Photocatalytic parameters and kinetic study for degradation of dichlorophenol-indophenol (DCPIP) dye using highly active mesoporous TiO₂ nanoparticles

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Highly active mesoporous TiO₂ of about 6 nm crystal size and 280.7 m²/g specific surface areas has been successfully synthesized via controlled hydrolysis of titanium butoxide at acidic medium. It was characterized by means of XRD (X-ray diffraction), SEM (scanning electron microscopy), TEM (transmission electron microscopy), FT-IR (Fourier transform infrared spectroscopy), TGA (thermovagametric analysis), DSC (differential scanning calorimetry) and BET (Brunauer-Emmett-Teller) surface area. The degradation of dichlorophenol-indophenol (DCPIP) dye under ultraviolet (UV) light was studied to evaluate the photocatalytic activity of samples. The effects of different parameters and kinetics were investigated. Accordingly, a complete degradation of DCPIP dye was achieved by applying the optimal operational conditions of 1 g/L of catalyst, 10 mg/L of DCPIP, pH of 3 and the temperature at 25 ± 3°C after 3 min under UV irradiation. Meanwhile, the Langmuir-Hinshelwood kinetic model described the variations in pure photocatalytic branch in consistent with a first order power law model. The results proved that the prepared TiO₂ nanoparticle has a photocatalytic activity significantly better than Degussa P-25.

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Introduction

Total water abstraction in Egypt is approximately 73 billion m³/year, which is nominally higher than the fresh water supply figure of 57.5 billion m³/year. The reason for this is that major agricultural, urban and industrial users are located on the banks of the Nile, where water is returned to the river and used more than once. The biggest user of water is agriculture, followed by industry and domestic users. Domestic water requirements in Egypt are increasing at a rapid rate and demand is expected to reach 7.6 billion m³/year by 2015, due to improvements in the standard of living and the increasing population. Industrial water needs are also increasing, and are forecast to reach 14.6 billion m³/year by 2015. The Ministry of Water Resources and Irrigation (MWRI) expects Egypt’s available water resources to reach 70.8 billion m³/year by 2025, following the implementation of new projects and the improvement of irrigation systems (Arab Republic of Egypt et al., 2005). Due to the large degree of aromatics present in dyes and the stability of these modern dyes, severe environmental pollution...
problems are created by releasing toxic and potential carcinogenic substances into the aqueous phase (Kansal et al., 2009). The adverse effects of these synthetic dyes on the environment include an increase of the color and toxicity of the waters, death of fish and zooplankton, and general affectation of ecosystems, especially on microorganisms, and its long degradation time in the environment is a cause for concern and widespread esthetic damage (Azbar et al., 2004; Sponza, 2006). These effects are persistent because the pollutants in wastewater streams in general have low biodegradability (Azbar et al., 2004; Sadik, 2007). There are a number of methods currently in use for removing pollutants from wastewater, some of which have environmental disadvantages. Air stripping, adsorption by activated carbon, chemical precipitation and ion exchange are merely a form of pollution conversion in which the original polluting materials are transformed from one phase to another, without destroying, and ultimately there is a disposal problem (Sadik, 2007). Heterogeneous photocatalysis has recently appeared as a new emerging “advanced oxidation process” (AOP) simultaneously able to be efficient in green chemistry (Blake, 2001).

The use of semiconductor oxide particles as photocatalysts is well established and has shown great utility in the complete mineralization of organic pollutants (Bianchia et al., 2014). Several semiconductors, such as TiO₂, Fe₂O₃, ZnO, ZnS, CdS, and WO₃, are known to have photocatalytic properties (Hasegawa and Mayo, 1986). Among various oxide semiconductors, TiO₂ has been intensively investigated because of insolubility, its biological and chemical inertness, strong oxidizing power, cost effectiveness, nontoxicity and long-term stability against photo and chemical corrosion under the reaction conditions (Liu et al., 2014; Lai and Sreekantan, 2012; Miranda-García et al., 2014). However, the fast recombination rate of photogenerated electron–hole pairs hinders the commercialization of this technology (Muthirulan et al., 2014). Anatase with large surface area, high crystallinity, and small crystal size is higher for photocatalytic activity, since higher crystallinity means fewer defects for the recombination of photogenerated electrons and holes (Li et al., 2009).

The following reactions summarize the possible mechanism steps. Generally speaking, from irradiation on TiO₂ photocatalyst to reduction of contaminants, the process undergoes six steps: (i) electron–hole generation; (ii) hole trapping from valence band (VB); (iii) electron transferring from the conduction band (CB); (iv) role of oxygen; (v) oxidation of organic contaminants; and (vi) charge carriers recombination (Mills et al., 1993; Herrmann, 1999). Therefore, it is of great importance to synthesize TiO₂ with particular properties, such as crystal sizes and phases, mesoporous structures and high surface areas, and to study their influence on the photocatalytic performance.

Mesoporous TiO₂ nanocrystals are promising materials for photocatalysis due to its continuous particle framework, which may be beneficial compared to the separated individual nanoparticles, especially for catalyst recovery (Ismail and Bahnemann, 2011). Mesoporous TiO₂ has a large surface area because of its confined porous structure and high surface to volume ratio. The most important factors affecting the photocatalytic activity of TiO₂ are its specific surface area in a continuous structure and its crystallinity. In the last decade, research efforts have been directed to enhance the activity of the mesoporous TiO₂ photocatalysts using various methods such as increasing catalyst surface-to-volume ratio, doping the catalyst with nonmetals such as nitrogen, carbon (Huang et al., 2008; Choi et al., 2007), transition metals (Sinha and Suzuki, 2005) and sensitization of the catalyst using dye molecules (Nagaveni et al., 2004).

