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Photocatalytic degradation of synthetic dye by immobilised doped nanoparticles on polyurethane foam reactor using RSM

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The aim of this work is to optimize the functional factors that influence the efficiency of the photodegradation of methylene blue using SiO_2–TiO_2 nanoparticles on polyurethane foam reactor by UV-TiO_2 photocatalytic process. The experimental factors like dye concentration, pH value, temperature, reaction time are analyzed by RSM (Response Surface Methodology) to achieve the efficacy of the best textile dye decomposition. The effect of operational factors to check the photodegradation efficiency of the methylene blue (MB) for SiO_2 nanoparticles and SiO_2-TiO_2 nanoparticles are examined by response surface methodology and contour plots. The degradation percentage of MB by SiO_2 and SiO_2-TiO_2 nanoparticles are 40.32% and 67.01% respectively. The best values of MB decomposition is achieved by SiO_2-TiO_2 with 10 ppm initial dye concentration, pH 6.88, temperature of 32 °C and 480 min reaction time. The satisfactory results is obtained through the correlation of the experimental values and predicted data by regression analysis (R^2 = 0.9984).

Keywords: TiO_2. SiO_2 nanoparticles, Polyurethane foam, Photocatalytic degradation, Methylene blue, Response surface methodology.

Introduction

Efficient elimination and separation processes are important for purifying the polluted water resources in the environment. The water reservoirs are always polluted by reason of unsystematic methods implemented by the dyeing, textile, paper, pharmaceutical and sugar industries and so on, during the release of hazardous and toxic chemicals [1, 2]. Textile dye compounds are highly complicated and cannot be biodegraded using normal methods. But in a few occasions, conversion of carcinogenic byproducts takes place by partial degradation. Therefore, physicochemical and various biological methods were developed for the decomposition of textile dye liquid waste from industries. Coagulation, precipitation, as well as oxidizing agents were utilized for degradation of various organic dyes. Significant limitations of chemical treatment techniques are that this process needs costly chemical compounds and the yield produced after textile dye effluent process are also highly contaminating the water bodies. Furthermore, they occasionally form a secondary pollution that requires chemical oxidation and additional techniques. Newly, an Advanced Oxidation Process (AOP) used to increase the complete degradation of organic pollutants [3-5]. AOP is an emerging process for the photodegradation of various contaminants in air and water because of the highly efficient, non-solubility, non-toxicity, feasibility at low pressure and temperature, and low fabrication cost [6-9]. Various semiconductors (sulfides and oxides) like TiO_2, ZnO, WO_3, SiO_2, $SrTiO_3$, CdS and ZnS are typically utilized as photocatalysts for pollutant degradation [10-16].

To enhance the degradation efficiency optimization of various factors such as pH, concentration, time and temperature plays a very important role in degradation system. Conventional wastewater treatment methods are multivariable and the optimization using the classical methods are unreliable, inflexible and time-consuming [17-19]. Hence, an alternative process which will be more effective and can be adapted for parameter optimization of different wastewater treatment methods is preferred. RSM is most efficient and extensively used method. RSM can be utilized to optimize and examine the effects of many independent variables on treatment method to attain the maximum output and system performance optimization [20-22]. RSM has been utilized to optimize various types of the wastewater treatment methods for industries like paper, tannery, textile etc [23-27]. In present trend the direction of replacing this ineffective operation with effective methods (chemometric), namely RSM, DOEs (statistical designs of experiments) [24]. This practical approach to achieve the most favorable factors is an proficient practice for use under a multivariable setup. RSM

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being effectively applied to several methods to attain optimization by experimental designs, together with titania coated/UV light photo oxidation [28, 29]. Some studies have been already stated the photodegradation and decolorization efficiency of textile dye using immobilized titanium dioxide nanoparticles on poly Polyurethane Foam Reactor [5, 30, 31].

Various studies have been explained for the enhancement of the catalytic activity of bare titania [11]. Investigation of photocatalytic operations are broadly performed in slurry methods operating using TiO_2 powder materials [14, 17]. The major difficulty in this process is the recycling and isolation of titania powder particles after degradation treatment, which is costly process and time consuming. To avoid this recycling issues, photocatalytic materials are immobilized on larger surfaces such as polymer foam, polymer spheres, ceramic foam [5, 15]. For large scale water treatment process this type of photocatalytic degradation system is greatly advantageous. Although, currently small development has been completed in the improvement in large scale applications of photocatalytic water treatment technology. The existence of various system conditions that need fast treatment testing is the one scientific barriers to enhance photocatalytic treatment technology.

In the current work, doped SiO_2-TiO_2 nanoparticles on polyurethane foam reactor is employed to photocatalytic degradation. This photocatalytic reactor is highly useful for large scale water treatment. The optimization efficiency of the photodegradation of methylene blue by immobilized SiO_2-TiO_2 nanoparticles on polyurethane foam reactor the pH, initial dye concentration, temperature, reaction time have considerable effects on the decomposition of textile dye in photodegradation method [32, 33]. Hence, these factors taken into account as independent variables, RSM was utilized to investigate their impacts and to upgrade the effectiveness of the photodegradation of MB.

Materials and Synthetic Procedures

Materials

In this study, analytical grade reagents such as titanium isopropoxide, ammonium hydroxide, ethanol, tetraethyl ortho silicate, hydrochloric acid, isopropanol, tetrahydrofuran, α-terpineol, ethyl cellulose are procured from Merck Specialties Private Ltd, Mumbai and these chemicals utilized in pure form. All the solutions were made-up with triple distilled water. Methylene blue is a synthetic dye. $C_{16}H_{18}N_3SCl$. MB dye sample was acted as model pollutant for degradation studies.

The MB dye chemical structure is shown in Fig. 1.

Synthesis of pure SiO_2

Pure SiO_2 was synthesized by hydrolysis of the TEOS at room temperature in alkaline medium. About

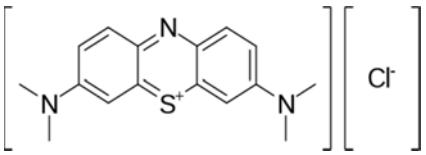


Fig. 1. Structure of MB.

15 ml of H_2O and 4 ml of NH_4OH were mixed with 100 ml of ethanol into Teflon coated reactor and stirring with magnetic stirrer for 20 min. After that TEOS (3 ml) were added instantly to above said reaction mixture and magnetic stirring continued for another 1 h. Afterwards hydrolysis polycondensation process, the reaction mixture used to be neutralized by 5 mol per litre hydrochloric acid and centrifuged for 10 min at 3,000 rpm. The supernatant was not needed and the precipitate washed thrice with distilled water. The obtained residue was dried by 70 ºC for 15 h.

