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Optimization studies of Ultrasonication assisted Catalytic Treatment of Rhodamine G in aqueous solution

Amisha Patel[1, a)], Shivendu Saxena[2, b)] and Vishal Kumar Sandhwar[3, c)]

[1]*Department of Industrial Chemistry, Parul Institute of Applied Sciences, Parul University, Vadodara, Gujarat 391760, India*
[2,3]*Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, Gujarat 391760, India*
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Abstract

In this study,the treatment of rhodamine G in aqueous solution was carried out by ultrasonication-basedcatalytic treatment.The study focuses on the synthesis of TiO_2 and its application for rhodamine G from aqueous solution. The catalytic treatment was optimized using response surface methodology to get maximum removal efficiency. The influence of operating parameters like pH, treatment time and catalyst amount were investigated and optimized during the study. At optimal operating conditions (pH:6.7 time:104.81, catalyst amount:50.75)the maximal removal efficiency of 55.5% was obtained.

Keywords:Nanoparticle, Ultrasonication, Catalytic Treatment, Textile wastewater, Optimization.

1. Introduction:

One of the broadest and most intricate industrial networks in the manufacturing sector is the textile industry. The mechanical processing steps involved in producing a textile, such as spinning, knitting, weaving, and garment manufacturing, appear to be isolated from the wet treatment processes, such as sizing, desiring, scouring, bleaching, mercerizing, dyeing, printing, and finishing operations. However, there is a significant relationship between the two [1].There are rigorous regulations for the release of wastewater since it is bad for the environment and people. Because to variations in the raw materials utilized, various types of dyes, technology, and equipment, the standards of wastewater discharge (Table 1) have far too many characteristics. Based on the regional environment and variable environmental safety requirements, these criteria are set by the national environmental protection department of the Central Pollution Control Board (CPCB)[2].

The organic contaminants, colour, and heavy metal ions are the first things to take into account for printing and dyeing wastewater. In light of the recent water shortage, wastewater recovery should be taken into account. As a result, the effluent from printing and dyeing increased significantly in decolourization [2].COD, BOD, pH, SS, DS, chloride, sodium, fats, oil, nitrogen, phosphorus, sulphate, and TSS are the parameters in textile wastewater that are most crucial to monitor [3]. High BOD, COD, pH, and colour values are characteristics of effluent from the textile industry[4]. Wastewater from the textile sector is distinguished by its highly apparent hue, high BOD, COD, and alkaline pH (5.5–10.5) [5].

The concentrations of sulphate, phosphate, nitrate, chloride, calcium, magnesium, and metals/ppm,

chemical oxygen demand/ppm (COD), and dissolved oxygen/ppm are among the chemical characteristics that are crucial for evaluating the treated wastewater[7].The major two sources of metals in textile wastewater are soil and water. These are the dye materials and impurities of chemicals used in the various phases of the textile business, including caustic soda, sodium carbonate, and salts. Chromium, zinc, iron, mercury, and lead are the metals that the World Health Organization deems to be of the greatest immediate concern [7].The visible light (solar or artificial light)/ZnO and visible light (solar or artificial light)/TiO_2 systems might be employed well for the treatment of textile industrial effluent, according to the Arab Science and Technology Foundation [8,9].

The textile industries that work with paper processing, resizing, cosmetics, blanching, colouring, leather, and wrapping have rapidly increased and include numerous steps of material creation and processing before they are converted into fabric and other industrial products. The wet processes used in the textile industry—particularly the dyeing stage—are what have the biggest negative effects on the environment. The tissues are given colour at this stage, and significant amounts of water and energy are consumed. Per kilogramme of completed product, dyeing procedures can consume up to 170 L of water, 1.1kW of electricity, and 16 MJ of heat energy[1-3].Both discontinuous and continuous dyeing processes are possible with the aid of various tools and methods. Discontinuous staining involves placing a specific amount of tissue on a dyeing machine and bringing it into balance with a dyeing compound solution. The dye is then fixed to the fibre using heat and chemical products, and the fabric is then washed to remove the non-fixed dye content and other chemical products. The materials are continually fed into a bath during continuous dyeing procedures, when fixing agents, heat, and colour are added in proportion to the incoming cloth. Hence, complex mixes of products like metals, salts, acids, and colours are present in the textile effluent.