The main purpose of the present study is to synthesize uniform highly active mesoporous TiO₂ nanoparticle by increasing surface to volume ratio without any templates, surfactants, structure directing agent, sensitization or doping via a sol–gel method/hydrothermal routes. Photocatalytic degradation of dichlorophenol-indophenol (DCPIP) in aqueous TiO₂ dispersions and comparison with that on Degussa P-25 under UV irradiation as well as the dependence of dye photo-oxidation rate on the following parameters: (i) Degussa P-25 and TiO₂; (ii) substrate concentration; (iii) catalyst amount; and (iv) pH were also investigated. The optimum condition to achieve the maximum degradation was determined.

### 1. Materials and Methods

#### 1.1. Materials

Chemicals used in this study are in analytical grade. An anatase-rutile mixture TiO₂ powder (P25) was kindly supplied by Degussa Corporation (Degussa Corporation, Germany). Titanium butoxide (Ti(OBu)₄, 97%) was obtained from Aldrich chemicals (Aldrich Chemicals, Germany), acetylacetone (CH₃(COCH₃)₂, 99%) was supplied from Alfa aesar (Germany), nitric acid (HNO₃, 65%) was supplied from Pharo Company (Pharo Company, Egypt). Hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH, Min. 99%) were supplied from ADWIC-El-Nasr company (ADWIC-El-Nasr company, Egypt). 2,6 Dichlorophenol-indophenol-sodium salt (C₁₂H₆Cl₂NO₂·Na, 97%) was supplied from Sigma (Sigma company, USA). Properties and structure of DCPIP dye are shown in Table 1.

#### 1.2. Preparation of Highly Active Mesoporous TiO₂ Nanoparticles

In a typical preparation procedure, titanium butoxide (Ti(OBu)₄) was used as a titanium precursor, and an acetyl acetone (acac) as a complexing agent was used to control the rate of hydrolysis and condensation reaction of the precursor. De-ionized water is used as solvent (18.2 MΩ-cm, TKA-Genpure, UK). Nitric acid

<table>
<thead>
<tr>
<th>Name</th>
<th>2,6 Dichlorophenol-indophenol (DCPIP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature</td>
<td>Anionic</td>
</tr>
<tr>
<td>λ max (nm)</td>
<td>600</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>209.09</td>
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<td>Molecular Structure</td>
<td><img src="image" alt="Molecular Structure" /></td>
</tr>
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</table>
(10%) was used as a catalyst and then was added to the mixture at a magnetic stirrer (Model Agimatric-ND, Selecta, Spain). The molar ratios of the ingredients were as follows: titanium precursor/acac/10% HNO3/De-ionized water = 1:1:3:20. The pH value of resulting solution is 3. The final solution was stirred for 6 hr at room temperature. The resulting sol was placed in an 80 mL Teflon lined stainless steel autoclave, which was then placed in an oven (Model TR60, Nabetherm, Germany) for hydrothermal treatment at 170°C for 72 hr.

1.3. Physicochemical Characterization

1.3.1. X-ray Diffraction (XRD)
Crystal phases and crystallite size of as prepared samples were obtained by an X-ray diffractometer (XRD) (XRD-Shimidzu 7000, Shimadzu, Japan) operating at room temperature with Cu (Kα) radiations of wavelength (λ = 1.5406 Å), generated at 30 kV and 30 mA. The 2θ range for all samples are in the range of scan step size 10° < 2θ < 80° with a scan speed of 4°/min.

The average crystallite size was estimated by applying the Scherrer equation (Eq. (1)) to the apparent full width at half maximum intensity (FWHM) of the (101) peak of anatase TiO2 or the (110) peak of rutile TiO2:

\[
L = \frac{K\lambda}{\beta \cos \theta}
\]  

(1)

where, \(L\) (Å) is the crystallite size, \(\lambda\) (Å) is the wavelength of the X-ray radiation, \(K\) is usually taken as 0.89, \(\beta\) (radians) is the line width at half-maximum height and \(\theta\) (degree) is the diffraction angle.

The phase composition of the samples can be calculated from Eq. (2).

\[
X_R = 1 - \frac{1}{1 + \frac{1.26P}{I_K}}
\]

(2)

where, \(X_R\) is the weight fraction of rutile in the mixture, and \(I_R\) and \(I_K\) are the relative intensities of the strongest diffraction peaks rutile and anatase, respectively.

1.3.2. Morphological Characterization
The prepared samples were examined with a scanning electron microscope (SEM) (Model JSM-6360 LA, JEOL, Japan) to investigate the homogeneity and the morphology of samples. Prior to the investigation, the samples were coated with gold using sputtering coater (model: S150B, Edwards High Vacuum Ltd., UK) in order to avoid the build-up of local electrical charges.

Crystallite sizes and shapes of the prepared samples were confirmed by transmission electron microscopy which was performed on a transmission electron microscopy (TEM) (JEM-1230, JEOL, Japan) with Max. Mag. 600,000× and resolution 0.2 nm. Samples for TEM measurements were suspended in ethanol and ultrasonically dispersed. Drops of the suspensions were placed on a copper grid coated with carbon.

The compositional and elemental analyses of the prepared TiO2 nanoparticle were determined by energy dispersive X-Ray analysis (EDAX) combined with the scanning electron microscopy (Model JSM-6360 LA, JEOL, Japan). The inner most electron shell was called the K shell and the next inner most shell was L shell, where all shells had subshells (\(\alpha\) and \(\beta\)).

FT-IR (Fourier transform infrared spectroscopy) spectra of titanium dioxide recorded using a FT-IR spectrophotometer (8400 S, Shimadzu, Japan). IR transmission spectra were taken from test samples, which were pressed into KBr-supported disks, in the range from 400 to 4000 cm⁻¹. The scanning rate was 2 cm⁻¹ sec⁻¹.

Stability and weight loss from the as prepared samples were investigated by TGA (thermogravimetric analysis) using apparatus (TGA-50 H, Shimadzu, Japan) with heating rate of 10°C/min under a flow of N2 (30 mL/min) up to 600°C and DSC (differential scanning calorimetry) was performed for samples with the heat flux Shimadzu (DSC-60 A, Shimadzu, Japan), in an inert atmosphere of nitrogen flowing at the rate of 30 mL/min with the temperature scanned in the range of 30–600°C and heating rate of 10°C/min. DSC was used to determine the peak of endothermic or exothermic and specific heat.