Synthesis of SiO_2-TiO_2

Powdered silica material was dried by 110 ºC for 1hour and 0.2gram taken from it, that diffused in 30 ml 2-propanol by sonication process for 1 hour. This SiO_2 suspension then shifted to Teflon coated reactor and 50 ml of 2-propanol were mixed and allowed for 5 min under constant stirring. Then 18.2 g of Titanium isopropoxide were immediately added and then lid was firmly closed in the reactor. The reaction mixture was stirred further another 19 h with magnetic stirring. Then 9 ml alcohol-water mixture (6 ml 2-propanol: 3 ml H_2O) was added gradually and stirring continued another 1 h. The suspension (colloidal gel) of SiO_2-TiO_2 was then centrifuged for 10 min at 3,000 rpm, the supernatant was not needed and the precipitate washed with 2-propanol once and with double distilled water twice. The amorphous TiO_2 was crystallized using hydrothermal technique. The obtained amorphous mixture were suspended with 50 ml water and applied to hydrothermal process at 105 ºC for 24 h in a homemade air-proof teflon coated reactor. After hydrothermal process the samples were centrifuged once again for 10 min at 3,000 rpm and that precipitate were dried in air at 100 ºC.

Synthesis of pure SiO_2 and doped SiO_2-TiO_2

SiO_2 paste was prepared by adding 1 g of SiO_2, 2.5 g of α-terpineol ($C_{10}H_{18}O$), 12 ml of ethanol (C_2H_5OH) and 0.25 g of ethyl cellulose in a beaker and kept under constant stirring in magnetic stirrer for about 24 hrs. This process can be repeated for SiO_2-TiO_2 nanoparticles. This paste is used for fixing in the polyurethane foams.

Synthesis of dye

Methylene blue is a heterocyclic aromatic chemical compound. The methylene blue was collected from

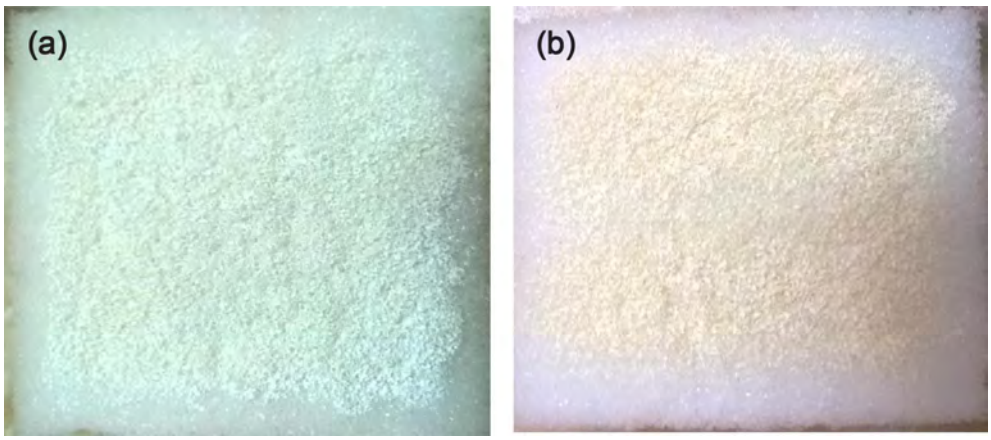


Fig. 2. (a) SiO_2 pasted PU foams. (b) SiO_2- TiO_2 PU foams.

laboratory. The prepared stock solution of methylene blue by dissolving dye (MB 10 g) in 1 L of double distilled water. The different concentration solutions of MB were prepared with serial mixing.

Photocatalyst characterization

There are various techniques existing for characterization of nanoparticles. X-Ray diffraction analysis of the synthesized materials was characterized by the XPERT-PRO, Field emission scanning electron microscopic image nanomaterials were captured by ZEISS instruments, metal composition of the SiO_2 and SiO_2-TiO_2 nano-particles taken by ZEISS SEM attached with EDAX by Oxford Instruments, UV-Vis spectra of the prepared catalysts were analyzed by UV–visible spectrophotometer (model AU2701).

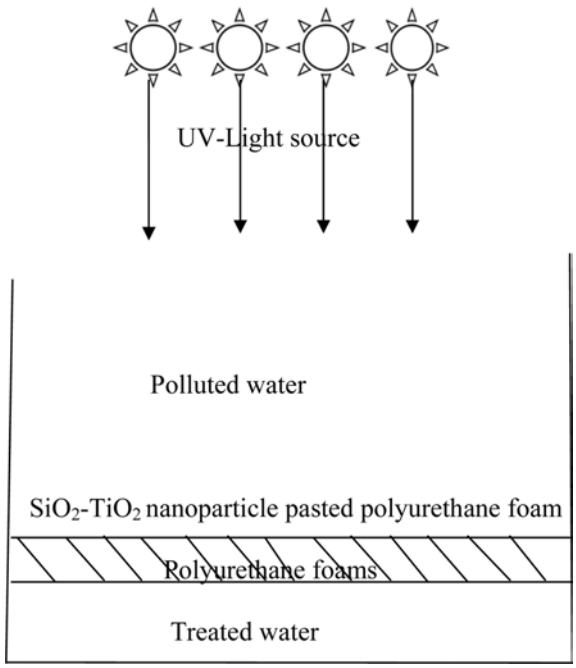


Fig. 3. Photo catalytic reactor set up.

Photoreactor and experimental procedure

Photochemical reactor, Philips TUV lamp, high pressure pump, polyurethane foams, nanoparticles paste, Reactor setup, 1/4" tubes. The SiO_2-TiO_2 nanoparticle pasted polyurethane foam was acted as the photocatalyst for the degradation of MB. The design of photo reactor are fixed in two certain position reduce nanoparticles to escape from the reactor. This type of reactor can be created for SiO_2 and SiO_2-TiO_2 separately. The reactor have the capacity of 1,500 ml and the effluent tank have a capacity of 5000 ml.

The fixed SiO_2 pasted polyurethane foams in the reactor was placed in the photochemical reactor with the setup of Ultraviolet Lamps and connected with high pressure pump to the Effluent tank. This setup is used for circulating the effluent in the reactor setup for about 8 hours and the UV-VIS spectroscopy can be done for each hours and for each reactors. This same process is to be repeated for Reactor with the SiO_2-TiO_2 paste coated polyurethane foams.

Results and Discussion

XRD analysis

Different factors such as particle size, dislocation density and strain were calculated by XRD. The XRD patterns of SiO_2 and SiO_2-TiO_2 nanoparticles were shown in the Fig. 4(a) and 4(b) respectively. On comparing the SiO_2 peak with the SiO_2-TiO_2, SiO_2-TiO_2 shows a slight deviation which shows the presence of TiO_2 material as a dopant over SiO_2, due to this the particle size are increased. The miller indices (hkl) values which are given the graph based on the reference JCPDC-02-0406.