Rhodamine dyes are fluorescent chemicals that have exceptional brightness, exceptional photostability, and a high fluorescence quantum yield. By substituting other substances, one can change their features. Rhodamine dyes have outstanding characteristics that make them adaptable for application in microarray analysis, fluorescence spectroscopy, whole-body imaging, and immunodiagnostics[10].

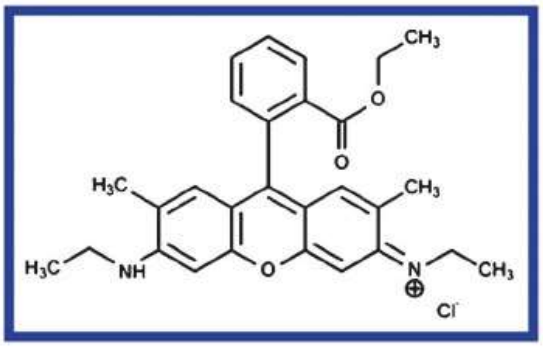


Figure 1: Rhodamine G

Due to its widespread use in the biological and chemical sectors, copper ion (Cu^{2+}) is a significant metal contaminant. This study examines how three rhodamine dyes' photophysical characteristics are affected by copper. Also, the effect of copper on rhodamine dye-sensitized solar cells' performance is assessed.

Using the use of SCAPS-1D software, the experimentally generated data were confirmed by a theoretical investigation. The electrical and optical properties of TiO2 nanostructures are altered by oxygen vacancies (VO). TiO2 loses its crystallinity and becomes more amorphous with rising VO concentrations[11–13]. Oxygen vacancies produce a mixed state of titanium consisting of Ti^{4+} and Ti^{3+}, and the transition from Ti^{4+} to Ti^{3+} accelerates as the defect density of VO rises[14].

2. Materials & Methods:

2.1 Reagents and Chemicals:

Titaniumtetraisopropoxide(TTIP), Isopropanol, Deionizedwater, Niticacid. Chemicals are being used without any extra filtration. 0.1 N NaOH, 0.1 N HCL, (for pH maintain) Distilled water. TiO_2 nanoparticles, Rhodamine G.

2.2Sol-GelMethodforCatalystPreparation:

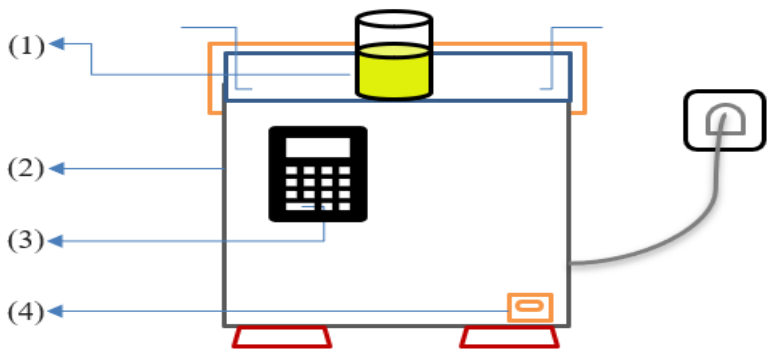
The manufacturing of nano composite materials may be done using the wet-chemical sol-gel method. As the name implies, this process involves the solution gradually moving towards the formation of a network resembling a gel that contains both liquid and solid phases.

