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Photocatalytic degradation of methylene blue in aqueous solution: Parametric optimization

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Abstract
In the present study degradation of methylene blue in aqueous solution was carried out by photocatalytic technique. The study focuses on the synthesis, and characterization of silica and its application for the degradation of methylene blue, moreover the catalytic treatment process was optimized to get maximum degradation efficiency of methylene blue in aqueous solution. The effect of process variables such as pH, doses, and reaction time were studied and optimized during the study. Maximum degradation efficiency was achieved by 60% at pH 5.8, reaction time 106.02 min and catalyst doses 68.01mg/lit.

Keywords:Nanoparticle, UV Photocatalyst, Day wastewater, Optimization and central composite Design

1. Introduction
1.1 Textile wastewater

Textile wastewater (TWW) is characterized by its color and high concentration of chemicals and stabilizers (used during the dye solubility process), which significantly harm aquatic ecosystems and the environment and limit photo activity. The textile industry generates a lot of highly colored effluents that are typically toxic and resistant to biological breakdown.Being largely non-biodegradable in both organic and waste disposal plant conditions, textile wastewater is a potential environmental annoyance.Coloured wastewater is a significance of batch processes both in the dye developed industries and, in the dye, consuming industries. The staining and environmental persistence of textile dyes are two qualities that define them. They are made to be extremely stable against oxidising chemicals, microbial attacks, sunlight, heat, and reflector.Complex chemical structures and one or more aromatic rings are frequently found in the molecules that give colour its shade. By using dynamic material in conventional effluent treatment, they are typically not eradicated from the water since they are difficult to decompose. Apart from colour, several textile dyes have the potential to cause pollution because of their harmful effects and cancer [1], as some of them contain the carcinogenic benzidine and other heterocyclic compounds. In the textile dyeing, the impacts of the dyes are improved by substances like oxidising, reluctant, light scattering agents, or gelling agents. These substances contribute to improving the impacts of water performance characteristics like total solids, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and overall oxide [2].10% of manufactured colours are lost after being discharged directly into aqueous effluent at a rate of 2% during the process of textile colouring.Wastewater has grown as one of the most significant environmental problems facing nations like China or India as they strive to rank among the world's major industrialised nations.China's textile sector is booming, contributing 7.6% of the nation's total commercial output in 2010. Yet, water pollution in China is among the worst in the world.

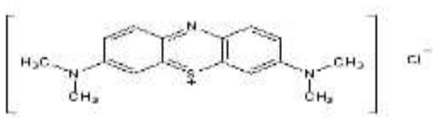
The main environmental problems caused by the textile industry include water pollution, Air pollution and soil waste pollution. The high volume of water discarded in the textile producing process are responsible for aquatic life toxicity. Air pollutant produced by the textile industry include in nitrous oxide, sulphurdioxide, hydrogen sulphide in the energy production stages. The waste produced ends up in water bodies, causing environment issues. Textile industry in harmful chemicals used they are damages our skin, they can allergic reaction, carcinogenic and mutagenic on human health. This industry is responsible for10 % of global carbon emission.

The many types of technique to treatment of textile waste water: the textile effluent collected was characterized to determine the pH, temperature, electric conductivity, biochemical oxygen demand, total dissolved solids, UV absorbers, photo catalytic treatment.

As the purpose of removing colours from water, hybrid silica and silica-based nanoparticles are being explored with significant interest. The presence of surface silanols that can complex the dyes, the simplicity of grafting additional functionalities to improve the complexation, the potential for grafting a photo catalyst to accelerate dye degradation, and good chemical stability are the causes of the silica nanoparticles' excellent efficacy at removing dyes from water.Silica is a crystalline compound that is an extremely common constituent is most minerals and sand. Silica is used a variety of industrial application.These silanols give the particles functionality since hydroxyl molecules can specifically complex particular substances or metal ions. By adjusting the pH level, the interactions of different molecules with ethyl-hydroxy-dimethyl silane can be improved.

