TiO_2 Nanoparticles as Bifunctional Adsorbent/Photocatalyst for Degradation of Effluent from Local Dairy in Telangana

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Abstract

Contamination of precious life sources with industrial waste including dairy effluent is an increasing concern worldwide. Over the past few years, titanium dioxide nanoparticles have drawn worldwide attention as an efficient photocatalyst and adsorbent for wastewater treatment. The current study refers to the potential of nitrogen doped titanium dioxide nanoparticles as an adsorbent and photocatalyst to purify wastewater from the local dairy to meet the quality of wastewater discharged into public sewers. The Nitrogen doped titanium dioxide (TiO_2) Nano Materials were prepared by sol-gel technique and calcined at various temperatures. Characterization techniques such as SEM, XRD and FTIR were performed and Zeta potential was estimated. Efficiency of degradation as applied to dairy effluent has been examined varying the parameters such as time of exposure and dose of nanoparticles along with solution pH variation monitored during study. A good reduction in COD of about 99 % was observed after treatment under visible light. It is observed that calcining temperature affects activity of TiO_2 nano particles. Furthermore, statistical analysis that represent experimental response as a function of independent parameters as well as analyse the interaction between the parameters was successfully employed. The results showed that TiO_2 nanoparticles can be employed as adsorbents for the treatment of dairy waste water.

Keywords: Adsorbent, Chemical oxygen demand, Dairy effluent, Doping, nanoparticles, TiO_2

1. Introduction

The rate of water pollution has increased due to expanding industrialization and rapid urbanization. This is an important limitation as the natural deposits of water are diminishing and uncompromising regulatory prohibitions for wastewater discharge quality have been imposed by environmental protection agencies [1]. Wastewaters from industries based on agriculture and farming are characterised by chemical oxygen demand (COD) that is high due to their high level of organic contents [2]. The dairy industry generates a huge amount of wastewaters: approximately 0.2 L to 10 L of waste per litre of milk that is processed [2]. Different pollutants for instance organic matter, nutrients of spilled milk, microorganisms, detergents , alkalis, and acids are contained in these effluents [3]. Attributing to the highly dissimilar nature of this industry, wastes of different quality and quantity are created in product processing, handling, and packaging operations. If such waste is not treated, it could lead to increased disposal and severe pollution problems [4]. All chemical, physical and biological methods used to treat wastewater set limits based on implementation, efficiency, and cost [1, 5]. The factors such as, restrict pH range, swift organic-load variations, and the effluent's physical-chemical characteristics check the degradation efficiency of the biological processes that have been widely used for dairy wastewater treatment [5, 6]. Adsorption is a promising technique because of its ease of use, increased proficiency, low-cost requirements, and great reproducibility [7]. Furthermore, because the process is usually reversible, the adsorbents can be readily regenerated and reused [8]. Additionally, the availability of a diverse spectrum of adsorbents makes the adsorption process adaptable to specific requirements [9].

Considering the wide band gap (3.2 eV) under ultraviolet light of titanium dioxide, it is verified to be one of the most reliable n- type semiconductors. This widely researched material has high physical stability, chemical stability, refractive index and it finds application in fields such as photocatalysis, solar cells, sensors, self-cleaning, and bactericidal action as a result of its optical and electronic properties [10]. Ti02 absorbs light of wavelength 400 nm or shorter [11]. To make the most effective use of sunlight or radiation from synthetic sources in photocatalytic reactions, photocatalysts with strong visible region absorption must be developed. For this purpose, doping of Ti02 with transition metals has been investigated [12]. Few of the photocatalytic reactions would advance under visible light by treating TiO_2 powder with hydrogen peroxide or chelating agents [11]. N-doped TiO_2 shows photo absorption at wavelengths 400 nm or longer [13].