2.3 Synthesis Procedure of TiO_2 Particles:

When magnetic stirring is being employed, drops of an isopropanol/deionized water solution (Misopropanol: MTTIP: MH2O = 1: 2: 12) were added to the TTIP solution.The aqueous solution was reconstituted with nitric acid when the titration process was finished. The pH of the solution was held constant at 2.0.The acid slows the hydrolysis process, which in turn regulates grain growth. The mixture was continually agitated for a further hour, and it was overnight peptized.Afterpeptization,atwo-layersolutionwasfoundtodevelop,withtheorganicoutputofthehydrolysis in the top layer and a titanic acid gel in the lower layer of the precipitate.The gelwas then filtered off and heated at 110°C for a number of hours, generating yellow blockcrystals.Usingacrusherand,thesecrystalswerebrokendownintoafinepowder,itwasfurthercalcined at 400°C for three hours.

2.4 Experimental Set-up:

The process of using sound energy to stir up particles or discontinuous fibres in a liquid is known as sonication. Since ultrasonic frequencies (>20 kHz) are typically employed, the procedure is also referred to as ultrasonication. To determine the effectiveness of dye removal, the impact of sonication combined with agitation and stirring alone (150 rpm) was tested. The sonication mechanism is employed in ultrasonic cleaning, which also involves the removal of particles from surfaces.



1. Beaker (Dye Solution + TiO_2 Nanoparticle)
2. Stainless steel tank
3. Operational condition board
4. Power Switch

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Figure 2: Experimental Set-up

2.5 Analytical characterization:

SEM (scanning electron microscope) producing various signals that contain information about the surface topography and composition of the sample.XRD (X-Ray diffraction analysis) istechnique that provides detailed information about physical properties of a material. BET (Brunauer-Emmett-Teller) analysis technique for the measurement of the specific surface area of materials.Calibration of the UV spectrophotometer including control of absorbance using potassium dichromate solution, resolution power using toluene in hexane, limit of stray light and wavelength accuracy.

2.6 Treatment of textile wastewater using sonication:

20 mg/l (20 ppm) of Rhodamine G dye is added to 1 litre of distilled water. To ensure adequate mixing and dissolution, stir thoroughly. TiO_2 nanoparticles 0.4 grammes should be added to the mixture. Once more, mix thoroughly to distribute the nanoparticles. With the help of a suitable container, collect 200 ml of the prepared solution. The collected solution should be placed in an ultrasonic bath. Remove 20 ml samples of the solution at intervals of 60, 90, and 120 minutes following the ultrasonication treatment. The analysis of these samples will be conducted. Put some filter paper in a funnel arrangement andfilter 20 ml of different samples. Give the samples an hour to filter. After filtering, measure the results with a UV spectrometer.By following above process and just varying the amountofTiO_2we got a differentresult.

Table 1: Operating parameters and their levels obtained from statistical software for catalytic with TiO_2

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Central composite design characteristics			
Levels	Parameter (Range)		
	pH (3→7)	Doses(mg/l) (40→80)	Time (min) (60→120)
-1(-α)	3	40	60
0	5	60	90
+1(α)	7	80	120

Table 2: CCD predicted experimental set for catalytic of TiO_2

Sr No	pH	Dosage	Minutes
1	3	40	90
2	7	40	90
3	3	80	90
4	7	80	90
5	3	60	60
6	7	60	60
7	3	60	120
8	7	60	120

9	5	40	60
10	5	80	60
11	5	40	120
12	5	80	120
13	5	60	90
14	5	60	90
15	5	60	90
16	5	60	90
17	5	60	90

3. Result & Discussion:

3.1 Characterization of Titanium Dioxide:

3.1.1 XRD (X-Ray diffraction):

An XRD (X-Ray diffraction) examination of TiO2 produced using the Sol-Gel (SGL) process reveals that the crystal size of the particles may be determined. The Scherrer equation, which includes figuring out the crystal diameter, was used to analyse X-ray peak-broadening. The formula is: D=k/Cos; it takes into account a constant (k) with a value of 0.9, the radiation's wavelength (0.15418 nm), the peak's full width at half maximum (FWHM), the peak's Bragg's angle of diffraction, and the wavelength of the radiation employed. The table below shows the calculated TiO2 crystal sizes using the Scherrer equation for various 2 values and complete width at half maximum.