1.2 Types of Dye:

Methylene blue (MB) is a representative cationic dye used by the textile industry for a variety of uses, including the colouring of paper, the dying of cotton, wool, silk, and leather, as well as the coating of photo paper. A thiazine dye with a basic makeup is methylene blue. Nucleic acids and other negatively charged cell components are stained by methylene blue. The effect of methyl blue is Industrial waste from colour dyestuff causes water contamination, which is a serious global concern. Dyeing is a common practise in multiple industries, including the leather and textile sectors. The finishing and colouring process in the textile industry was the main polluting process [3]. As dyes are resistant organic compounds that resist natural deterioration and are stable to light, dye-containing wastewater is especially challenging to treat. Textile wastewaters can be removed using a variety of techniques. Three broad categories can be used to classify dye removal techniques: biological mechanisms both chemical and inorganic [4].Methylene blue (MB), one of these dyes, poses the greatest risk to environment protection as well as human health due to its toxicity, nontoxicity, and non-biodegradability.Thus the, MB extraction from wastewater involves the development of an effective, ecologically friendly technology. For the elimination of MB, photo catalysis is a popular chemical oxidation method.A popular advanced treatment technique to eliminate MB is photo degradation.



1.3 Catalyst/Nanocatalyst:

The synthesis of nanoparticles for various methods are available such as: 1. Chemical vapour deposition,2. Micro emulsion processing, 3. combustion synthesis,4. Hydrothermal technique, 5. Plasma synthesis,6. Sol-Gel processing. Among these processes, sol-gel process is cheap technique and popular method for synthesis of nanoparticles. The scientific world has paid particular attention to silica nanoparticles because of its numerous uses in things like electronic devices, insulators, catalysis, and medicines. Because they differ from their bulk counterparts in having good electrical, optical, and magnetic properties, the oxide nanoparticles produced by various ways appear to be more beneficial [5].

2. Materials & Methods

2.1 Reagents and Chemicals:

Ammonia (NH_3), absolute ethanol, Tetraethoxsilane (TEOS) and distilled water have been used in this work.Chemicals are being used without any extra filtration. 0.1 M NaOH and 0.1 M HCl is used for pH maintenance.Distilled water is used for dilution purpose.

2.2 Synthesis Procedure of Silica Particles:

Some conventional process is used to create silica nanoparticles, and the process parameters are listed in this.Take 30mL of pure ethanol and 5 mL of TEOS were combined and then dissolved under low frequency ultrasound at room temperature for10 min.Then, to aid in the hydrolysis of TEOS in the ultrasonic bath, 1 mL of distilled water was added to the reaction medium at a feed rate of 0.2 mL min-1. At a feed rate of 0.01 mL min-1, 2 mL of ammonia (the catalyst) was added to the reaction mixture after 1.5 hours.The sonication continued for three hours. Gelation was permitted for one hour. After centrifuging, the gel was cleaned with ethanol and distilled water.Drying was done either in a regular oven set to 70 degree Celsius for 24 hours. Drying could have been done in a standard oven for a full day at 70 ° C.

2.3 Analytical Characterization:

Scanning Electron Microscopy (SEM): SEM is produce images of samples and particles size. X-Ray diffraction (XRD): XRD finds of properties such as crystalline phase, crystalline structure and pressure. Brunauer-Emmet -Teller(BET): The BET analysis is commonly used for surface area, pore volume and pore size of nanoparticles. UV spectrophotometer is use for wavelength accuracy and absorption.

2.4 Experimental Set-up:

The dye waste water was used at a concentration of 20 ppm, and after silica powder was diluted in it for the various doses while maintaining the various pH levels, the solution for the various doses was placed in the magnetic stirrer for the various periods of time and it was required to be present in the UV reactor that shows in the figure 1. After that we was analyzed to absorption of sample from spectrophotometer.