Surface area was determined using a Coulter SA 3100 nitrogen adsorption apparatus (Coulter SA 3100 nitrogen adsorption apparatus, Coulter, USA). Specific surface areas were used to determine an automated N2 adsorption manifold. Adsorption and desorption of samples were performed at 77 K to a relative pressure (\(P/P_0\)) of approximately 0.95. Standard procedures for this out gassing step usually required holding samples in a vacuum at 200°C for about 4 hr.

UV/Vis (Ultraviolet/visible) spectrophotometer was used to monitor the electronic energy level of a molecule. After preparation of samples, the wavelength and absorbance were measured using an ultraviolet-visible spectrophotometer (Spectro UV-Vis Double Beam PC Scanning, Model UVD-2960, Labomed, Inc.).

1.4. Bench Scale Slurry Photoreactor
Dye and catalyst were placed in a glass container (1 L) and agitated by means of a magnetic stirrer. Dry air was fed into the solution as a source of oxygen. A tubular low pressure mercury vapor source (total rating 43 W, total UV output at 254 nm 13.4 W, length 120 cm, VALBER LOURMAT, Germany) was used to irradiate the solution which was located 10 cm from the surface of the source. The total intensity reaching the slurry solution was measured by a UVX radiometer (UV products Ltd., Cambridge, UK) equipped with a sensor with the peak sensitivity at 254 nm being 4 mW/cm². The local volumetric rate of energy reaching the solutions was 2.1 µEinstein/(sec·L) at 254 nm. Schematic representation of the bench slurry photoreactor is shown in Fig. 1.

1.5. Determination of the Photocatalytic Activities
The photocatalytic performance of the as prepared TiO2 was used to determine by using the photocatalytic decomposition of DCPIP in aqueous solution under ultraviolet irradiation.

The degradation reaction was carried out in a slurry photocatalytic reactor. Polluted waste water was prepared by dissolving a known weight of dye in distilled water. The reaction mixture was maintained as a suspension by
magnetic stirring. Then, the mixture was placed inside the photoreactor and air was fed into vessel with a rate of 4 L/min. The reaction was conducted under vigorous agitation to ensure uniform distribution throughout the reacting medium. At different time intervals, aliquots were taken out with the help of a syringe and then filtered through a Millipore sterile syringe filter of 0.2 μm (NY 14831, Corning, Germany). These experiments were carried out at a natural pH, which was 6.7 and the reaction temperature was kept constant at room temperature as 25 ± 3°C. The pH value was adjusted using 0.5 mol/L HCl or 0.5 mol/L NaOH. The photodegradation efficiency \( R \), % of 2,6 dichloroindophenol dye could be calculated according to Eq. (3):

\[
R = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\%
\]

where, \( C_0 \) (mg/L) is the initial concentration of dye solution, \( C_t \) (mg/L) is the concentration of dye solution after photoirradiation at time \( t \) (min), \( A_0 \) is the value of absorbance of dye aqueous solution after adsorption in the dark, and \( A \) is the value of absorbance of dye aqueous solution after reaction.

Photocatalytic reactions are affected by many factors, each of which has the potential to influence the reaction rate. Optimization of these conditions has the ability to increase the process efficiency and is important in enabling complete contaminant degradation in a shorter time. The photocatalytic oxidation of DCPIP dye was carried out in aqueous suspensions of polycrystalline TiO\(_2\) (anatase) irradiated by UV light. The dependence of dye photo-oxidation rate on catalyst type, catalyst amount, substrate concentration and pH was investigated.

![Schematic diagram of bench slurry photoreactor.](image1)

**Fig. 1** – Schematic diagram of bench slurry photoreactor.

### 2. Results and Discussion

#### 2.1. Characterization of the Photocatalysts

**2.1.1. X-ray Diffraction Studies**

Wide angle X-ray diffraction patterns were measured to determine the TiO\(_2\) crystal composition as shown in Fig. 2a. The main peaks corresponding to standard anatase TiO\(_2\), including (101), (004), (200), (105), (201), (204), (116), (215), were observed. The broaden diffraction peak was with a crystallite size of about 6 nm and the most phase was anatase without rutile. The diffraction peak of P25 had anatase and rutile structure, and its crystal size was approximately 18 nm with anatase and 23.29 nm for rutile phase. Degussa P-25 contained 24.68% for the rutile phase. The photocatalytic structure of as prepared sample was confirmed by the low angle XRD patterns, as shown in Fig. 2b. A broad peak was observed, indicating the existence of worm-like mesoporous structure in the sample (Yu et al., 2003) and in Degussa P-25 the peak was weak and broad as compared to as prepared titania, and shifted to a higher 2\( \theta \) angle.

**2.1.2. Electron Microscopy Studies**

Fig. 3a and b shows the SEM images of synthesized material and TiO\(_2\) Degussa P-25. The morphology of synthesized material and TiO\(_2\) Degussa P-25 had spherical shape with high homogeneity and low aggregation, but grain size in synthesized materials was smaller than TiO\(_2\) Degussa P-25. This may be due to further hydrolysis and condensation of titanium precursors leading to the growth of larger TiO\(_2\) nanoparticles, which slowly aggregate to one another. As TiO\(_2\) nanoparticles further aggregate, the TiO\(_2\) particles become microscopic particles. Similar aggregation of nanoparticles leading to mesoporous sphere was also studied by Yang and Zeng (2004). The TEM images of mesoporous TiO\(_2\) nanoparticles (with average crystallite size of about 6 nm as determined by XRD) are shown in Fig. 3c and d. The distribution of particles in TEM showed particles sizes of 5-8 nm for this specimen. This is a good agreement with XRD crystallite size. Most of the particles appearing spherical in shape are also present as shown in the TEM images.