The calculated crystallite size for the production of tio2 powder was 11.612 nm based on the facts stated above. Temperatures can reach up to 700°C when titanium (IV) n-butoxide is used, and the crystallite size can shift from 13.96 nm to 35.07 nm.

Table 3: Crystal size of TiO_2.

SR.NO.	Diffraction angle (2θ)	FWHM (Degree)	Crystal size (nm)
1	27.5510	0.7506	10.90586
2	36.2864	0.5411	15.46192
3	41.3687	0.7506	11.32197
4	54.4591	0.6667	13.41136
5	69.1962	1.3874	6.961611

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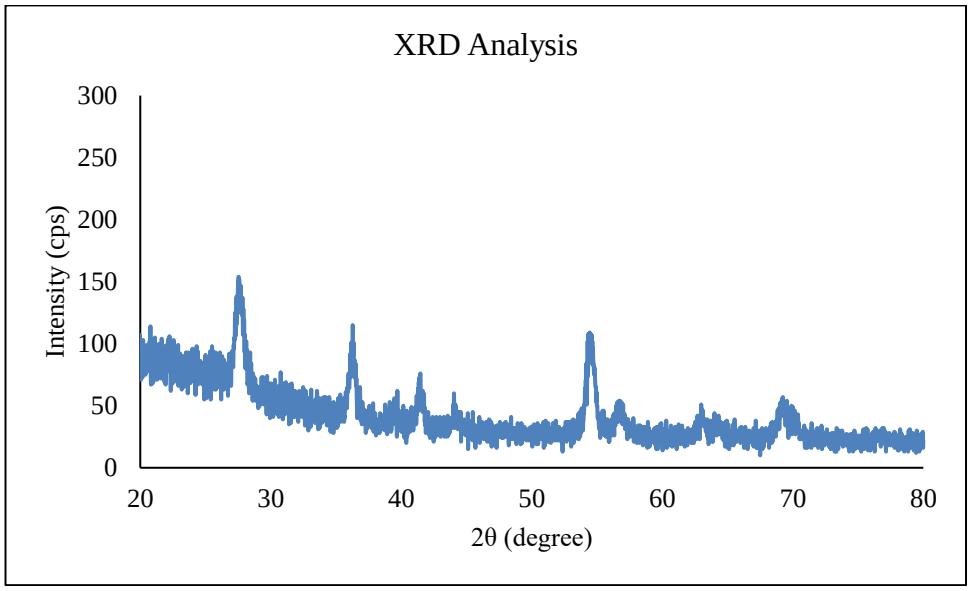


Figure 3: XRD Analysis

3.1.2 BET surface area analysis:

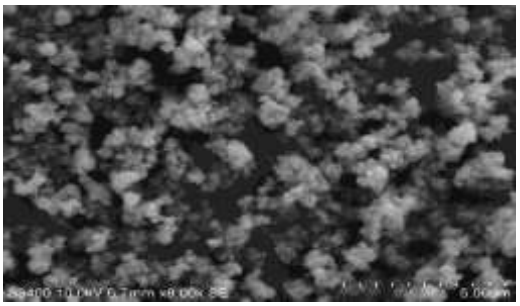
Sol-Gel (SGL)-prepared samples of TiO_2 were tested to BET adsorption of nitrogen gas for surface area analysis at liquid nitrogen temperature. The BET surface area of the synthesize TiO_2 was determined to be 34.8599 m^2/g. The average pore diameters of adsorption and desorption were 172.838Å and the pore volume of absorption and desorption was 0.150 cm^3/g.