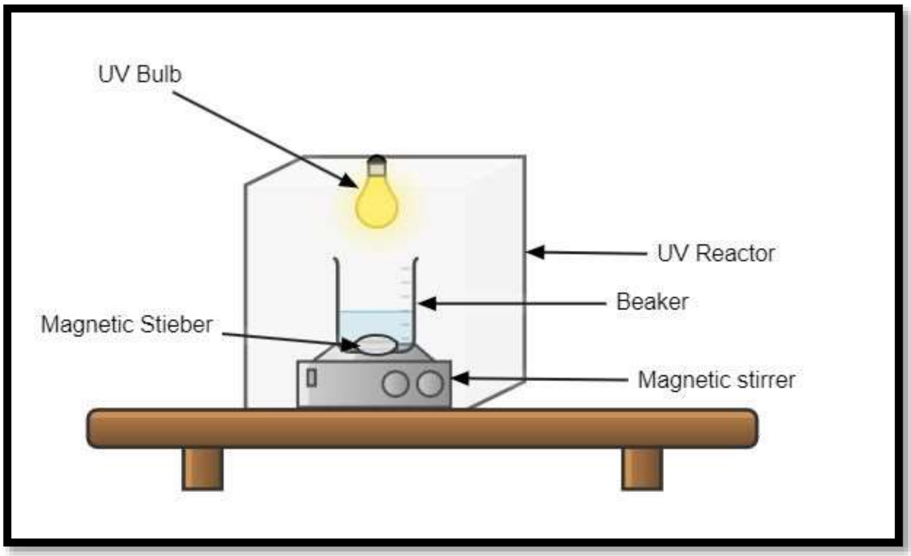


Figure 1: Experimental set-up

2. 5 Treatment of textile wastewater using Photo catalysis:

This waste constitutes a substantial danger to environmental and human health toxic and carcinogenic of textile dyes.There are several accepted methods for reducing these types of pollutants, including evaporation, aerobic conditions therapies, gelation, cell wall nuclear energy and absorption, etc. [6-10].In addition to these techniques, Photo catalyst connected with nanoparticles have shown promise for the removal of organic pollutants. In the recent years, a variety of microelectronic metallic nanoparticles, nanowires, and Nano flowers have been used as photo catalysts to XRD breakdown the assortment of neural dyes made from waste water and UV radiation.Due to the fact that dyes are thought to be the most prevalent industrial toxins, they also are the substrates that have been tested the most in photo catalytic degradation when exposed to solar light [11-12]**.**

2.6 Experimental Design:

Response of surface methodology is an effective statistical tool for processing optimization. The various operating parameter are viz. pH (3 – 7), time (60-120min) and dosages of silica(40-80mg/L) during the treatment of photo catalytic with silica as shown in Table 1. Around 17 experimental sets were given by CCD tool as shown in Table 2.

Table 1: Operating parameters and their levels obtained from the statistical software for Photo catalytic with Silica

Central Composite Design Characteristics			
level	**Parameter Range**		
	X1	**X2**	**X3**
	pH (3-7)	Dosage (mg/L) (40-80)	Time (60-120) (min)
-1	3	40	60
0	5	60	90
+1	7	80	120

Table 2: CCD predicted experimental sets for photocatalytic of silica

No	pH	Doses	Time
1	3	40mg	90min
2	7	40mg	90min
3	3	80mg	90min
4	7	80mg	90min
5	3	60mg	60min
6	7	60mg	60min
7	3	40mg	120min
8	7	80mg	120min
9	5	40mg	60min
10	5	80mg	60min
11	5	60mg	120min
12	5	60mg	120min
13	5	60mg	90min
14	5	60mg	90min
15	5	60mg	90min
16	5	60mg	90min
17	5	60mg	90min

3. Result & Discussion

3.1 Silica particle characterization:

3.1.1 X-Ray diffraction (XRD):

X-ray diffraction patterns have been extensively employed in nanoparticle research as a major characterization tool for obtaining crucial properties such as crystalline phase, crystalline structure, and pressure.The smallest unfiled regions or sequentially reflecting areas of such substance are measured by the size derived from the broadening of the x-ray diffraction peak.Figure 2 shows various peaks from the XRD analysis.