The EDS of mesoporous TiO\(_2\) is expected to contain only Ti and O elements. The percentage of oxygen was 70.65 wt.% in the titania. The EDS spectrum of the prepared titania was

![XRD patterns of as prepared mesoporous TiO\(_2\) and Degussa P-25.](image2)

**Fig. 2** – (a) Wide and (b) low angle XRD patterns of as prepared mesoporous TiO\(_2\) and Degussa P-25. XRD: X-ray diffraction.
shown by a strong Ti signal at 4.5 eV with atomic percentage of 29.35%, confirming that the external shell was principally composed of TiO$_2$. No vague peaks associated with other crystal structures were observed (figure not included).

2.1.3. Surface and Pore Studies

Fig. 4 shows N$_2$-adsorption isotherm of the TiO$_2$ as prepared with their corresponding pore size distribution curves (inset) calculated from the desorption branch of the N$_2$ sorption isotherms by the BJH (Barrett-Joyner-Halenda) method. A type IV isotherm with a broad hysteresis loop was observed in the middle range of relative pressure, typical of mesoporous solids. The isotherm showed a typical IUPAC type IV pattern with a sharp inflection of nitrogen adsorbed volume at $P/P_o$ about 0.98 (type H$_2$ hysteresis loop). The sharp decline in the desorption curves was an indication of mesoporosity, and had a bimodal pore size distribution in the mesoporous region. The pore size distribution plot exhibited a mean average pore diameter of 0.6-6 nm with a narrow distribution. The large specific surface area at 280.7 m$^2$/g, total pore volume at 0.193 cm$^3$/g, and high volume fraction of atoms located both on the surface and at the grain boundaries resulted in an increased surface energy. Therefore, the surface of nanocrystalline TiO$_2$ provides an active substrate for catalysis (Grover et al., 2013).

For comparing the prepared TiO$_2$ to Degussa P-25, the surface area of the parent P-25 powder was 52 m$^2$/g, which is in good agreement with a value of 55 m$^2$/g reported by Minero et al. (1992), but larger than that reported by Sclafani et al. (1990) (44 m$^2$/g). Its pore volume was only 0.0246 m$^3$/g. Since Degussa P-25 consists of agglomerates of crystallites, such a low porosity means that the surface area is largely external to the agglomerates and the pore volume measured is mainly located between the agglomerates (interagglomerate pores) (Zhang et al., 2006). It can be observed that as prepared TiO$_2$ exhibited type II nitrogen isotherms. This type of isotherm is indicative of non-porous or macroporous material. These results are similar to those obtained by Saadoun et al. (2000) who reported that Degussa TiO$_2$ P25 was a non-porous powder mixture of anatase and rutile phases, as denoted by the hysteresis loop in its adsorption–desorption isotherm. However, a hysteresis loop with a stepwise adsorption and desorption branch was not observed in the case of P25. However, the pore size distribution of P25 was not observed and pore volume was not also counted (Porter et al., 1999).

2.1.4. FT-IR Spectroscopy Studies

The FT-IR spectra of as prepared mesoporous nano-TiO$_2$ and Degussa P-25 with scan ranged from 450 to 4000 cm$^{-1}$ are shown in Fig. 5. The IR results showed that major broad absorbance at 3949 cm$^{-1}$ accompanied by weak shoulders at 3720 cm$^{-1}$, indicating the presence of different types of isolated hydroxyl groups on the surface of the gel (Fig. 5b), which was not found in the synthesized mesoporous TiO$_2$ (Fig. 5a). The weak band at
Fig. 4 – Nitrogen adsorption–desorption isotherms and BJH (Barrett-Joyner-Halenda) pore-size distribution plot (inset) for as prepared mesoporous TiO₂.

2349.14 cm⁻¹ was attributed to νOH mode of interacting hydroxyl groups (i.e., involved in hydrogen bonds) and the symmetric and asymmetric νOH modes of molecular water coordinated to Ti[^{4+}] cations (Maira et al., 2001; Puddu et al., 2010). The presence of water was evidenced by the appearance of the bending mode at 1640 cm⁻¹ and the stretching mode at 3400 cm⁻¹ (Liu et al., 2004). The intensity bands at 1436 and 1394 cm⁻¹ were assigned to –CH₂– and tertiary C–OH bending respectively. It is bonded to Ti from the presence of alkyl groups that can ascribed to the characteristic frequencies of residual organics species. The broad peak at 490 cm⁻¹ was attributed to ν(Ti–O–Ti) stretching vibration in the anatase phase, which indicated characteristic strong absorbance of TiO₂ due to Ti–O stretching Ti–O–Ti bridge stretching vibration or bending vibration (Musić et al., 1997).