Table 4: BET Analysis

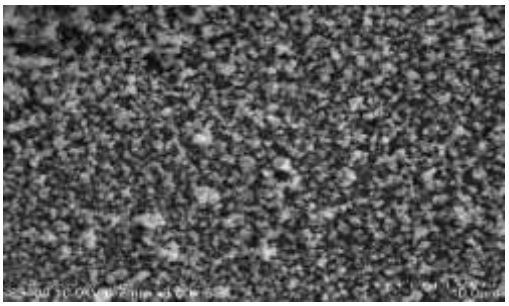
Sr.No.	BET Analysis	Result
1	Surface area	35 m^2/g
2	Pore volume	0.15 cm^3/g
3	Pore average diameter	17.2838 nm
4	BJH desorption average pore width	15.4138 nm

3.1.3 SEM (scanning electron microscope):

It is the best method for creating a magnified image of the sample for analysis following scanning it with an electron beam. TiO_2 is synthesized using the Sol-Gel (SGL) process, and SEM morphology shows the effect of the different magnitude states.



(a)



(b)

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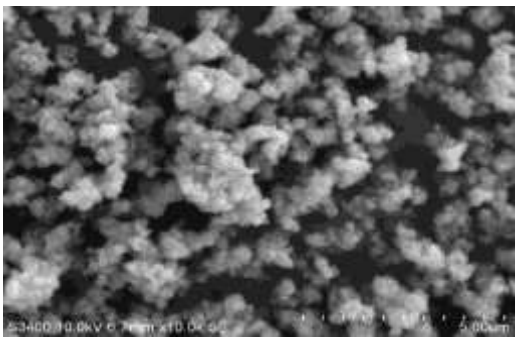

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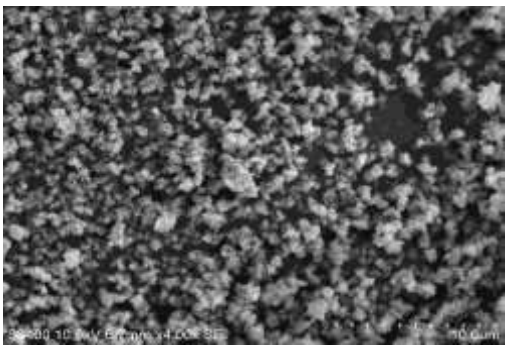

(d)

Figure 4: SEM image for the different magnification stated and different scale

A different magnification stated indicated as 8.0k and 10.0k scale of 5.0 μm is shown in figure 5 images (a) and image (c) above the SEM image, and a different magnification stated as 3.0k and 4.0k scale of 10.0 is shown in above figure images (b) and (d), respectively. The SEM image shows in below figure, which specified magnification is 6.0k, identifies some of the particle sizes present in the image below. `

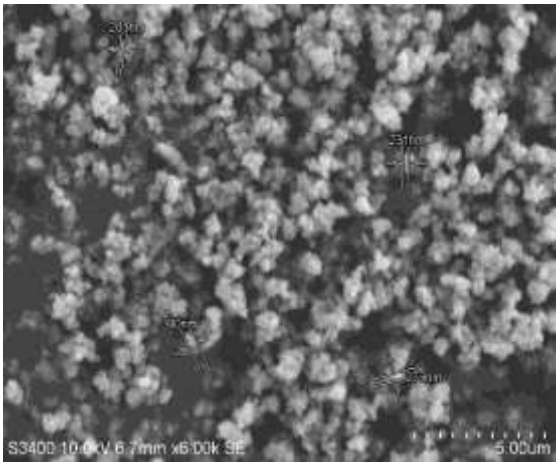

Figure 5: SEM image

3.2 Effect of pH, Time and Dosage of TiO_2on percentage removal of rhodamine G:-

The effect of pH (3-7), catalytic doses (40-80mg/lit) and treatment time (60-120min) were examined for removal of rhodamine G from aqueous solution as presented in figure:6,6.1and 6.2.From the following figures it can be observed that the maximum removal of rhodamine G was achieved at pH 6.7, 50.75mg/lit of TiO_2 dose and after104.81min of ultrasonication treatment of synthetic solution of rhodamine G. The maximum degradation of rhodamine G was observed at 55.5% at optimal parameters as presented in table5.