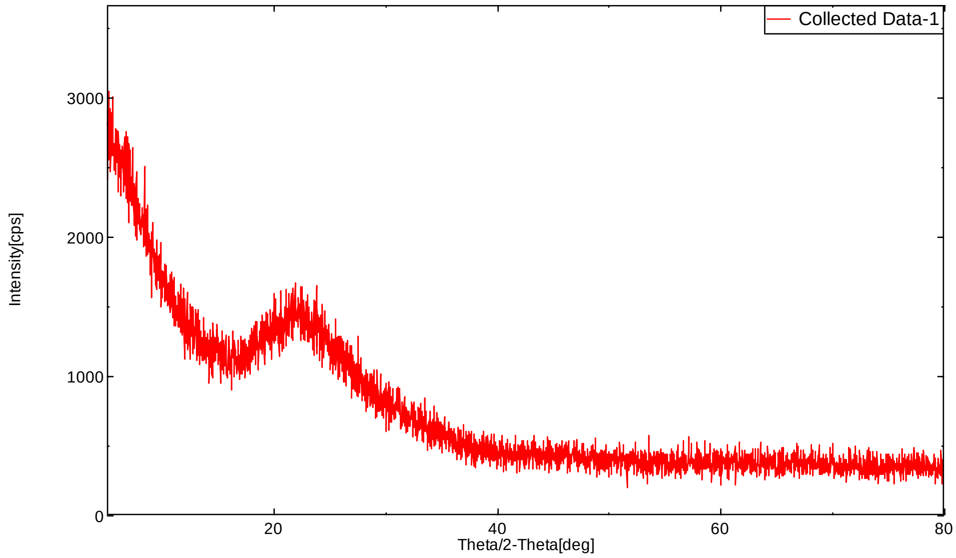
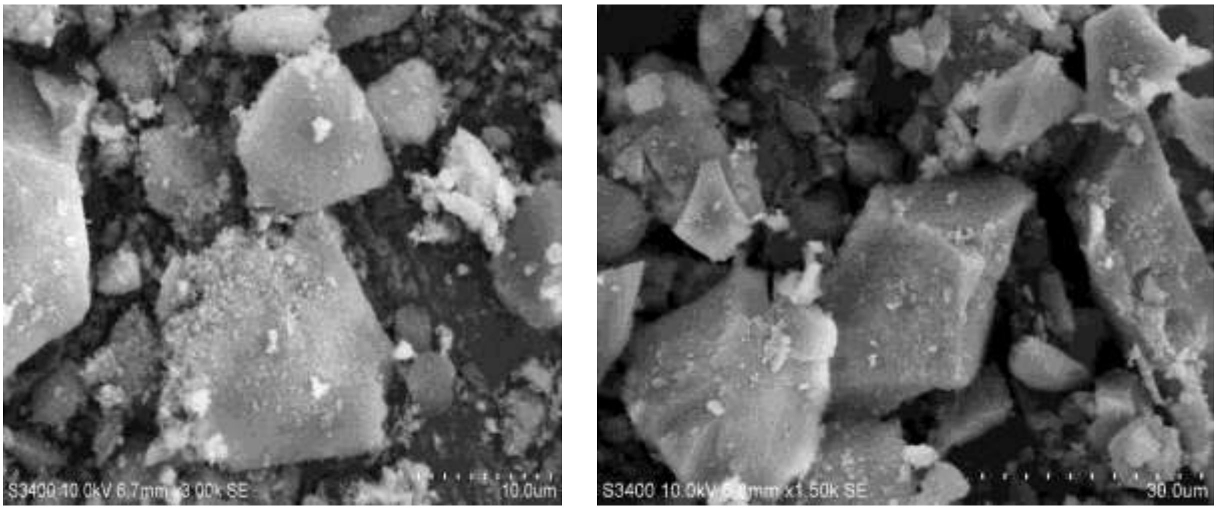


Figure 2: XRD Analysis

3.1.2 Scanning Electron Microscopy (SEM):

The distribution of silica nanoparticles generated in extract is clearly seen in the SEM scans in Figure. The resulting powders varied in particle size from below 7-50 nm with slight variations, and they were uniform and agglomerated. Below the SEM image was represented by the different magnitude and different scale show in below figure 3.