2.1.5. Thermal Studies

Fig. 6a shows the TGA results of the sample prepared with a flow rate of 20 mL/min. The weight loss consisted of five distinct steps in the curves. The first stage (up to 100°C) corresponded to rapid loss (about 5.63%) due to non-dissociatively physically absorbed water molecules as well as water held on the surface by hydrogen bonding (Maira et al., 2001). The second weight loss of 1.73% in the temperature range of 100–245°C was attributed to the loss of small molecular compounds such as desorbed hydroxyl and water molecules, isopropanol, and oxidation of organics such as alk oxy group and acetyl acetone, corresponding to a gradual exothermic process from DSC curve ended at 111°C with specific heat of 155.77 J/g attributed to the release of organic compound from the TiO₂ (Sivakumar et al., 2004). In DSC curve (Fig. 6b), a broad exothermic peak was attributed to hydration and loss of water, and these characteristic results are similar to that found in (Musić et al., 1997). Also, it seems that the decompositions of organics (possibly alk ox y groups) occurred at a low temperature around 200°C where the rate of weight loss was very low (Lee et al., 2004). In the temperature range of 245–322°C, there is a third weight loss of about 1.9%, corresponding to the decomposition of trapped alkyl groups which were difficult to remove and loss of crystal water. The decomposition of organic species also gave an endothermic peak at 322°C in the DSC curve. A considerable weight loss (5%) was observed in the temperature range between 200 and 400°C. The weight loss is due to the loss of crystal water and the decomposition of nitrate ions. This is consistent with a previous study (Sivakumar et al., 2004), in which the decomposition of nitrate ions was performed at around 230–400°C. The fourth weight loss was 2.9% in the range of 322–480°C, attributed to the gradual removal of the organic residues consisting of dehydroxylat ion of the gel and decomposition of nitrate ions. However, direct observation of the endothermic effect in the DSC curve was difficult, probably because the crystallization temperature is usually close to the decomposition temperatures of residual organics and removal of chemisorbed water, which are demonstrated as endothermic effect (Grover et al., 2013). Finally, both TGA and DSC curves showed little change in the range of 480–600°C. This indicates that the residues were removed and a stable phase structure was formed. High thermal stability and specific surface area of anatase TiO₂ could be ascribed to two-fold as follows: first, according to the previous researchers, the thermodynamic phase stability of TiO₂ is actually a function of particle size, and when the particle size decreases below ~14 nm, anatase becomes more stable than rutile even at high temperature; second, an autoclave was employed to obtain a high temperature and pressure for the nucleation and crystallization of nanoparticles. This method is favorable for better crystallization and smaller size TiO₂ nanoparticles (Mguniet al., 2013).

2.2. Photocatalytic Activity

2.2.1. Dye Degradation Kinetics

Experimental results of TiO₂ photocatalytic oxidation of several organic contaminants showed that the corresponding data fit the Langmuir–Hinshelwood (L–H) kinetic model (Eq. (4)):

\[
\frac{1}{r} = \frac{1}{k_d} + \frac{1}{k_cC}
\]
where, $r$ (mg/(L·min)) is the decomposition rate of the reactant, $C$ (mg/L) is the concentration of the reactant, $K$ represents the equilibrium constant for adsorption of the dye on TiO2 particles (Langmuir constant) and $k_i$ (mg/(L·min)) represents the specific reaction rate constant for the oxidation of the reactant. However, adsorption/desorption equilibrium is to be established under irradiation and in catalysis achievements, which is a major issue requirement for the validity of the L–H model. When the chemical concentration $C$ is millimolar solution, the integrated form of Eq. (5) is an apparent first order equation:

$$\ln \frac{C_0}{C_t} = k_i K t = k_{app} t$$  \hspace{1cm} (5)

where, $k_{app}$ represents apparent first order rate constant of the photocatalytic degradation, and $t$ is reaction time. A plot of $\ln(C_0/C_t)$ versus time represents a straight line, the slope of which upon linear regression equals the apparent first order rate constant $k_{app}$. Generally, first order kinetics is appropriate for several studies, which were reasonably well fitted by this kinetic model. The experimental half life time ($t_{1/2}$) of the first order reaction is the time required for the reactants to be degraded to the half of their initial concentration. The relationship between $t_{1/2}$ and $k_{app}$ is given by Eq. (6).

$$t_{1/2} = \frac{0.693}{k_{app}}$$  \hspace{1cm} (6)

The following equation indicates that plot of $t_{1/2}$ (estimated half life time) versus initial concentration of 2,6 dichlorophenol-indophenol should be linear:

$$t_{1/2} = \frac{0.5C_0}{k} + \ln \frac{2}{kK}$$  \hspace{1cm} (7)

where, $K$ is Langmuir adsorption constant and $k$ is the reactivity constant. By substituting the value of $k$ and $K$ into Eq. (7), the estimated half life time is obtained and listed in Table 4.

2.2.2. Comparison Between as Prepared TiO2 and Degussa P-25

Fig. 7 and Table 2 show the decolorization of DCPIP dye as a function of time with a constant dye concentration of $1 \times 10^{-4}$ mol/L and 1 g/L TiO2 at natural pH (6.7). As prepared TiO2 served as an efficient photocatalyst as compared with TiO2 Degussa P-25. It may be noted that as prepared TiO2 possesses a high degree of crystallinity, i.e., the amorphous content must be either zero or negligible, mostly anatase phase, a high surface hydroxylation, and mesoporous structure, which are consistent with our XRD and BET results. TiO2 with high crystallinity is characterized by longer charge carrier lifetime, thus associated with more efficient electron–hole utilization and decrease in the content of amorphous TiO2, increasing the photocatalytic activity of TiO2. High degree and quality of crystallization means the presence of fewer TiO2 bulk defects, where photoexcited electron and holes can recombine. Meanwhile, the porosity and surface hydroxylation affect the transport and higher capacity of oxygen adsorption on the catalyst active site (Liu et al., 2004). Such a physical property of large surface area and high crystallinity with nanocrystalline aggregated is indicative of a good candidate material for high photocatalytic activity (Machado et al., 2003).

**Fig. 6** – (a) TGA (thermogravimetric analysis) and (b) DSC (differential scanning calorimetry) patterns of as prepared mesoporous TiO2 nanoparticles.

**Fig. 7** – Comparison of photocatalytic activity between as prepared mesoporous TiO2 and Degussa P-25. $C_o$ and $C_t$ refer to the concentration of dye solution at initial and after photoirradiation at time t.
The photodegradation rates of these photocatalysts obeyed the following order of as prepared TiO₂ > Degussa P-25. Thus, it can be concluded that the lower activity of Degussa P-25 was more likely attributable to an increase in rutile content in the sample rather than the reduction in surface area. Pigmentory grade particles were in the micron range and their photoactivity decreased due to low surface area to volume ratio. This is contrary to the increased heterogeneous catalytic activity observed with increasing surface to volume ratio for nano-sized particles. The efficiency of the surface trapping of photo-generated holes increased in smaller particle sizes due to availability of more active sites. This translates into their ability to better promote photocatalyzed processes on the surface of the catalyst (Farbod and Kajbafvvala, 2013).