The S-doped Ti02 particles showed strong absorption in the visible light region and high activity to degrade aqueous solution of methylene blue under light beam at wavelengths of 440 nm or more [11]. The nitrogen doped TiO_2, displayed higher photocatalytic performance under imitated sunlight, and 100% removal of Flumequine a typical water pollutant was achieved in 4 hours of exposure [14]. Under visible light irradiation, TiO_2 doped with N, demonstrated photocatalytic activity for 2-propanol decomposition in aqueous solution. A higher absorption in the visible light region was observed [15]. Most studies related to nano-TiO_2 have focused more on the photocatalytic degradation of pollutants. However, of the adsorbent properties of nano-TiO_2 should also be taken into consideration, as efficient nano-TiO_2 adsorbent might facilitate better contact between substrate molecules and surfaces of reactive species on nano-TiO_2 in the pre-photocatalysis phase [16]. To reduce the dependency on photocatalysis, the structure of nano-TiO_2 could be modified to increase the number of adsorption sites [16]. The present study reports the synthesis of Nitrogen doped and calcined TiO_2 nanoparticles and their efficiency of degradation of dairy effluent under visible light.

2. Material

The dairy effluent was generously provided by a local industry, Vijaya dairy in the city of Secundarabad, India. It was refrigerated for subsequent use. The physico-chemical data of the collected diary industry effluent is presented in Table 1. Other chemicals used in the study such as Titanium Isopropoxide, Zinc nitrate, Cetyl trimethylammonium bromide (CTAB), Ammonia solution, Iso propyl alcohol, potassium dichromate ($K_2Cr_2O_7$), ferroin indicator, and Ammonium ferrous sulfate were analytical reagent grade and procured from Hychem laboratories, Hyderabad. Purified water was used for all the experiments.

Table 1: Physiochemical parameters of dairy effluent

Parameters	Value Range
Color	Whitish Grey
pH	5.3
Total dissolved solids, TDS	920 PPM
Chemical oxygen demand, COD	936 PPM

3. Experimental

3.1 Synthesis and characterization of TiO_2 nanoparticles

The procedure mentioned in our previous work [17] was followed for the synthesis and characterization of doped and calcined titanium dioxide nanoparticles. In addition physical properties of TiO_2 nanoparticles including size and polydispersity index have been illustrated for different samples.

3.2 Treatment of dairy effluent

Batch experiments were conducted for degradation of procured dairy effluent using doped TiO_2 nanoparticles. Each experiment was performed by adding known amount of nanoparticle to 20 mL of dairy effluent of known pH and initial concentration (COD=936 PPM). The above suspension was magnetically stirred for 30 minutes in the dark to obtain an adsorption-desorption equilibrium and to eliminate the error due to any initial adsorption effect Next the dairy effluent sample was irradiated with fluorescent tube, a low-pressure mercury-vapor gas-discharge lamp that uses fluorescence to produce visible light and was maintained at this condition for the predetermined time. After settling the supernatant was filtered through whattmann filter paper and analyzed for COD. Variation in the pH of the suspension was recorded. It is preferable to have a pH independent adsorbent with highest adsorption capacity at pH near to a given water. The use of expensive chemicals to alter the pH might be eliminated, especially for large plants.

3.3 Analytical methods

For analysis of Chemical Oxygen Demand, mixture of $K_2Cr_2O_7$ is added to waste water sample and digested employing a heater. Once the bubbles appear, Ferroin Indicator is added. Pale green colour is observed. It is cooled and then titrated against Ammonium Ferrous Sulphate (FAS) until it turns blue, followed by wine red finally. The burette reading gives the amount of the ammonium ferrous sulphate required to degrade the excess $K_2Cr_2O_7$. COD is calculated from equation (1) and % COD removal from effluent after treatment is calculated from equation 2.

$$COD = ((\text{Blank titre value} - \text{waste water titre value}) * \text{N} * 8 * 1000)/\text{V} \quad (1)$$

$$\%\ \text{COD removal} = \frac{\text{C}_\text{o} - \text{C}_\text{t}}{\text{C}_\text{o}} * 100 \quad (2)$$

Where N is the normality of FAS, V is the volume of FAS, C_o is the initial effluent concentration (mg/L) and C_t is the concentration of the dairy sample at time t.

4. Statistical technique:

Data analysis was performed using Minitab. The adsorption capacity is influenced by several factors, such as, adsorbent concentration, time of exposure, temperature, stirring rate and pH [18]. Among these, the influence of, time of exposure, adsorbent dose and calcining temperature of the nanoparticles are verified, and the adsorption process is optimized through statistical technique, response surface [18]. Dependent parameter (% COD removal) was measured as response to conduct an adequate analysis of the process. The quadratic equation, equation 3, for forecasting optimum conditions is expressed as follows:

$$Y = \beta_o \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{i\,i} X_i^2 + \sum_{i<j}^{k} \sum_{j}^{k} \beta_{i\,j} X_i X_j + --- + e \quad (3)$$

where Y is the response, X_i and X_j are the variables, β_0 is a constant coefficient, $\beta_i,\ \beta_{i\,i}, and\ \beta_{i\,j}$ are the interaction coefficients of the linear, quadratic, and second-order terms, respectively, *k* is the number of studied factors, and *e* is the error. The quality of the fit polynomial model was expressed by the coefficient of determination R^2.