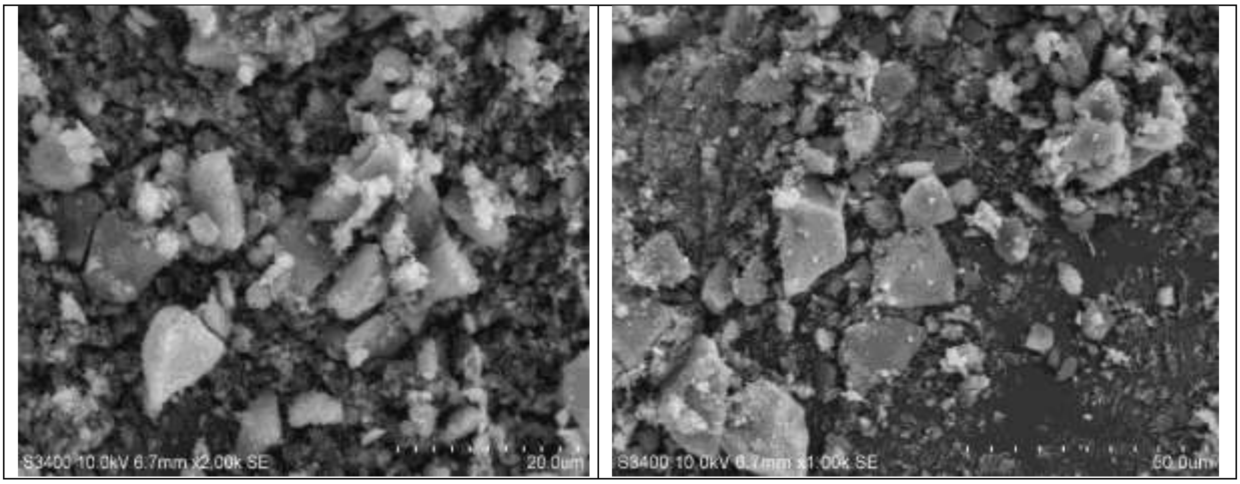


Figure 3: SEM analysis

3.1.3 BET(Brunauer-Emmet-Teller) Analysis:

It is the nanoparticles' large specific area that determines a totalization of the visible surfaces' surface areas for each energy unit of the particles. The opposite exists. Surface and crystallite size relationships space.The total surface area is calculated using this bet technique shown in the table 3.

Sr. NO.	BET Analysis	Result
1	Surface area	203.9580 m^2/g
2	Pore volume	1.169393 cm^3/g
3	Pore size	22.940 nm

Table 3: BET Analysis

3.2 Effect of operating parameters: pH, treatment time, and catalyst doses:

The effect of ph (3-7), catalytic doses (40-80mg/lit) and treatment time (60-120min) work examine for degradation of methylene blue as presented in figure: 4(a), 4(b), 4(c) from the following figures it can be observed that the maximum degradation of methylene blue was achieved at pH 5.8, 68.01mg/lit of photo catalytic does and approximately 106min of photo catalytic treatment of aqueous solution of methylene blue. The maximum degradation of methylene blue was observed at 60% at optimal parameters as presented in table no.4

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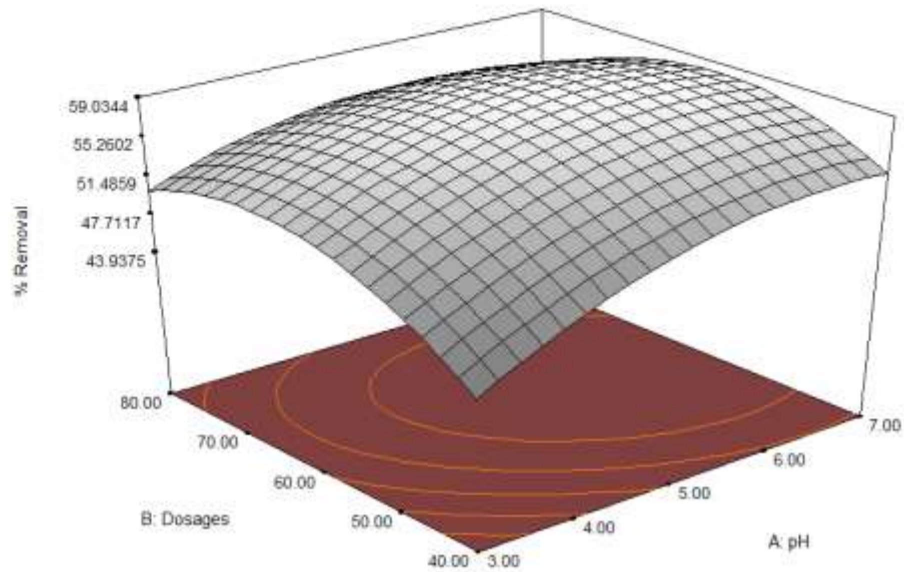