2.2.3. Effect of TiO₂ Loading

Fig. 8a shows the effect of the increasing TiO₂ loading on the decolorization of the studied dye as a function of time with a constant dye concentration of 1 × 10⁻⁴ mol/L at natural pH 6.7. It was observed that initial slopes of the curves rapidly increased by increasing catalyst loading from 0.4 to 1 g/L (degradation efficiency equal 95.32% for 1 g/L), so that the reaction rates were enhanced and t½ value was decreased as shown in Table 3. This may be due to the increase in the number of photons absorbed by TiO₂ particles from the UV source leading to excitation of more electrons from the valance to the conduction band. The concentration of holes would be increased and so was the number of active sites such as .OH and superoxide radicals adsorbed on the TiO₂ surface with increase in catalyst loading (Sadik et al., 2007).

After above a certain level, TiO₂ particles were in excess. When using higher amounts of nano-TiO₂ (over 0.6 g/L nano-TiO₂), no further reacting molecules were available for adsorption and the k₁ value decreased with t½ value increased. Two reasons are responsible: firstly, the excess catalyst prevented the illumination, .OH radical, a primary oxidant in the photocatalytic system decreased and the efficiency of the degradation reduced accordingly (Akpan and Hameed, 2009); Secondly, the light scattering increased and consequently, the UV light penetration reduced through the solution (the UV light penetration was hindered by excess catalyst particles). However, it remained almost constant beyond certain level, as shown in Fig. 8b. Besides, as the nano-TiO₂ loading increased, it could provoke the extensive aggregation. Hence, the specific surface areas of the catalyst were reduced, and consequently, reducing the photodegradation efficiency (Zainudin et al., 2009).

The observed decrease in the rate of degradation at higher catalyst loading may be due to the deactivation of activated molecules by collision with ground state catalysts. Shielding of TiO₂ may also take place according to Eq. (8):

\[
\text{TiO}_2^- + \text{TiO}_2^- \rightarrow \text{TiO}_2^# + \text{TiO}_2 \\
(8)
\]

where, TiO₂ has active species adsorbs on its surface and TiO₂ is the deactivated form of TiO₂. Since agglomeration and sedimentation of TiO₂ under large catalyst loadings would also take place (San et al., 2007), it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering and opacity. Consequently, the final effect is a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystal size (nm)</th>
<th>Apparent rate constant ((k_{app}) (\text{s}^{-1}))</th>
<th>Decolorization (%)</th>
<th>Time (min)</th>
<th>Half life time (t_{½} \text{(min)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Prepared</td>
<td>6.03</td>
<td>0.862</td>
<td>90.77</td>
<td>3</td>
<td>0.804</td>
</tr>
<tr>
<td>Degussa P-25</td>
<td>18.17</td>
<td>0.0459</td>
<td>16.11</td>
<td>3</td>
<td>15.098</td>
</tr>
</tbody>
</table>

Table 2 - Kinetic parameters of as prepared TiO₂ and Degussa P-25 on DCPIP photodegradation using a bench scale batch photoreactor.

Fig. 8 – Effects of (a) TiO₂ loading at 1 × 10⁻⁴ mol/L of 2,6 dichlorophenol-indophenol (DCPIP) dye and (b) initial concentration of DCPIP dye by 1 g/L TiO₂ on photodegradation at pH 6.7.
Table 3 – Effect of TiO₂ loading on the kinetics parameters of degradation values of DCPIP photodegradation in bench scale photoreactor over as prepared TiO₂.

<table>
<thead>
<tr>
<th>Catalyst concentration (g/L)</th>
<th>DCPIP concentration (10⁻⁴ mol/L)</th>
<th>pH</th>
<th>Apparent rate constant (k&lt;sub&gt;app&lt;/sub&gt;) (min⁻¹)</th>
<th>Reaction order (n) according to power law model</th>
<th>Degradation (%)</th>
<th>Time (min)</th>
<th>Half life time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>1</td>
<td>6.7</td>
<td>0.0326</td>
<td>3.725</td>
<td>19.26</td>
<td>4</td>
<td>21.28</td>
</tr>
<tr>
<td>0.6</td>
<td>1</td>
<td>6.7</td>
<td>0.0966</td>
<td>3.326</td>
<td>33.92</td>
<td>4</td>
<td>7.18</td>
</tr>
<tr>
<td>0.8</td>
<td>1</td>
<td>6.7</td>
<td>0.476</td>
<td>88.04</td>
<td>1.46</td>
<td>4</td>
<td>1.46</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>6.7</td>
<td>0.862</td>
<td>95.32</td>
<td>4</td>
<td>1</td>
<td>0.80</td>
</tr>
</tbody>
</table>

reduction of the number of activated sites in the aqueous medium (Zhu et al., 2012).

The assumption that first order kinetics applies allowed further analysis to be made of the data. The results of the effects of TiO₂ concentration were analyzed according to a power law model (Eq. (9)).

\[
\ln k_{app} = \ln K + n \ln [\text{TiO}_2]
\]  

where, \(k_{app}\) the is apparent rate constant, \(K\) is the true rate constant, \([\text{TiO}_2]\) is the concentration of TiO₂, and \(n\) is an exponent. The results are illustrated in Table 3. A plot of ln\(k_{app}\) versus ln \([\text{TiO}_2]\) represents a straight line with slope \(n\). The reaction rate order with respect to TiO₂ concentration is 3.725 (figure not included).

2.2.4. Effect of Initial DCPIP Concentration

As the effect of pollutant concentration is of importance in any process of water treatment, it is necessary to investigate the effect of initial concentration on the photocatalytic degradation of DCPIP dye. Fig. 8b and Table 4 show the effect of initial DCPIP concentrations on photocatalytic degradation efficiency at pH 6.7 and catalyst amount 1 g/L. The straight-line relationship of \(\ln (C_t/C_0)\) versus irradiation time was obtained. This photodegradation followed a first-order expression up to an initial concentration of DCPIP dye. As the concentration of the dye increased from \(1 \times 10^{-4}\) to \(4 \times 10^{-4}\) mol/L, the apparent rate of photodegradation decreased. This negative effect can be commented as follows.