5. Results and Discussion

The zeta potential (mean) of the nanoparticles calcined at various temperatures is shown in the table 2. Nanoparticle calcined at 800 ^oC has a zeta potential of -48 mV, indicating good dispersion and interaction with the effluent solution [17].

5.1 Effect of nanoparticle amount

The consequence of varying amount of TiO_2 nanoparticle used, with regard to degradation of the dairy effluent was examined and the results are shown in figure 1. The COD removal efficiency proliferated with the build-up in the amount of nanoparticles. The concentration of 5 g/L of doped TiO_2 degraded around 94.1% of photocatalyst in 120 min. However with increase in the concentration of TiO_2 the percentage COD removal reduced first and then remained constant [19, 20, 21]. The cause of this may be the fact that the light penetration depth is smaller for an effluent- photocatalyst suspension with higher concentration of photocatalyst as compared to a suspension of 5 g/L of photocatalyst [19]. Hence the turbidity of the concentrated suspension may inhibit the penetration of light [19]. Also it has been reported that, with the increase in dose, the adsorbent particle can agglomerate leading to the reduction in surface area available for adsorption and higher diffusion path length [22]. Solution pH varied from 7.4 to 7.7 during the study.

Table 2: Physical properties of TiO_2 nanoparticles

Sample No.	Calcining temperature (^{o} C)	Intensity weighted mean hydrodynamic size of particles, Z average, nm	Polydispersity index	Zeta potential (mV)
1	200	176.6	0.5	-34.5
2	400	169	0.6	-32.1
3	600	162.6	0.7	-37.7
4	800	197	0.4	- 48.1

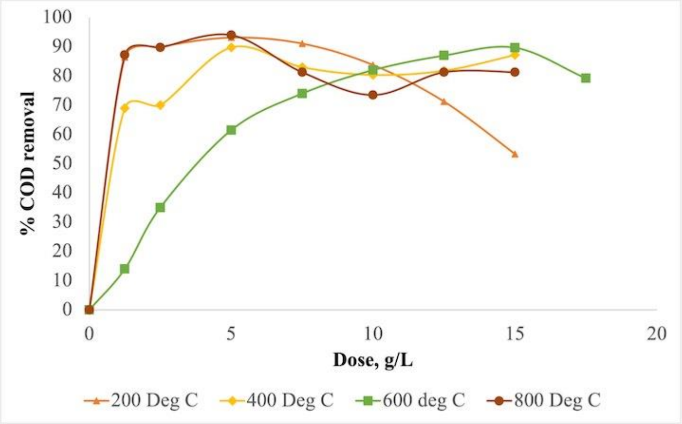

Figure 1: The effect of nanoparticle dose on COD removal from dairy effluent

5.2 Effect of time of exposure

Figure 2 shows the percentage COD removal of dairy effluent with 5 g/L of doped TiO_2 nano particles calcined at different temperatures for various time of exposure. It is noticeable that degradation increases with increasing time. This concentration of doped TiO_2 achieved about 99 % of COD removal in 150 min. The mixture pH varied from 7.2 to 7.9 during the study. It was noticed that activity decreased with high exposure time after around 3.5 h. The reason behind this may be that some released by-products covered the catalyst active sites or the doped N may have been released from the TiO_2 nanoparticle surface [15, 19].

