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Review on Biosynthesis of Tio2-Sio2 Nanocomposites Towards Photocatalytic Purpose of Wastewater Treatment

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Abstract: This research is conducted to analyse the capability of TiO2-SiO2 nanocomposite in eliminating methylene blue dye, lead ions and contaminant in water stream such as river and sea. Review research is performed as a primary prevention to remove the issue of polluted water by treating the contaminated water generated by consumers as well as clean water that can be used. TiO2 has been extensively used as photocatalyst due to its non-toxicity, low cost and photochemical stability. Titanium Oxide nanoparticles also exhibit unique surface chemistry and morphologies. The addition of other oxides such as silicon dioxide, SiO2 is establish to enhance the thermal stability and photocatalytic activity of titanium dioxide. This is partially explained by the intimate interaction of TiO2 and SiO2, which results in new structural and physicochemical properties such as quantum-sized crystallinity, high surface area, high adsorption capacity or high acidity. Mostly TiO2-SiO2 nanocomposite are produced via physicochemical methods like chemical vapor deposition, micro emulsion, chemical precipitation, hydrothermal crystallization, and sol–gel methods. Hydrothermal method is used in synthesizing the TiO2-SiO2 nanocomposite in order to enhance the adsorption ability and photocatalytic activity in wastewater treatment. The FTIR (Fourier transform infrared spectroscopy) and Energy Dispersive and X-ray (EDX) was used to determine crystallinity and phase. The Field Emission Scanning Electron Microscope (FESEM) was used for surface morphology and analysis on the nanoparticles.

Keywords: Photocatalytic, Hydrothermal, Synthesizing, TiO2-SiO2, Waste Water Treatment

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1. Introduction

In recent years, there has been great concern over the many serious environmental problems and a lack of natural energy resources we appearance on a global scale. The increase in world population and industrial development have all led to accelerated energy consumption and the unabated release of toxic agents into the air and water, prominent to such critical effects as pollution that related to diseases and global warming (Kitano et al., 2007). Dyes are one of the main pollutants due to their stable aromatic structures and less decomposition speed under biological process.

Titanium Dioxide (TiO2) and Silica Oxide (SiO2) nanoparticles can also be made in a continuous hydrothermal system for photocatalyst applications. As we know this process is one of the effective processes that able to degrade dyes from wastewater using photocatalysts. Similarly in hydrothermal flow, morphology can easily be changed depending on the mixing methods and additives such as SiO2 particles. The TiO2-SiO2 nanocomposites can be utilized in a variety of applications, including purification of polluted water and air, decomposition of H2O into H2 and O2, and self-cleaning (Dong et al., 2018).

Now days, contamination of chemical substances such as dyes, paint, oil that generated from industry and human activities has create a serious problem to the main water source system such as river and sea. The accumulation of dyes and other chemical substances not only contaminated the water system but also reduce the absorption and reflection of sunlight entering the water that able to decrease the production of algae and disturb water ecosystem. This effect not only will reduce the aquatic life but also reduce the quality of the water.

The ability of inorganic particles such as TiO2-SiO2 with assistant sunlight to conduct photocatalytic process ease the elimination of organic substances and able to protect the environment system. Thus, this work will focus on the review of the synthetization of Titanium dioxide (TiO2) and Silica Oxide (SiO2) nanoparticles for wastewater treatment through hydrothermal technique as well as others green approaches such as biosynthesis approaches towards degradation and antibacterial properties.

2. Methodology

More conventional nanoparticles synthesis methods such as sol-gel and co-precipitation techniques, are slow, require multiple steps and need very precise control of several reaction parameters such as pH, temperature, concentration. Since the hydrothermal method appears to be a promising method for synthesizing TiO2-SiO2 nanocomposite with various properties and findings for the best photocatalytic activity outcome, it is safe to conclude that this research paper analysis is the best approach.

2.1 Materials

2.1.1 Titanium Dioxide (TiO2)

Titanium dioxide (TiO2) is one of the most basic materials in our daily life. It has emerged as an excellent photocatalyst materials for environment purification. TiO2 is the most widely investigated photocatalyst due to high photo-activity, low cost, stable against photo corrosion and chemical resistance(J. Wang et al., 2019). Other properties of Ti02 are non-toxic to environment and human, high turnover, complete mineralization of organic pollutants, high catalytic activity and strong oxidizing power. Ti02 can be supported on various substrates.

2.1.2 Silicon Dioxide (SiO2)

Silicon dioxide, also known as silica is an oxide of silicon. It is the most abundant mineral in the Earth's crust. Si02 appears in white or colourless non-water soluble crystalline solid. Si02 has a giant covalent structure. Si02 is lightweight and it is highly porous material (Rahmani et al., 2011). It played an important role in absorbents for organic pollutants removal. Si02 was believed to be a very good medium that facilitates adsorbing organics.

2.1.3 Chitosan (CS)

Chitosan is the second most abundant biopolymer after cellulose. It is a copolymer that is obtained by the deacetylation of chitin. Chitosan is a low cost natural polysaccharide material(Shao et al., 2019b). Chitosan can remove metal cations efficiently in acidic or near-neutral solutions due to it contains a number of amino groups. Chitosan is able to be made into a variety of useful forms such as films, fibres and beads. Its unique chemical and biological properties make chitosan has high chemical reactivity, chirality, chelation and adsorption capacity(Bergamonti et al., 2019). Chitosan is also non-toxic, biocompatible and high porosity which are very attractive biomaterial for enzyme immobilization.