Figure 4: (a) Effect of pH, Dosages and % removal

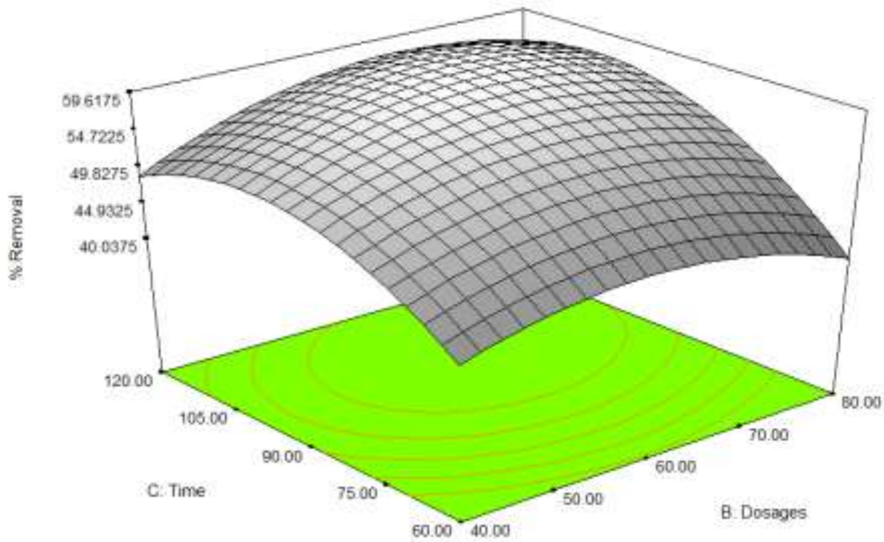

Figure 4: (b) effect of Dosages, time and %removal

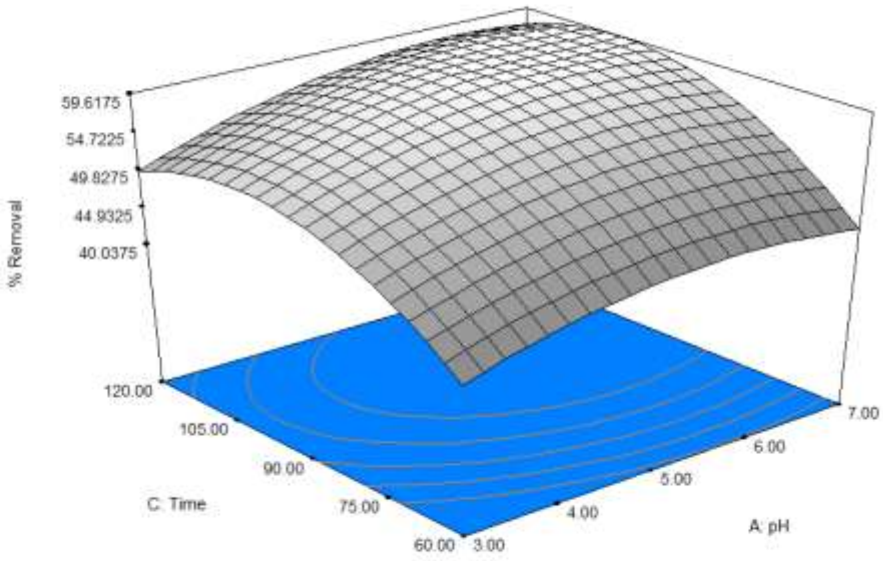

Figure 4: (c) effect of pH, time and %removal

4. Optimization:

Expert softwareto examine the combine effect of operating parameters such as pH, catalyst doses, and treatment time, number of experiments were conducted for the given sets of experimental conditions given by design. Photo catalytic degradation of methylene blue was optimize to get maximum removal of methylene blue from aqueous solution. Central Composite Design (CCD) model has predicted the optimum parameters as presented in Table4. The optimum operating parameters given by the CCD model were further examined by conducting the experiments. The values of the maximum % removal of methylene blue predicted by CCD model and achieved by experiments were almost the same as shown in the table which presents the efficiency of CCD model.

Table 4: Optimum operating conditions predicted by CCD and experimental test

pH	Time (min)	Dosage(mg/L)	% Removal of Methylene Blue	
			CCD Pre.	Test run
5.8	106.02	68.01	60	58.3

5. Conclusion

This thesis investigated the decolonization of textile wastewater using silica nanoparticles. Sol-gel processes were used to create the silica, resulting in nanostructured compounds. The efficacy of nanoparticles were tested to degrade the methylene blue from the aqueous solution. Finding the optimized dose of silica particle for a particular set of process variables, such as duration, pH, dosage type, and concentration, was the goal of the research. It was observed that the surface area of silica particles is 203.9580 m^2/g and pore volume is 1.169393cm^3/g by BET analysis. The effect of process variables such as pH, doses, and reaction time was studied and optimize during the study. Maximum degradation efficiency was achieved 60% at pH 5.8 reaction time 106.02 min photo catalyst doses 68.01mg/lit. The maximum % removal of methylene blue predicted by CCD model and achieved by experiments were almost same which represents the efficiency of CCD model.

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