96%, respectively.

Fig.5(a). The Effect of initial dye concentration in the hybrid system [Catalyst loading = 0.2 g/L, pH=5]. 5(b). Effect of initial dye concentration on percentage decolorization of MB dye in hybrid system [Initial concentration=500 mg/L, catalyst loading = 0.2 g/L]

From the experimental outcomes it was noticed that the decolourization of dye declined with the escalation of dye concentration. The constant illumination time and light intensity, and catalyst surface are the rationale for this decline. Based on the surface given by the catalyst, the dye has been adsorbed on its surface. The O_2^- and OH which were developed on the photocatalyst surface were also persistent. Due to this reason, when the dye concentration enhances, the strength of the O_2^- and OH declines, which eventually leads to decrease in photo-degradation efficiency. As the active sites are protected by the dye ions, at high dye concentrations the OH⁻ radicals generation on the catalyst surface is reduced [32–38].

4. Model Development, Regression analysis and optimization through RSM

In the past few decades, many researchers have focused their efforts in the field of optimization of wastewater treatment technologies using various models. However, RSM methodology was shown to be an effective optimization model for the operating parameters. Wang et al. [43] applied the response surface process (RSM) to optimise the initial parameters such as pH, flocculent and coagulant dosage for the treatment of paper recycling wastewater. The confirmation experiments have revealed the RSM as the best suitable method for the optimization of initial parameters of coagulation–flocculation process. Moghaddam et al. [44] examined the functioning of $FeCl_3$ sludge for the acid red 119 (AR119) dye removal. The three operating variables such as initial dye concentration, coagulant dosage and initial pH of coagulation/flocculation process were optimised by using response surface methodology (RSM). 96.53% of dye removal was observed in this experimental study, and this was very close to the RSM results. This study has concluded

that, for the optimization of operating variables of coagulation/flocculation process, the RSM is considered as a cogent tool. Salahi A et al. [45] worked on the oily wastewater treatment in a desalter plant by using a 10 nm nominal pore size nano-porous membrane (PAN) sheet. The initial operating variables such as pH, cross-flow velocity (CFV), salt concentration, feed temperature, and trans-membrane pressure (TMP) were optimized by employing response surface methodology (RSM). The experimental results are likewise to the RSM results. Hence it was mentioned that the RSM as an efficient method for the optimization process which reduces capital and saves time. Yuliwati E et al. [46] studied the impact of operating parameters on the treatment of refinery wastewater in submerged ultrafiltration. In this study, various parameters including pH, mixed liquor suspended solids (MLSS) concentration, hydraulic retention time (HRT), air bubble flow rate (ABFR) were optimized by using response surface methodology (RSM). From the obtained results it was observed that the application of RSM had surpassed the removal of COD and water flux.

In this study, ANOVA for Response Surface Quadratic Model was used to design and analyse the operating parameters for the MB dye degradation using photocatalysis and nanofiltration.

Three factors CCD matrices were designed for this work. Final Equation in Terms of Coded Factors:

$$\% \text{ MB dye decolourization} = 94.08 - 0.16A + 1.20B + 2.04C + 0.090AB + 0.81AC + 0.55BC - 6.54A^2 - 7.41B^2 - 0.64C^2 \quad (3)$$

From the results, it was noticed that the experimental and predicted values are in good agreement with each other. The mutuality between the predicted and the experimental data was quantitatively assessed by the R^2 value. The generated equation (3) was used to compare the predicted and experimental data. From the mathematical model it was observed that the experimental results were effectively agreed with the correlation coefficient ($R^2=0.9898$). From the model it is also observed that the adjusted R^2 ($\text{Adj-}R^2=0.9806$) value was near to that of the R^2 value and it is also in a good fit.

The ANOVA for Response surface quadratic model was performed and included in table 3. The Predicted responses were in good agreement with the experimental outcomes. In the ANOVA test, the model variance can be compared with the residual variance using the F-test. The lack of fit is known to be notable if $\text{Prob}>F$ -value. F Value in this test is 107.61 with a parallel p-value of < 0.0001 indicating A, B and C are significant models. The R^2 values in this test were preferable because of a good fit of the model [47].