The calculated values are shown in the Table 1. The average size of the particle for pure SiO_2 is 3.372 nm, for SiO_2-TiO_2 nanoparticles the particle size increased to 3.572 nm. This confirms that size of the particle increases with increasing concentration. Also particle size increases with doping on TiO_2 and the consequent

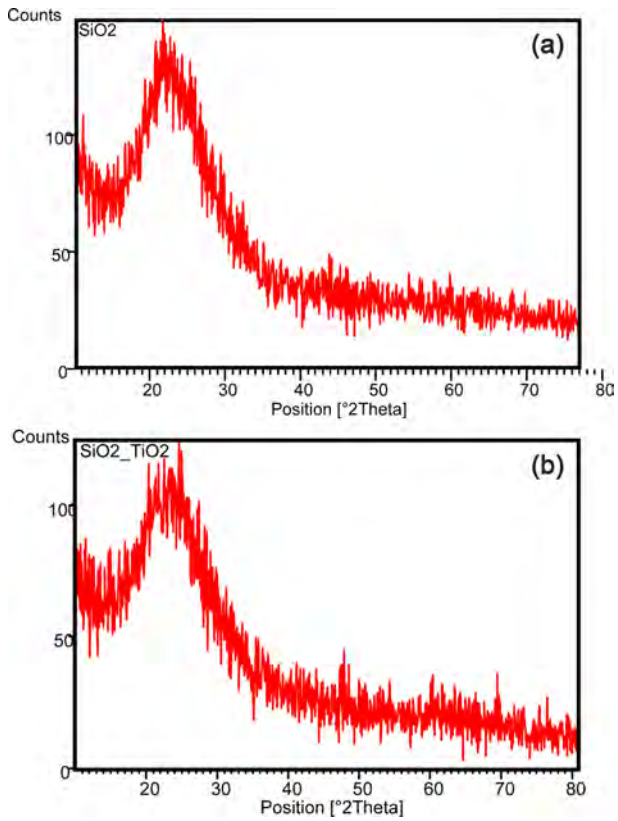


Fig. 4. (a) XRD patterns for SiO_2 nanoparticles and (b) XRD patterns of SiO_2 – TiO_2 nanoparticles.

reduction of bandgap causes red shift in absorption spectrum.

FESEM analysis

The FESEM images of SiO_2 and SiO_2-TiO_2 nanoparticles are shown in the Fig. 5(a) & 5(b). These typical FESEM analysis was visibly confirmed that synthesized samples are nanoparticles. Surface structure of nanomaterial plays a very important responsibility in the photocatalytic applications. The FESEM images shows that surface morphology of nanoparticless, and its size. The size of SiO_2 and SiO_2-TiO_2 which is shown on line integration of the FESEM software nano-sized particles.

EDAX analysis

The EDAX analysis of SiO_2 and SiO_2-TiO_2 nanoparticles are shown in the Fig. 6(a) & 6(b). EDAX technique is used to identify the composition of elements in the prepared nanomaterials. The EDAX analysis of SiO_2-TiO_2 nanoparticles revealed that the existence of all elements with proper composition. According to the outcomes, the dopant SiO_2 completely incorporated into TiO_2 lattice with good interaction.

Ultraviolet-Visible spectra of prepared nanoparticles

The UV-Visible Spectrophotometry of prepared catalysts are shown in Fig. 7. Optical properties of produced nanoparticles are recognized using UV-Visible double beam spectroscopy. UV-Visible spectra of SiO_2 and SiO_2-TiO_2 nanoparticles were analyzed from 190 to 700 nm wavelength range. Pure SiO_2 and SiO_2-TiO_2 illustrates the absorption spectral lines at 345 nm and 355 nm. The minute change in absorption spectra is in accordance with doping of SiO_2 in TiO_2. The bandgap (E_g) values of SiO_2 and SiO_2-TiO_2 were estimated using the following formula

$$E = hc/\lambda,$$

Where h is the Plank's constant, c is the light velocity and λ is the light wavelength. Bandgap of SiO_2 and SiO_2-TiO_2 were identified to 3.59 eV and 3.54 eV respectively.

Photocatalytic degradation using SiO_2 and SiO_2-TiO_2 nanoparticles

The systematic behavior of the synthetic nanoparticles are analyzed in the unique reactor which are fitted with the photochemical reactor setup. The aliquots are withdrawn each 1 h and the readings are taken in the UV-VIS Spectrophotometry for each reactors separately. This shows the photocatalytic degradation which causes changes in the dye concentration. The treatment of dye can leads to no wastage of nanoparticless during reaction, effective photocatalytic degradation with nanoparticles.

Fig. 8(a) shows the hour wise absorbance of dye samples using SiO_2 pasted polyurethane reactor, 1 hour residence time is allowed for getting each samples. Samples collected are instantaneously placed in the UV-VIS Spectrophotometer for getting instantaneous absorbance values with the form of graph. Totally 8hrs gone through to get a sets of the readings for the SiO_2 pasted polyurethane reactor. The maximum degradation obtained after completion of 8 hrs.

The method followed in the above procedure is repeated for the SiO_2-TiO_2 nanoparticle and UV-VIS reading is repeated for each hour to analyse the degradation value and shown in the Fig. 8(b). Totally 8 hrs gone through to get a sets of the readings for the SiO_2 – TiO_2 pasted polyurethane reactor. The maximum degradation obtained after completion of the 8 hrs, this degradation value is high when compared to SiO_2 catalyst.

Table 1. XRD results of SiO_2 and SiO_2-TiO_2.

Samples	2θ (deg)	FWHM	d-spacing [Å]	Particle size D (nm)	Strain (Lines/m^2)
SiO_2	21.693	2.4	4.09345	3.372127	0.01027942
SiO_2-TiO_2	20.693	2.4	3.09345	3.572127	0.00334833