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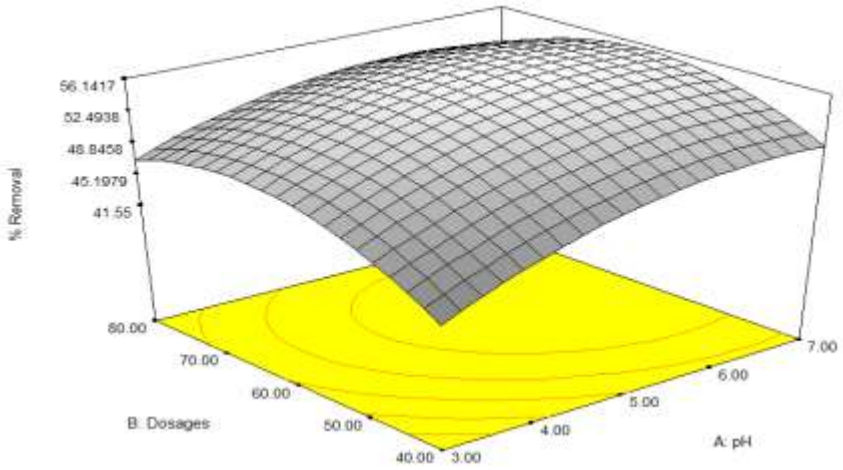