Table 3: ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	898.64	9	99.85	107.61	< 0.0001
A-Catalyst Loading	0.26	1	0.26	0.28	0.6086
B-pH	14.47	1	14.47	15.60	0.0027
C-Time	41.53	1	41.53	44.76	<0.0001
AB	0.065	1	0.65	0.070	0.7969
AC	5.22	1	5.22	5.62	0.0392
BC	2.44	1	2.44	2.63	0.1358
A²	117.56	1	117.56	126.70	<0.0001
B²	150.92	1	150.92	162.66	<0.0001
C²	1.14	1	1.14	1.23	0.2941
Residual	9.28	10	0.93		
Lack of Fit	7.32	5	1.46	3.73	0.0875
Pure Error	1.96	5	0.39		
Cor Total	907.92	19

Fig. 6(a) Normal plot of Residuals, (b) Residuals vs Predicted

Besides R^2 , the effectiveness of the models was also analyzed using residuals. The normality of the residuals can be determined by using normal probability plots. The residuals present in the above Fig. (6a) were represented against the anticipated value. Feasible results can be observed in Fig.6b.

The purpose of this work is to generate the optimized input operating parameter values for the textile dye wastewater treatment using photocatalysis combined with the ceramic

nanofiltration system. Experimental design models were employed to optimize the input operating factors. The desirable values of the process variables for the utmost decolorization ability were found to be 0.2 g/L, 5.26, 94.23 for catalyst loading (A), pH (B) and Time (C) respectively. At these optimum values, the predicted and observed MB dye % color removal was 94.8752 and 94%, respectively.

Fig. 7: Response surface plot showing mutual interactions between the input parameters to enhance % CV decolorization. 7(a) pH Vs catalyst loading, 7(c) Time Vs catalyst loading, 7(e) Time Vs pH and 7(b)(d)(f) are contour plots

Fig 8: CCD Matrix

Figures 7 and 8 explain the response surfaces, contours and the CCD matrix developed for the optimization of operating parameters for dye decolorization using combined system.

The maximum decolorization was achieved when the experiments were conducted at the obtained optimum values. This can be concluded as the best approach for the effective MB dye decolorization using optimized operating parameters designed in the RSM experimental model. Hence this study is termed as successful.

5. Comparison of individual and combined systems

Individual operations were executed to explore the effect of various operating conditions on decolorization of MB dye. Initially, the equilibrium adsorption for ZnO catalyst was accessed before further experiments.

Fig.9 (a) Effect of initial concentration of dye in hybrid system [Catalyst loading = 0.2 g/L, pH=5.26, Time 94.23 min]. 9(b). Effect of the initial concentration of dye on Percentage decolorization of MB dye in hybrid system

For this, initially, 0.2 g/L of catalyst was supplemented to 1.0 L of MB dye solution. The solution was further blended using a magnetic stirrer in an unilluminated space to avoid passage of light. The above procedure was continued until the equilibrium adsorption was achieved. Within 60 min, 0.2 g/L of ZnO reached the equilibrium state by adsorbing and degrading 90% of MB dye approximately. The effect of ZnO dosage on nanofiltration performance for the removal of dye was studied at optimized parameters such as 0.2 g/L of ZnO and pH 5.26. Nanofiltration experiments were carried with 5 L of 500 mg/L of dye mixture. By using a centrifugal pump of 0.87 HP, the feed was pumped into the ceramic nanofiltration membrane at the desired pressure.

The pressure and the desired flow rate were adjusted using the manual control valve fixed in the main line. Alternatively, a circumvent line was provided to maintain the desired pressure at the inlet of the membrane. The influence of inlet pressure on the nanofiltration alone was also studied for the removal of MB dye at inlet pressures ranged from 2 to 4 bars. The performance of integrated nanofiltration and photocatalysis on dye reclamation was carried out with optimized operating factors; 0.2 g/L of ZnO dosage and pH 5.26. It was perceived that the integration of photocatalysis with nanofiltration process shows 94% decolorization of MB dye. It was also noted that the hybrid system had shown the synergistic effect by the integration of photocatalysis with nanofiltration, as compared to individual operations. Fig.9a and 9b illustrate the effect of individual and combined systems on removal of MB dye. Moradi et al. [48] were attempted with commercial nanofiltration membrane to treat the textile wastewater for reuse. In this work, the central composite face-centred technique of RSM methodology was used to design and optimize experimental conditions including pH (3–9), pressure (3–6 bar), and dye concentration (10–50 mg/l). From this study, it was concluded that large amount of dye rejection and clear water was attained in the permeate flux under acidic and alkaline conditions. The authors have concluded that the RSM design was efficient approach for optimizing the experimental conditions and attaining the desired outcomes. Askari et al. [49] worked on treatment of textile wastewater by employing thin-film composite Nanofiltration (NF) membrane. Box-Behnken design of RSM method was employed to analyse the optimum operating conditions of the experiment including pressure, pH and dye concentration. At primary dye concentration of 180 mg/L and pH 10 showed 92% of acid blue 25 and 91% of disperse red 73 were removed. At primary dye concentration of 40 mg/L and pH 3, 86% of MB dye was removed.