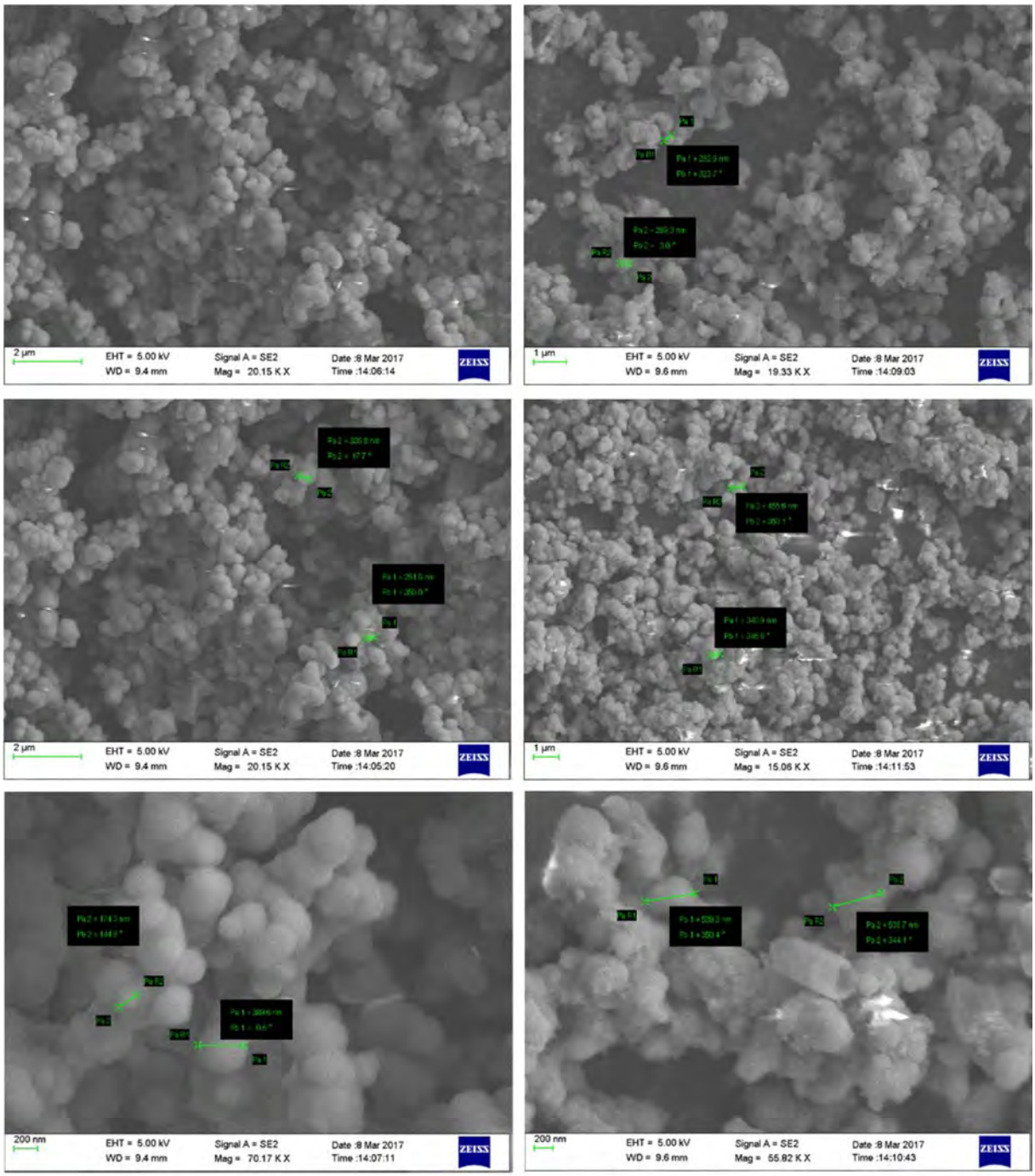


Fig. 5. (a) FESEM images and sizing of Pure SiO_2 and (b) FESEM images and sizing of SiO_2–TiO_2.

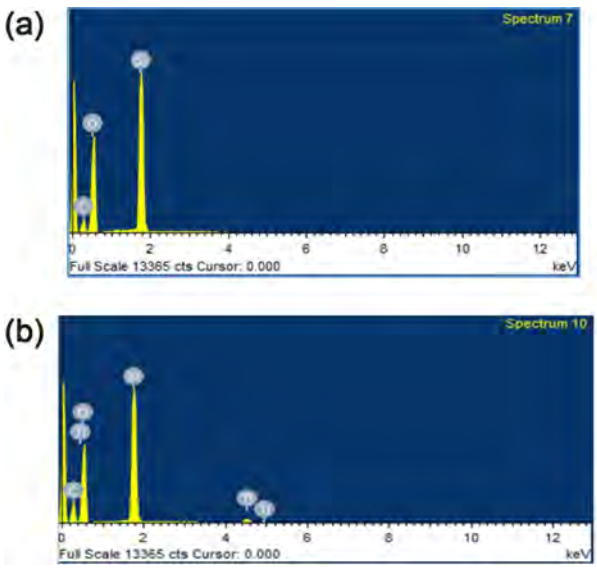
Comparing the SiO_2 and SiO_2-TiO_2 nanoparticles the photodegradation of methylene blue is given in the Table 2. From the above value it is infer that, SiO_2 and SiO_2-TiO_2 have degradation value of 40.32% and 67.01% respectively.

Effect of temperature

Temperature plays most significant role in the degradation process. So the percentage of decolourisation was investigated for every 1 °C rise in temperature and the investigated report is shown in Fig. 9. Decolourization efficiency of MB was high for at 38 °C@ SiO_2, 32 °C@ SiO_2-TiO_2. So decolourisation efficiency of SiO_2-TiO_2 was high at low temperature when compared to SiO_2 alone.

Effect of pH

The effect of pH on percentage decolourisation of



Element	Weight%	Atomic%	Compounds%	Formula
C K	16.23	22.23	59.46	CO_2
Si K	18.95	11.10	40.54	SiO_2
O	64.82	66.67		
Totals	100.00			

Element	Weight%	Atomic%	Compounds%	Formula
C K	18.67	24.98	68.39	CO_2
Si K	14.07	8.05	30.11	SiO_2
Ti K	0.90	0.30	1.50	TiO_2
O	66.36	66.67		
Totals	100.00			

Fig. 6. (a) EDAX composition result of SiO_2 and (b) EDAX composition result of SiO_2-TiO_2.

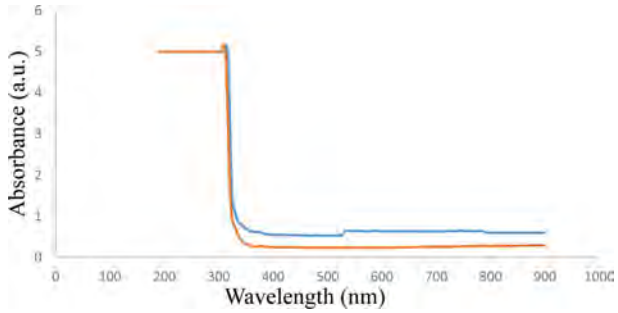


Fig. 7. UV-VIS spectra synthesized nanoparticles.

Table 2. Degradation percentage using SiO_2 and $SiO_2 - TiO_2$ Nanoparticles

Time (hr)	Decolourisation (%) by SiO_2	Decolourisation (%) by SiO_2– TiO_2
0	0	0
1	0.32	31.37
2	0.44	63.39
3	0.48	63.56
4	0.60	63.56
5	0.84	63.64
6	23.80	63.98
7	36.12	64.56
8	40.32	67.01

MB was conducted with different values of pH. From the Fig. 10 it is known that the percentage decolourization efficiency of methylene blue for SiO_2 and SiO_2-TiO_2 nanoparticles was evaluated, decolourization of MB is high at pH 5.42 and 6.88 respectively.