When the initial dye concentration increased, more and more dye molecules were adsorbed on the surface of TiO₂, which was thought to have an inhibitive effect on the reaction of dye molecules because of the lack of any direct contact between them. Once the concentration of dye is increased, it causes the dye molecules to absorb light, and the path length of the photons entering the solution decreases; thus, the photocatalytic decolorization efficiency decreases and in low concentration the reverse effect is observed (Daneshvar et al., 2005; Zhu et al., 2012), thereby increasing the number of photons absorption by the catalyst in lower concentration. An increase in the photocatalytic activities was due to the higher adsorption area towards the organic substrates, in turn, making the organic molecules accessible to the active sites on the nano-TiO₂ surface (Zainudin et al., 2009). In general, low reactant concentrations exhibit a first order rate dependence and at higher concentration, rate is independent of concentrations and zero order dependence is suggested (Mehrotra et al., 2003).

Fig. 9 shows the change of reciprocal initial rate (1/R<sub>ini</sub>) with initial concentration on photodegradation of DCPIP at constant TiO₂ concentration (1 g/L) and a variable dye concentration of \((1-4) \times 10^{-4}\) mol/L. The apparent first-order constant \(k_{app}\) decreased with increasing the concentration of DCPIP when other parameters were also kept constant, as shown in Table 4.

In recent years, the Langmuir–Hinshelwood rate expression has been used successfully for heterogeneous photocatalytic degradation to describe the relationship between initial degradation rate and initial concentration (Eq. (5)). A linear expression can be conveniently obtained by plotting reciprocal initial rate against reciprocal initial concentration. The slope is \(1/(K_r K)\) and the intercept is \(1/K\) (Fig. 10). The linear transform of this expression yielded \(k 1.42 \times 10^{-4}\) mol/(L·min) and \(K 1.35 \times 10^{-8}\) L/mol.

The estimated half life time are obtained and listed in Table 4. Fig. 10 shows the dependence of \(t_{½}\) and \(t_{½}\) on the initial DCPIP dye concentration and their relationship was also straight line. Thus, the photocatalytic degradation of DCPIP dye fits well to the Langmuir–Hinshelwood model. It was also found that \(t_{½}\) and \(t_{½}\) are near to each other at low initial solute concentration and the gap between them increases with the increasing solute concentration. At low dye concentration \((1 \times 10^{-4}\) mol/L), the intermediate product

<table>
<thead>
<tr>
<th>Initial dye concentration (C₀) (M)</th>
<th>Apparent rate constant (k&lt;sub&gt;app&lt;/sub&gt;) (min⁻¹)</th>
<th>Initial reaction rate (R_{ini} = k_{app} \times C_0) (M/min)</th>
<th>Degradation after 4 min (%)</th>
<th>(t_{½}) (min)</th>
<th>(t_{½}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 \times 10^{-4})</td>
<td>0.8621</td>
<td>(8.62 \times 10^{-5})</td>
<td>95.32</td>
<td>0.80</td>
<td>1.69</td>
</tr>
<tr>
<td>(1.5 \times 10^{-4})</td>
<td>0.6997</td>
<td>(1.049 \times 10^{-4})</td>
<td>83.86</td>
<td>0.99</td>
<td>1.86</td>
</tr>
<tr>
<td>(3 \times 10^{-4})</td>
<td>0.4055</td>
<td>(1.217 \times 10^{-4})</td>
<td>74.84</td>
<td>1.71</td>
<td>2.39</td>
</tr>
<tr>
<td>(4 \times 10^{-4})</td>
<td>0.333</td>
<td>(1.33 \times 10^{-4})</td>
<td>68.60</td>
<td>2.08</td>
<td>2.74</td>
</tr>
</tbody>
</table>
concentration formed during the degradation of the parental dye was very low. They may compete with the dye molecules for the limited adsorption and catalytic sites on the TiO2 particles. This effect may be neglected as the intermediate concentration was very low, thus $t_{1/2}$ increased a bit relative to $t_{1/2}^*$. However, the difference between $t_{1/2}$ and $t_{1/2}^*$ increased with increasing initial dye concentrations (1 to $4 \times 10^{-4}$ mol/L) due to the increasing intermediates concentration and thus inhibited the dye degradation. Thus, $t_{1/2}$ will be increased compared to $t_{1/2}^*$ (Sadik et al., 2007). Another possible cause for such results is the UV-screening effect of the dye itself. At a high dye concentration, a low amount of UV may be absorbed by the TiO2 particles and thus reduces the efficiency of the catalytic reaction (Song et al., 2008).

2.2.5. Effect of pH

pH is an important operating parameter in the heterogeneous photocatalysis, since it determines the surface charge properties of the photocatalyst and therefore the adsorption behavior of the pollutant and also the size of aggregates it forms. The effect of pH on the photocatalytic decolorization efficiency of DCPIP dye at the pH 3, 5, 6.7 (natural), 9 and 11 respectively with a constant dye concentration ($1 \times 10^{-4}$ mol/L) and catalyst loading (1 g/L) were studied and illustrated in Fig. 11 and Table 5. Increasing the pH of the solution diminished the decolorization efficiency, which decreased rapidly after pH 6.7. From the factorial optimization it can be concluded that better results were obtained at pH 3. Photodegradation close to 96.42% was obtained in 3 min of photocatalytic treatment.

In general, medium pH has a complex effect on the photodegradation rates of chlorophenols depending on different molecular structures of chlorophenols as well as the semiconductors used in the oxidation process (Quan et al., 2007, Rauf and Ashraf, 2009). DCPIP is an anionic species in aqueous solution. The initial adsorption of the dye molecules onto the polyscale crystals greatly depends on the solution pH (Murov, 1973). The change in pH of the solution varies with the dissociation of the dye molecule and also the surface properties of the designer particles used.