In addition to MB dye decolorization, Total organic carbon (TOC) was also analyzed and observed that 70% of TOC was removed at optimum loading parameters. Fig.10 shows the percentage removal of TOC in various systems.

Fig.10. Percentage removal TOC of MB dye in various systems [Initial concentration=500 mg/L, Catalyst loading = 0.2 g/L, pH=5.26, Time 94.23 min]

Mortazavian et al. [50] worked on the breakdown of Acid Red 88 (AR 88) and Acid Blue 113 (AB 113) textile wastewater by employing TiO_2 based photocatalytic process. In this study, the experiments were designed and optimized by using Response surface methodology (RSM). The importance of experimental parameters like initial dye concentration and pH medium were determined by employing the analysis of variance (ANOVA). From the obtained experimental outcomes, it was perceived that dye concentration and its pH had drastic effect on AR 88 (99.6%) and AB 113 (98.7%) degradation. Abdullah et al. [51] studied the Methylene blue (MB) dye degradation by employing Visible-light active (BiVO_4) photocatalyst. In this study, authors have studied and optimized distinct operating parameters such as pH, concentration of dye and mass loading. Response surface modelling was employed as an experimental design and optimization methodology for the MB dye removal. The quadratic model which was developed using this technique shows a functional relationship between the experimental parameters and MB dye removal. 67.21% of MB dye removal was observed from the optimized experimental results.

The efficiency of the individual systems collated with the integrated process was represented by the synergetic index. The TOC removal by the individual as well as the combined hybrid

systems were explained in detail in the fig. 10. The synergetic effect was assessed by using this data.

The synergetic index (SI) plays a crucial part in the investigation of photocatalysis during the membrane filtration process. This synergetic index (SI) is determined by the following equation:

$$\begin{aligned}
 SI_{(PC+CM)} &= \frac{[\% \text{ TOC removal}]_{(PC+CM)}}{[\% \text{ TOC removal}]_{(PC)} + [\% \text{ TOC removal}]_{(CM)}} \quad (4) \\
 &= \frac{70}{26.5 + 35.03} \\
 &= 1.13
 \end{aligned}$$

The obtained result was more than 1 and it indicate the contaminant removal was higher in the integrated process than the removal observed in the individual systems together. The above obtained SI value expresses a notable synergy effect. Hence, it can be concluded that the combined hybrid technology is more efficient for the wastewater treatment than the individual systems.

6. Kinetic studies of MB dye decolorization

Fig 11. Pseudo-first-order decolorization of MB dye

During the Photocatalysis process, the OH radicals are generated, and these eventually degrade the organic pollutants present in the feed. These OH radicals are highly oxidative and readily react by attacking organic pollutants present in wastewater. Previous literature on photocatalysis for both decolorization and degradation of organic pollutants followed a

pseudo-first-order reaction. The results achieved in this work also confirmed the same. The rate constant of the degradation reaction of dye is achieved by the following equation:

$$\ln \frac{C_0}{C} = kt \quad (5)$$

Where C = Concentration of dye solution, mol/L, K = rate constant, min⁻¹, t = time, min.

Fig.11 depicts the pseudo-first-order decolorization of MB dye in photocatalytic process. It was confirmed from the plot of $\ln (C_0/C)$ Vs time (t) that a straight line is passing through the origin. From this plot, the decolorization rate constant (k) of MB dye was found to be 0.004 min⁻¹.

7. Conclusions

In this work, the performance of individual systems; nanofiltration, photocatalysis, and their combination was successfully investigated and discussed. From the results, it was observed that the preliminary dye wastewater treatment with photocatalysis and secondary treatment with nanofiltration was effective. At catalyst loading of 0.2 g/L and pH 5.26, the maximum dye removal was achieved. These are considered as the optimum operating conditions. Also, it was noticed that on increasing the initial dye concentration, the decolorization was decreased. And in the combined system 70% of TOC was removed in 94.23 min of operational time. The maximum decolorization was achieved when the experiments were conducted at the obtained optimum values. This can be concluded as the best approach for the effective MB dye decolorization using optimized operating parameters designed in the RSM experimental model. This experiment has utilized lower energy, less time, minimal membrane fouling because of the combined process and also economical. Hence, this study can be termed as successful.

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