Effect of concentration

Aiming to estimate the percentage of decolourisation versus concentrations strength of synthesized materials,

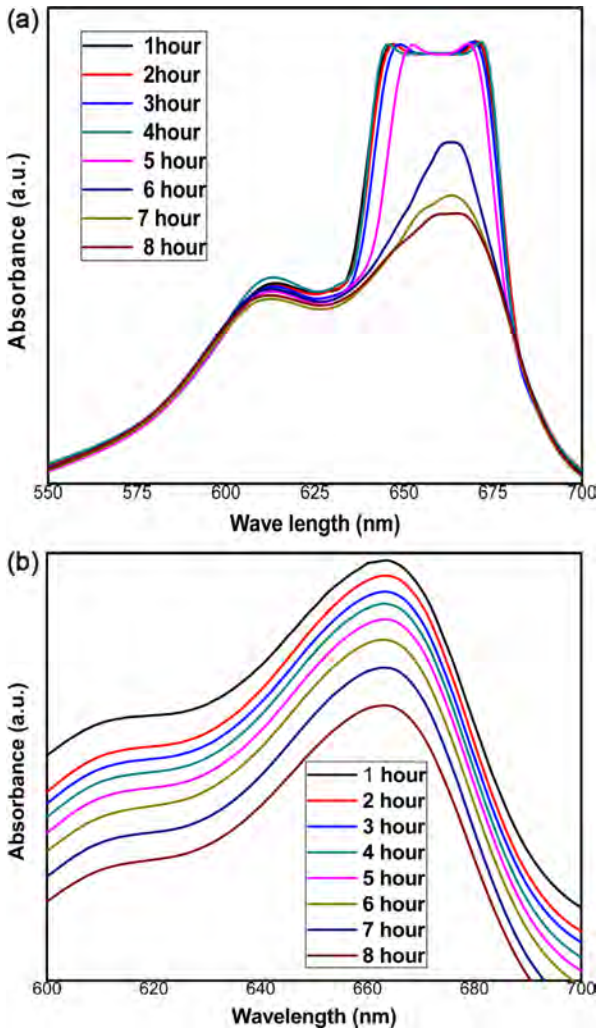


Fig. 8. (a) Hour wise Photo catalytic activity of SiO_2 pasted Polyurethane Foams in the reactor Placed in Photochemical Reactor for 8 hrs. (b) Hour wise Photo catalytic activity of SiO_2 – TiO_2 pasted Polyurethane Foams in the reactor Placed in Photochemical Reactor for 8 hrs.

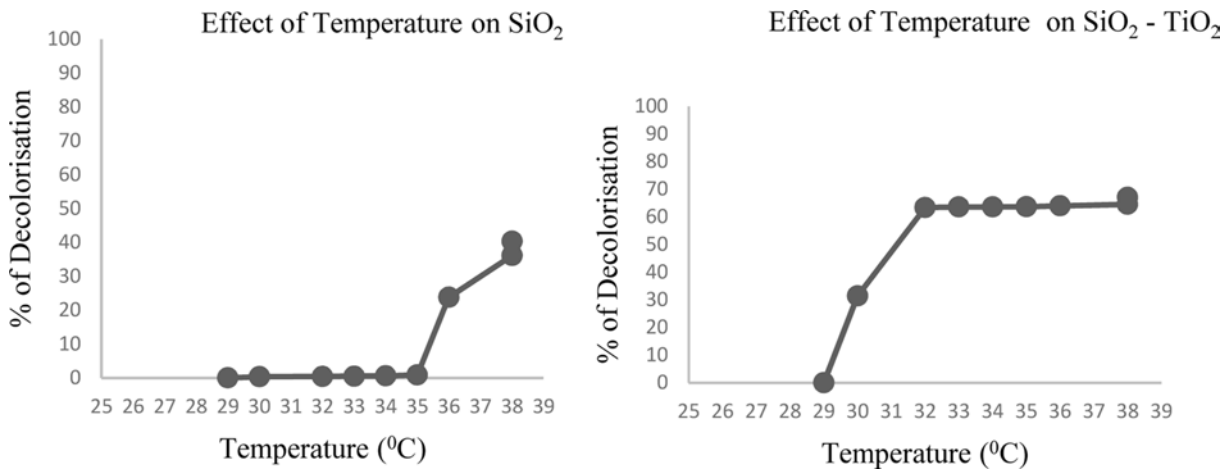


Fig. 9. Effect of temperature on decolourisation for SiO_2 nanoparticle and SiO_2-TiO_2 nanoparticles.

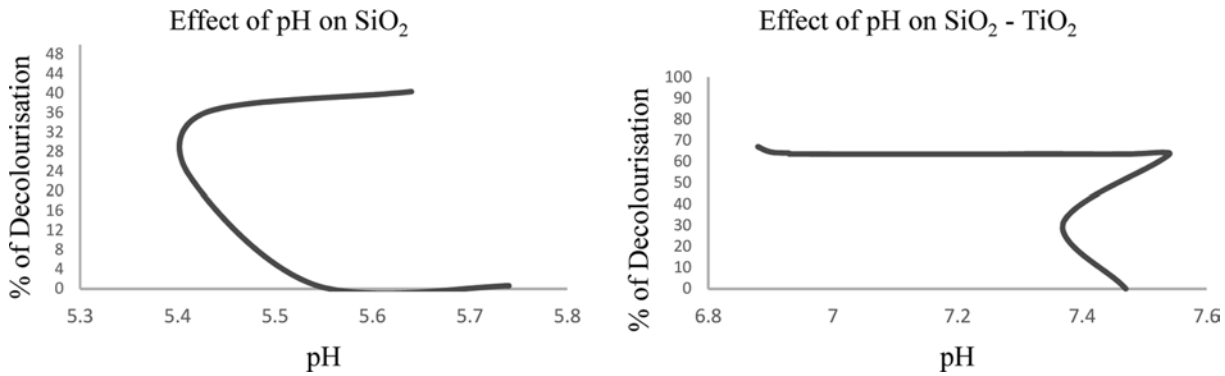


Fig. 10. Effect of pH on decolourisation for SiO_2 nanoparticle and SiO_2-TiO_2 nanoparticles.