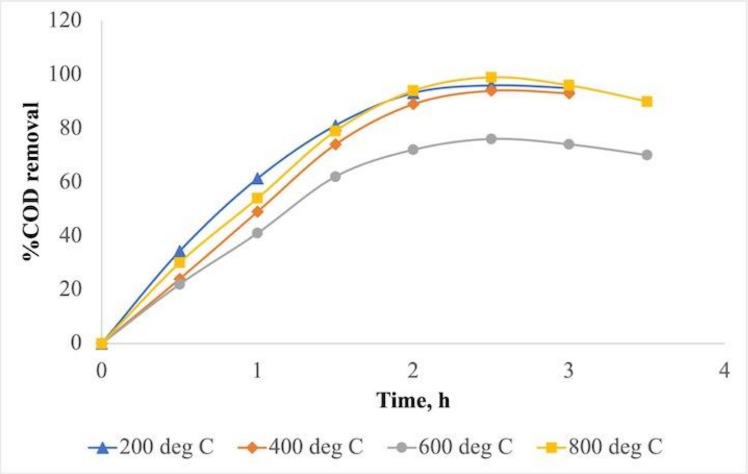

Figure 2: The effect of exposure time on COD removal from dairy effluent using doped and calcined TiO_2 nanoparticle

5.3 Effect of doping and calcining temperature

There have been reports that the calcining temperature effects the photocatalytic activity [21]. The results illustrated in figure 1 and 2 confirms that the doped TiO_2 photocatalytic nanoparticles calcined at 800 ^oC provides a good COD removal efficiency of about 99 %. Transformation of anatase to rutile phase in TiO_2 occurs at elevated temperature of around 850 ^oC [23] and may be lowered by the use of dopant [21]. Also there are reports that presence of mixture of anatase and rutile phase, having large surface area in TiO_2 and leads to improved activity [21]. These may explain the higher photocatalytic activity of TiO_2 calcined at 800 ^oC. Also doping with nitrogen modifies the surface of $TiO_{2,}$ provides more electrostatic binding sites for effluent molecules, and improves the activity of TiO_2 under visible light as confirmed by other authors [24].

5.4 Statistical analysis

The response variable % COD removal is denoted as Y and the independent variables namely dosage of the nano particles, calcination temperature and time of exposure are denoted as A, B and C respectively. The final constructed model is as shown in equation 4,

$$Y = 13.0 + 4.90 A - 0.1437 B + 70.5 C - 0.320 A^2 + 0.000144 B^2 - 13.24 C^2 - 0.00255 AB + 0.00274 BC \quad (4)$$

The coefficient of regression R^2 was used to validate the fitness of the model equation. For the R^2 value of 0.9279 showing that 92.79 % of the variability in the response can be explained. From the figure 3 it can be seen that the points are closely distributed to the straight line of the plot; it confirms that the selected model was adequate in predicting the response variables in the experimental values. The response surfaces are shown in the figure 4 A, B, and C. A surface plot contains the predictors on the x- and y-axes and a continuous surface that represents the response values on the z-axis. The peaks and valleys correspond with combinations of x and y that produce local maxima or minima. Minitab uses interpolation to create the surface area between the data point because a surface plot shows only two continuous variables at a time, any extra variables are held at a constant level. A The curved response surface means the model contains quadratic terms that are statistically significant.