Figure 6: Effect of pH, dosages % rhodamine removal

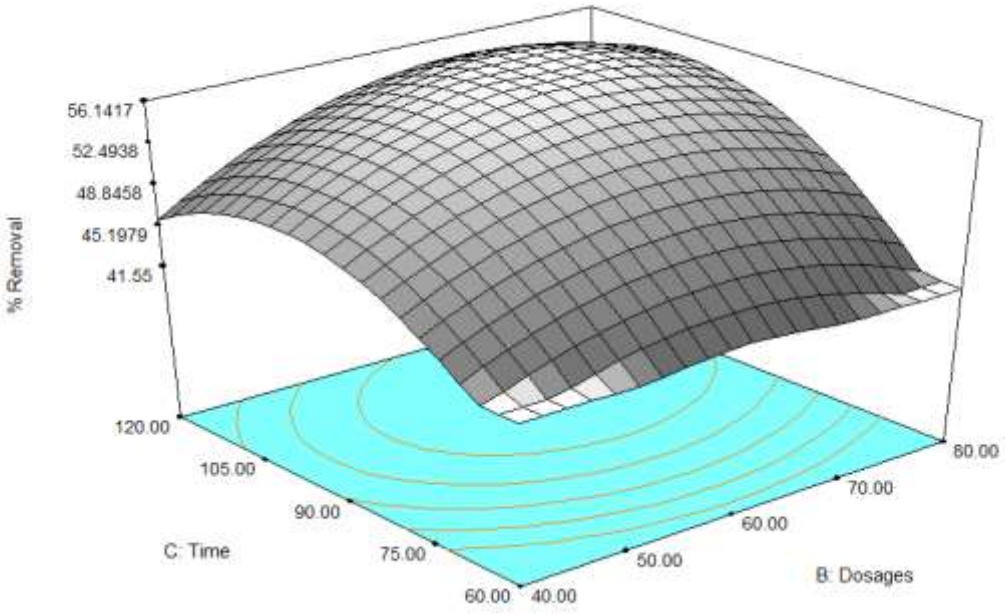

Figure 6.1: Effect of Time, dosages % rhodamine removal

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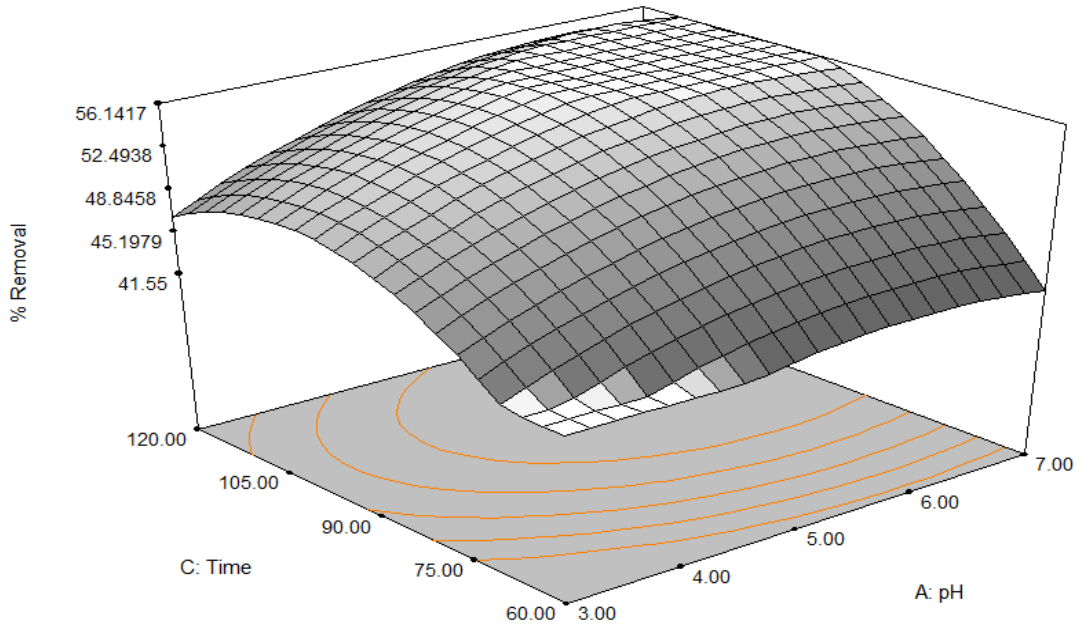

Figure 6.2: Effect of time, pH % rhodamine removal

4. Optimization:

A number of experiments were carried out for the specified sets of experimental settings provided by design expert software to investigate the combined influence of operating factors such as pH, catalyst dosages, and treatment time. Rhodamine G catalytic degradation was optimised to achieve maximal elimination of Rhodamine G from aqueous solution. The optimum parameters were predicted by the Central Composite Design (CCD) model, as shown in table 8. The trials were used to further investigate the best operating parameters provided by the CCD model. The maximum% elimination of Rhodamine G anticipated by the CCD model and attained by the trials were nearly identical, as indicated in the table that shows the efficiency of the CCD model.

Table 5: Optimum operating condition predicted by CCD and experimental test

pH	Time (min)	Catalyst dosage (mg/L)	% Removal of Rhodamine	
			CCD Pre.	Test run
6.7	104.81	50.75	55.50	54.3

5. Conclusion:

This thesis investigated the use of TiO_2 nanoparticles for the treatment of textile effluent using ultrasonication based catalytic treatment. Rhodamine G based textile wastewater was tested to see how well the particles treated the effluent. Finding the maximum removal efficiency at optimized condition for a particular set of process parameters, such as treatment time, pHand catalytic amount, was the aim of the research.TiO_2 nanoparticles were synthesised using the sol-gel method, and it was used inultrasonication based catalytictreatment process to purify wastewater. The sol-gel approach is

superior to alternative methods for creating metal oxide nanoparticles in several ways, including being simple, affordable, requiring no expensive equipment, ambient temperature, and no pressure. It was observed after characterization, TiO_2 has a surface area of 35 m^2/g, pore volume of 0.15cm^3/g and an average particles size is 259.60 nm. Maximum degradation efficiency 55.5% was achieved at pH 6.7 reaction time 104.81 min Sonication doses 50.75 mg/lit. The maximum % removal of Rhodamine G predicted by CCD model and achieved by experiments were almost same which represents the efficacy of CCD model.

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