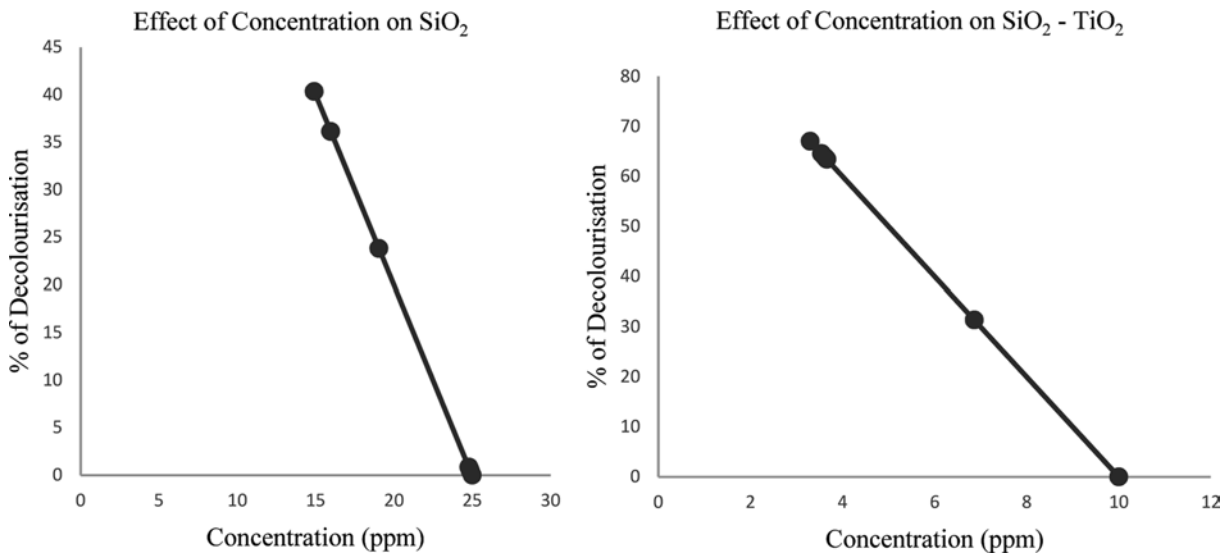


Fig. 11. Effect of concentration on decolourisation for SiO_2 and SiO_2-TiO_2 nanoparticles.

experiments were performed with catalytic material having different quantity shown in Fig. 11. When compare between undoped and doped SiO_2, the doped catalytic materials proved more effective photocatalytic activity using irradiation of UV light. This is due to the reducing bandgap of titania, less particle size and vast surface area, this resulting to absorb more quantity of dye compounds. Therefore, from the prepared photocatalyst

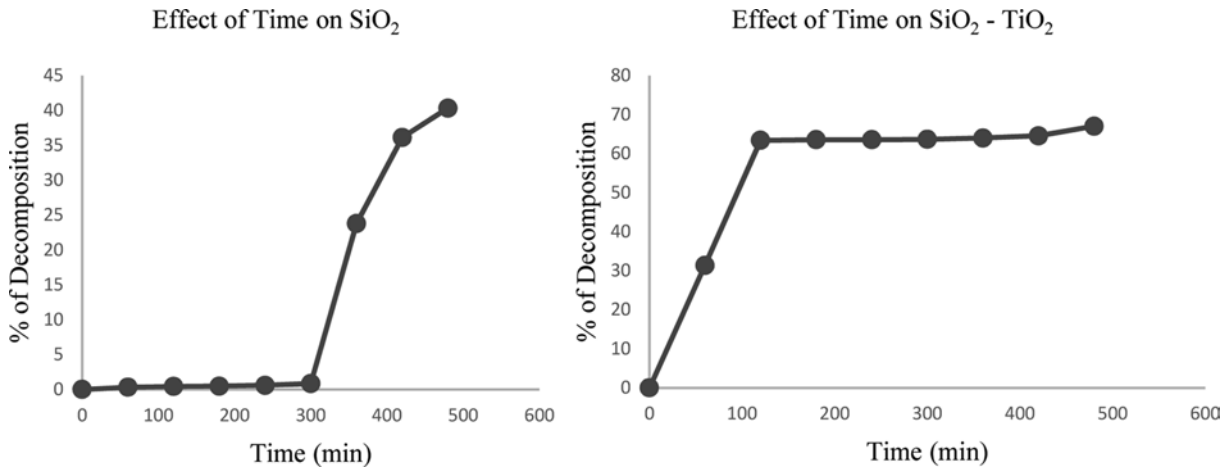


Fig. 12. Effect of time on decolourisation for SiO_2 nanoparticles and SiO_2-TiO_2 nanoparticles.

doped SiO_2-TiO_2 has shown 67.01% of degradation in 10 ppm (Fig. 11). The variations in the concentration value not only facilitate to access the decolourisation value, but also helps to determine the degradation of the dye. So the percentage of decolourisation was investigated for each concentration value with the help of Beer – Lamberts law and the investigated report is shown in figures.

Effect of time

Time also plays a most significant role in the degradation process. So the percentage of decolourisation was investigated for every 1 h and the investigated report is shown in the Fig. 12. From the grapes, it was observed that the percentage of decolourization efficiency of methylene blue for SiO_2 and SiO_2-TiO_2 nanoparticles was evaluated, decolourization of MB was high at time 480 mins for both.

Experimental design and optimization by RSM

RSM using CCD is worked in statistical design of the experiments, data analysis, clarifies to achieve the best parameters of independent factors, estimation of correlation between 4 important independent factors, these are concentration of the MB dye, pH, temperature and reaction time. All independent factors are diverse over two levels based on face centered CCD as -1 and +1, correspondingly at the defined ranges found on set of preface experiments. Number of test experiments carried out for 4 factors are calculated according to equation given below.

No. of Experiments = 2^k +2k + 6

Where, k is factors number.

In this study, number of test experiments carried out for 4 parameters is thirty with sixteen factorial points, eight axial points, six repetitions to evaluate the error and achieve a excellent value. The degradation and decolourisation are dependent factors (responses) under this practice. Efficiency is estimated by testing the percentage of degradation and decolourisation.

The conduct of the scheme is clarified through an empirical 2nd order polynomial model, as showed in below Equation

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{K} \beta_{ii} X_i^{\,2} + \sum_{i=1}^{K-1} \sum_{j=i+1}^{K} \beta_{ij} X_i X_j + \varepsilon$$

Y is response.

X_i, X_j are variables.

b is regression coefficient.

k is number of factors studied and optimize in the experiment.

e is random error.

Analysis of variance (ANOVA) for photocatalytic reaction by immobilized SiO_2 nanoparticles

A total of thirty runs are executed by the CCD relations among the 4 independent factors are believed in every run to examine the strength of photodegradation of MB dye using immobilized nano doped polyurethane foam reactor. The results are summarized in below Tables 3-6. The analysis of variance is utilized for graphical analysis of data to attain the relations among the process conditions and responses. To fit polynomial model is shown by coefficient of determination (R^2).

Table 3. Coded value for the SiO_2 nano ANOVA table.

FACTORS	LEVEL	
	-1 (low)	+1 (high)
Retention Time (min)	0	480
pH	5.41	5.74
Concentration (ppm)	14.92	25
Temperature (°C)	30	35

Table 4. Response value for the different experimental conditions of SiO_2 nanoparticle.