The surface charge of titania is a function of solution pH. When a nanoparticle is dispersed in an aqueous solution, the surface ionization and the adsorption of anions or cations result in production of the surface charge and an electric potential will be developed between the particle surface and the bulk of dispersion medium (Davis et al., 1978). The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively, as shown in the following equations (Eqs. (10) and (11)). TiOH represents the primary hydrated surface functionality of TiO2 (Hoffmann et al., 1995).

\[
\text{Acidic (pH < PZC)}:\quad \text{TiOH} + H^+ \rightarrow \text{TiO}^+ + \text{H}_2\text{O} \quad (10)
\]

\[
\text{Basic (pH > PZC)}:\quad \text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O} \quad (11)
\]
Due to the nature of TiO₂ catalyst used, any variation in the operating pH is known to affect the isoelectric point or the surface charge of the photocatalyst used. The pH at which the surface of titania is neutral is point of zero charge (PZC) or isoelectric point (IEP). If no specific adsorption of the ions presented in the solution takes place on the particle surface, the pH at PZC and IEP would be the same (Suttiponparnit et al., 2011). Many reports have used the point of zero charge (PZC) or the pH at which the photocatalyst used. The pH at which the isoelectric point or the operating pH is known to affect the isoelectric point or the surface charge of the photocatalyst used. The pH at which the interaction between the catalyst particles when irradiated by the light in the region of absorption charge-transfer bands. The primary e⁻/h⁺ pairs are generated from the UV irradiation in Eq. (12). Eqs. (13)–(15) are the three means of the hole trapping on the adsorbed organic species, adsorbed water molecules, and the surface hydroxyl groups. Dissolved oxygen can accept the excited electrons to form superoxide radical ions, which is another possible source of hydroxyl radicals (Eqs. (16)–(19)). Thus, hydroxyl radical .OHads species can be generated not only from VB hole trapping (Eqs. (12)–(13)), but also from the CB electron scavenging processes (Eqs. (12)–(13)), but also from the CB electron scavenging steps (Eqs. (17)–(19)). Finally, the radicals formed during this mechanism are responsible for the oxidation of DCPIP dye.

A mechanistic pathway based on hydroxyl radicals is the most popular for the description of photocatalytic degradation of DCPIP dye. DCPIP degradation mechanism using UV/mesoporous TiO₂ system is shown in Fig. 12. Firstly, direct photolysis involves the interaction of light with molecules, in addition to water, for dechlorination of DCPIP dye (Fig. 12a) (Brezová et al., 1991).

| Table 5 – Effect of pH on DCPIP solution and the kinetic parameters of photodegradation in bench scale photoreactor over as prepared TiO₂. |
|---|---|---|---|
| Apparent rate constant (k_{app}) | pH | Degradation (%) | Time (min) | Half life time (t_{1/2}) (min) |
| 1.35 | 3 | 96.42 | 3 | 0.515 |
| 1 | 5 | 94.9 | 3 | 0.693 |
| 0.862 | 6.7 | 90.77 | 3 | 0.804 |
| 0.183 | 9 | 5.06 | 3 | 3.78 |
| 6.72 × 10⁻³ | 11 | 0.065 | 3 | 103.14 |

The radical formation in the photodegradation mechanism is shown in reactions (12)–(20) (Carp et al., 2004). The key to photocatalysis is the electron–hole pair on the surface of the catalyst particles when irradiated by the light in the region of absorption charge-transfer bands. The primary e⁻/h⁺ pairs are derived from the UV irradiation in Eq. (12). Eqs. (13)–(15) are the three means of the hole trapping on the adsorbed organic species, adsorbed water molecules, and the surface hydroxyl groups. Dissolved oxygen can accept the excited electrons to form superoxide radical ions, which is another possible source of hydroxyl radicals (Eqs. (16)–(19)). Thus, hydroxyl radical .OHads species can be generated not only from VB hole trapping processes (Eqs. (12)–(13)), but also from the CB electron scavenging steps (Eqs. (17)–(19)). Finally, the radicals formed during this mechanism are responsible for the oxidation of DCPIP dye.

It was earlier demonstrated that the reaction pathways of photocatalytic degradation of DCPIP dye involve the formation of phenolic compounds as the primary intermediates. The formation of these intermediates were followed by the appearance of aromatic compounds like as hydroquinone, catechol and benzoquinone and then converted to acetic acid as aliphatic compound due to the opening of the benzene ring before completely mineralized to CO₂ and H₂O (Fig. 12b) (Tao et al., 2013).

3. Conclusions

Highly active mesoporous TiO₂ nanoparticles with anatase phase, 6 nm average crystallite size and high specific surface...
area of 280.7 m²/g have been successfully synthesized via sol–gel/hydrothermal route in acidic condition. The performance study of the degradation of DCPIP dye over the synthesized photocatalyst under the UV irradiation was performed in slurry reactor. The as prepared mesoporous TiO₂ has a higher life time than Degussa P-25 as a result of an enlarged surface area and porous structure. The photocatalytic degradation of DCPIP using titania nanoparticle irradiated by UV light followed Langmuir–Hinshelwood (L–H) kinetic model with reaction rates mostly of first order and the rate constants decreasing with an increase in the initial concentration of DCPIP, but increasing with decrease pH. The reaction rate constants also the increased with increased TiO₂ loading and reached a plateau at TiO₂ concentration of 1 g/L. The optimum photodegradation condition of DCPIP dye was mesoporous TiO₂, pH 3, and 1 × 10⁻⁴ mol/L of solute of DCPIP dye under UV illumination with degradation of 96.4% at 3 min. The described method is easily controlled and environmentally friendly, and provides an effective way for the preparation of mesoporous titania nanopowders with high photocatalytic activity.

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REFERENCES