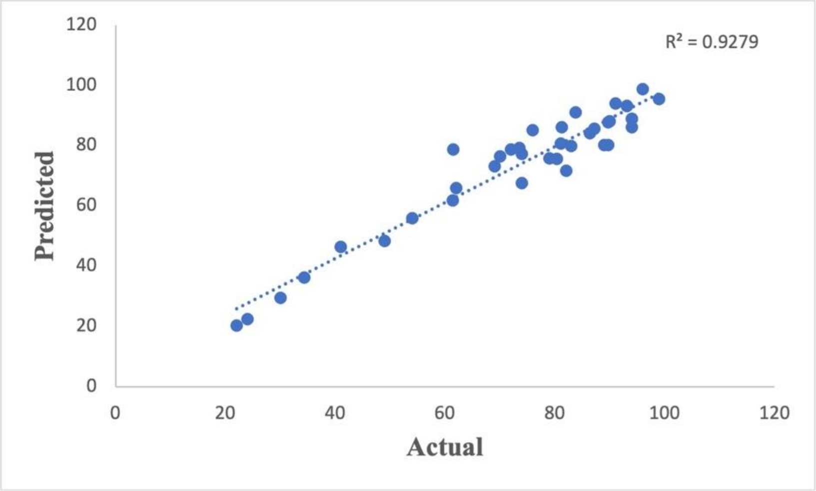

Figure 3: Predicted versus actual plot for COD removal with TiO2 nano particle

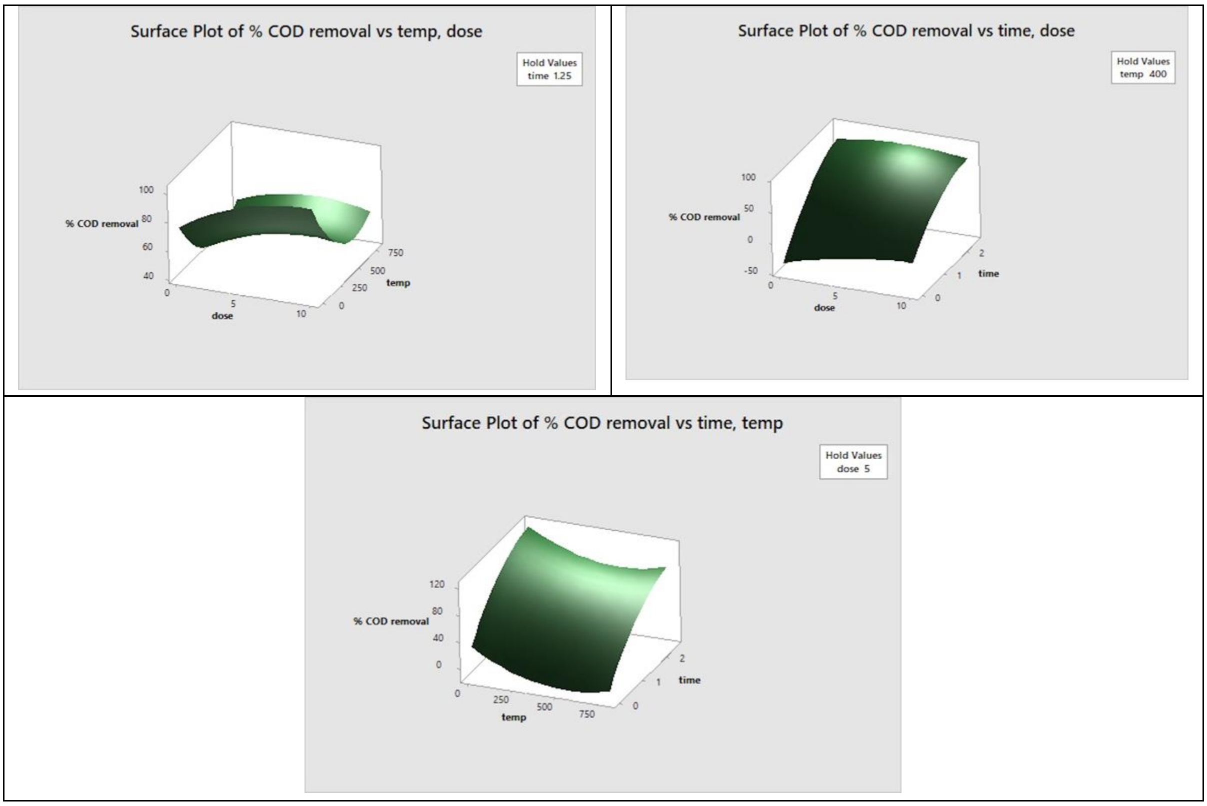

Figure 4: Combined effect of operational parameters (A) COD removal based on calcining temperature and dosage; (B) COD removal based on time and dosage; (C) COD removal based on calcining temperature of particles and time

6 Conclusions

In this work the effect of doped TiO_2 nanoparticles as adsorbent and photocatalyst under visible light for COD reduction of dairy industry effluent was investigated. The aim was to determine COD removal efficiency of the bi functional adsorbent/ photocatalyst under visible light and to optimize process parameters such as time of exposure, dosage of photocatalyst and calcining temperature of photocatalyst. Doping and calcination provides more surface area and electrostatic binding sites and improves the photocatalytic performance under visible light. The optimal operation parameters were adsorbent dose of 5 g/L, exposure time of 150 min, and calcination temperature of 800 ^{o}C. Under these conditions around 99 % degradation of the dairy effluent was achieved. The pH after treatment is 7.7 to 7.9, meets the quality of wastewater discharged into public sewers. Statistical analysis confirmed that the developed model was adequate in predicting the response variables in experimental values.

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