Run No	Factor-A Time (min)	Factor-B pH	Factor-C Temperature (°C)	Factor-D Concentration (ppm)	Response-1 % of Degaradation	Response-2 % of Decolourisation
1	240	5.575	32.5	19.96	79.75	78.00
2	480	5.740	35.0	25.00	15.62	61.83
3	240	5.575	27.5	19.96	72.35	66.95
4	0	5.410	35.0	25.00	55.37	51.91
5	240	5.575	32.5	9.88	69.04	79.58
6	240	5.575	32.5	19.96	83.28	79.14
7	480	5.740	30.0	14.92	83.99	80.93
8	0	5.740	30.0	14.92	71.15	70.88
9	480	5.410	30.0	14.92	76.22	96.62
10	240	5.575	32.5	19.96	85.24	79.09
11	0	5.740	30.0	25.00	60.37	55.19
12	240	5.575	32.5	19.96	79.28	79.07
13	240	5.575	32.5	30.04	41.39	65.4
14	240	5.245	32.5	19.96	63.29	73.75
15	480	5.410	35.0	14.92	67.37	76.29
16	0	5.410	30.0	25.00	64.69	93.38
17	240	5.905	32.5	19.96	56.09	56.18
18	240	5.575	32.5	19.96	79.19	79.22
19	720	5.575	32.5	19.96	76.57	79.20
20	480	5.740	35.0	14.92	68.86	95.45
21	480	5.740	30.0	25.00	63.96	72.08
22	480	5.410	30.0	25.00	83.05	71.80
23	0	5.410	30.0	14.92	39.74	75.16
24	480	5.410	35.0	25.00	57.69	75.36
25	0	5.410	35.0	14.92	56.07	60.73
26	0	5.740	35.0	14.92	75.23	90.38
27	240	5.575	37.5	19.96	48.62	42.98
28	240	5.575	32.5	19.96	77.78	81.35
29	240	5.575	32.5	19.96	80.89	76.38
30	0	5.740	35.0	25.00	35.07	53.73

Model conditions are evaluated using P-value by 95% of confidence level.

Analysis of variance (ANOVA) for photocatalytic reaction by immobilized SiO_2 -TiO_2 nanoparticles

Effects and optimum values of parameters

Response surface and counter plots are used to prove the impact of parameters on photocatalytic degradation and decolourisation efficiency for SiO_2 and SiO_2-TiO_2 Fig. 13(a-d). The percentage photodegradation of MB as function of the time & pH and temperature & concentration. It shows that percentage of degradation

Table 5. Coded value for the SiO_2 – TiO_2 ANOVA table.

FACTORS	LEVEL	
	-1 (low)	+1 (high)
Retention Time (min)	0	480
pH	6.88	7.54
Concentration (ppm)	3.29	10
Temperature (°C)	29	38

Table 6. Response value for the different experimental conditions of SiO_2–TiO_2 nanoparticles.

Run No	Factor-A Time (min)	Factor-B pH	Factor-C Temperature (°C)	Factor-D Concentration (ppm)	Response-1 % of Degaradation	Response-2 % of Decolourisation
1	480	7.54	29.0	3.2986	80.82	55.83
2	480	6.88	29.0	10	66.23	43.16
3	0	6.88	38.0	3.2986	41.60	42.67
4	240	7.21	33.5	6.6493	73.07	49.85
5	720	7.21	33.5	6.6493	59.21	86.84
6	0	6.88	29.0	10	23.70	74.58
7	240	7.21	33.5	6.6493	72.29	48.33
8	0	6.88	38.0	10	43.03	44.83
9	480	6.88	29.0	3.2986	84.12	45.95
10	0	7.54	29.0	3.2986	43.02	32.06
11	240	7.21	33.5	0.0521	70.57	31.36
12	240	7.21	33.5	6.6493	72.59	50.97
13	240	7.21	33.5	6.6493	72.94	48.74
14	0	6.88	29.0	3.2986	7.77	45.79
15	240	7.87	33.5	6.6493	45.24	8.997
16	0	7.54	29.0	10	52.05	51.17
17	240	7.21	33.5	6.6493	74.62	50.95
18	240	7.21	33.5	13.3507	45.14	22.34
19	240	6.55	33.5	6.6493	53.78	41.58
20	480	6.88	38.0	10	42.41	53.85
21	480	7.54	38.0	3.2986	44.68	74.29
22	240	7.21	33.5	6.6493	72.39	48.50
23	480	7.54	38.0	10	0.02579	33.53
24	0	7.54	38.0	10	41.05	3.029
25	480	7.54	29.0	10	53.73	46.19
26	240	7.21	42.5	6.6493	32.15	55.26
27	0	7.54	38.0	3.2986	46.76	8.748
28	240	7.21	33.5	6.6493	70.70	51.37
29	480	6.88	38.0	3.2986	79.26	82.86
30	240	7.21	24.5	6.6493	53.58	68.42

increases when the reaction temperature rises and time increases**.**

The above Fig. 14(a&b) shows the experimental and predictive values for methylene blue degradation and decolourisation. It shows that the high relationship between experimental values and predicted data (R^2 = 0.9984) proved the data fit with the model in the range calculated. At the same time, residual analysis was conducted in order to prove the capability of model.

Conclusion

From the experimental studies the photocatalytic degradation of aqueous methylene blue solution as a model pollutant from textile dyeing industries, was analyzed using SiO_2 and SiO_2-TiO_2 nanoparticles immobilised on polyurethane foam reactor. The value of decolourisation efficiency was calculated for SiO_2 and SiO_2-TiO_2 nanoparticles as 40.32% and 67.01% respectively. Effect of operational factors on the photocatalytic degradation efficiency of methylene blue

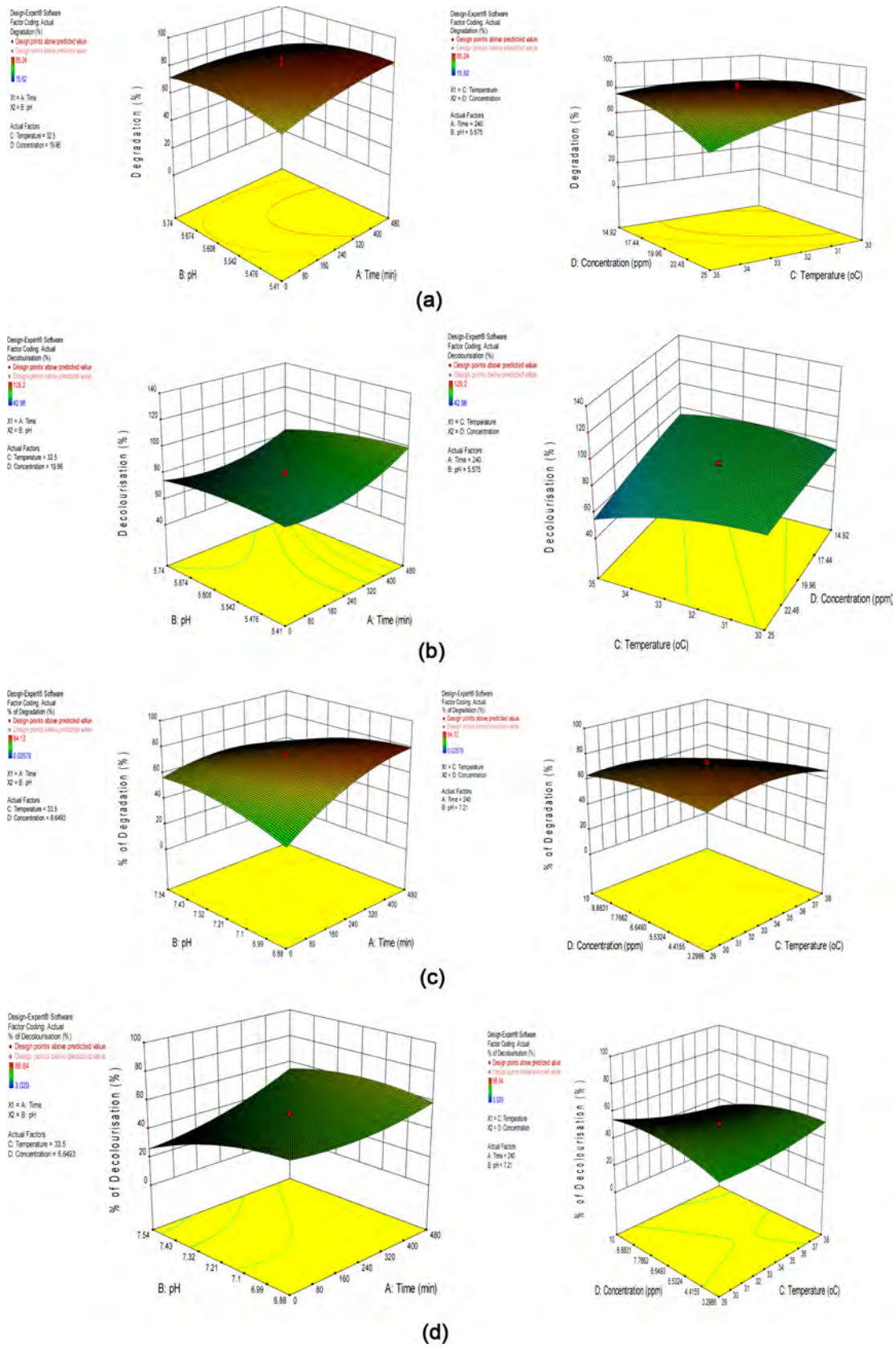


Fig. 13. (a) Response graph for the percentage of degradation of SiO_2 nanoparticles for the factor time and pH and temperature & concentration. (b) Response graph for the % of decolourisation of SiO_2 nanoparticles for the factor time & pH and temperature & concentration. (c) Response graph for the percentage of degradation of SiO_2 - TiO_2 nanoparticles for the factor time & pH and temperature & concentration. (d) Response graph for the percentage of decolourisation of SiO_2 - TiO_2 nanoparticles for the factor time & pH and temperature & concentration.

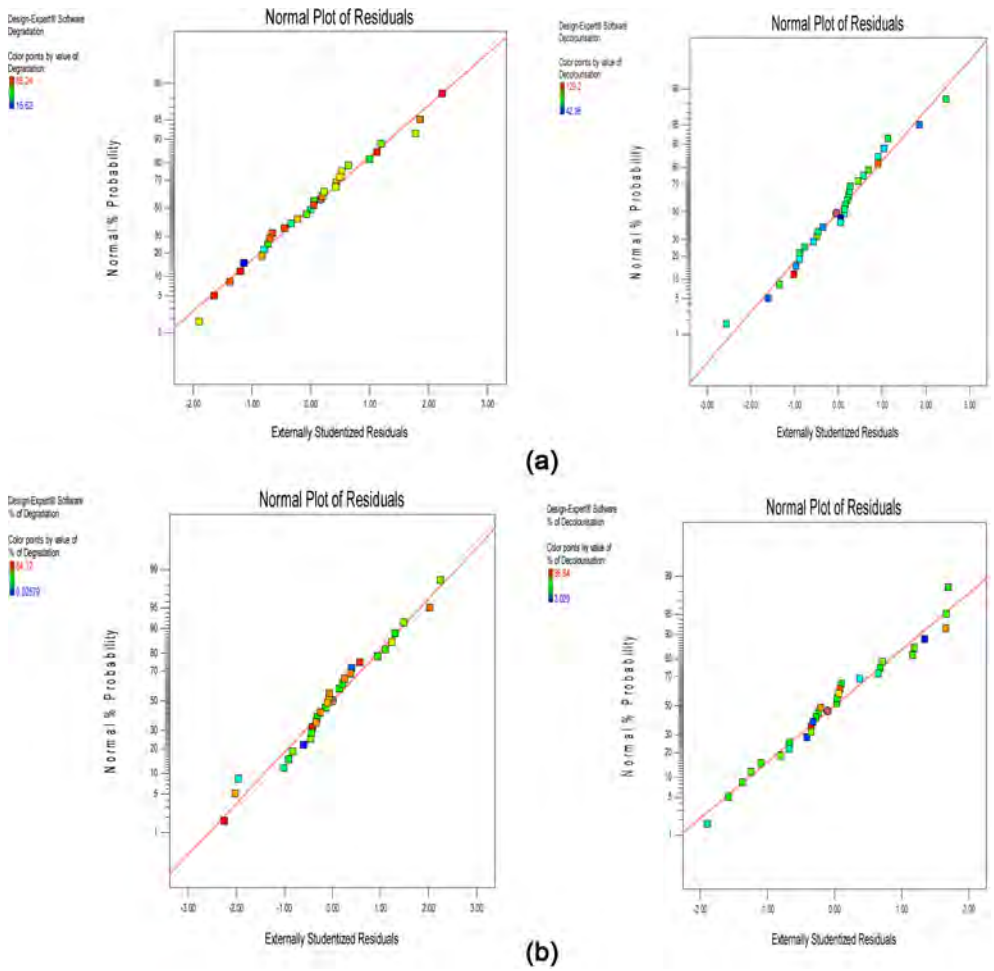


Fig. 14. (a) Normal plot of residuals for degradation of SiO_2 nanoparticles and decolourisation of SiO_2 nanoparticles. (b) Plot of residuals for degradation of SiO_2 - TiO_2 nanoparticles and decolourisation of SiO_2 - TiO_2 nanoparticles.

for SiO_2 and SiO_2-TiO_2 nanoparticles was analyzed by the contour plots and response surface methodology. The SiO_2 and SiO_2-TiO_2 optimum values of reaction time, pH, temperature and initial dye concentration were, 480 mins, 5.42, 38 °C, 14.42 ppm and 480 mins, 6.88, 32^{0}C, 10 ppm respectively. Regression analysis R^2 value of 0.9984 showed a good agreement between experimental results and predicted values.

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