2.1.4 Polyvinyl Alcohol (PVA)

PVA is an inexpensive, water-soluble synthetic polymer represented by the formula [CH2CH] (Fakoori et al., 2019). PVA has high elasticity, high mechanical strength. PVA is non-toxic and good biocompatibility. PVA is a semi-crystalline hydrophilic polymer and possesses material containing large amounts of hydroxide group(Hashim & Hamad, 2020). PVA is the commonly used for biomedical applications and water treatment. This is due to the hydroxyl groups present in PVA polymer structure that may contribute to the adsorption for heavy metal ions.

2.2 Methods

2.2.1 Experimental Method of Hydrothermal Synthesis

This chapter will explicitly focus on the processes used to synthesis the materials used in this photocatalysis procedure. The general methods of manufacturing processes and instrumentation used for the fabrication of nanocomposite will be discussed in this section. In addition, the photocatalytic results that obtained in all studies will be considered as the performance that will be used to measure the effectiveness of the chosen variables in getting the good composite structure of TiO_2-SiO_2 performance of specimen.

2.2.2 Overall Methodology of Sol-Gel

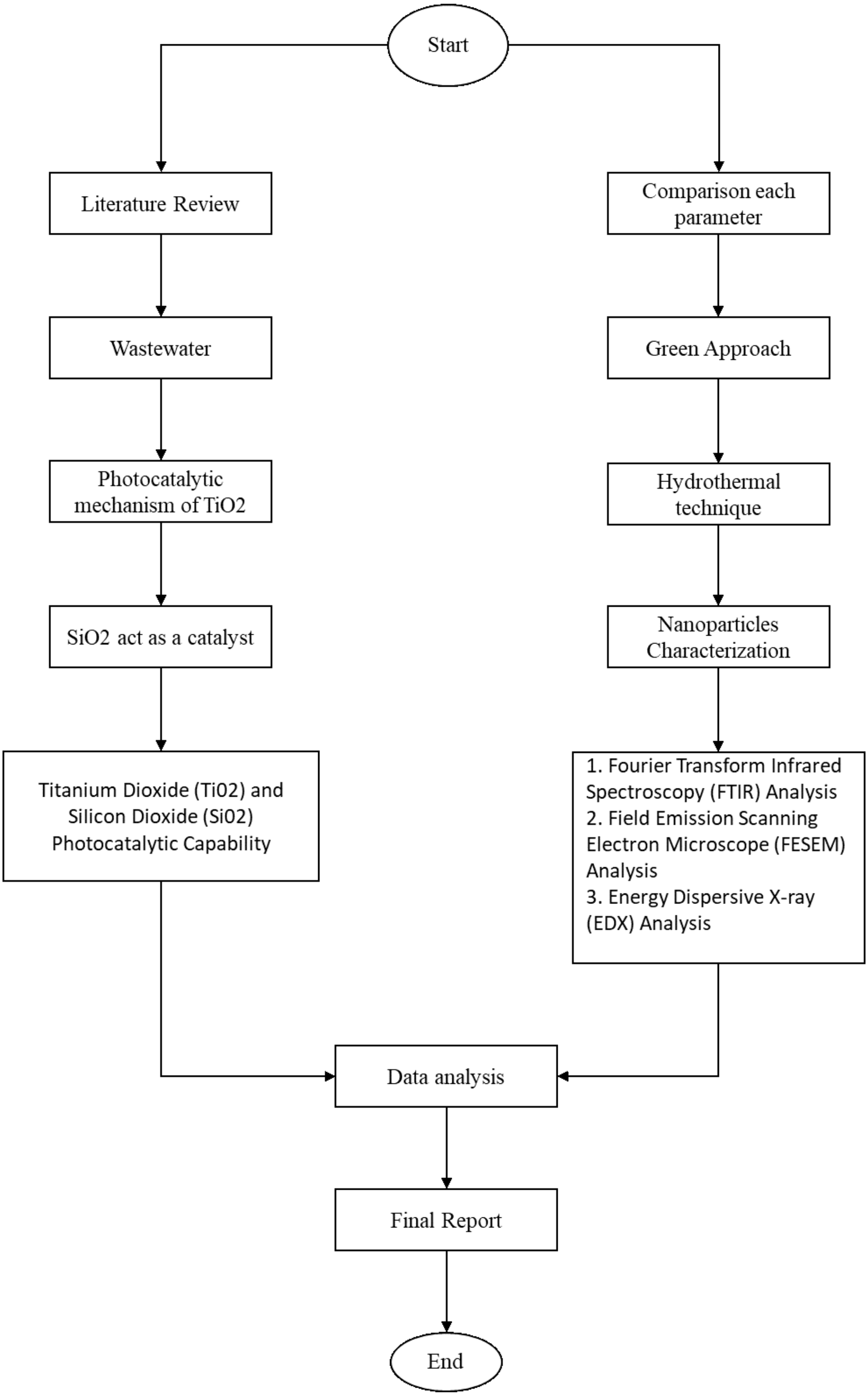

Figure 1: Flowchart of Overall Methodology of Hydrothermal Method

2.2.3 Structural Characteristics

X-ray diffraction (XRD) technology was used to analyze the crystal structure of the formulated TiO2-SiO2 nanocomposites. It is an instrument which collects x-ray emitted from a sample that has been bombarded by an electron beam. The x-rays are sorted by energy level and a spectrum of x-ray energy vs. frequency is which shows the elements present in the sample and of the concentration of plotted, which each element present(Kanna et al., 2018).

The result was obtained by:

1. During sample exposure to rays, the applied current of 100 mA and the accelerating voltage of 40 kV were applied.
2. In a diffraction angle range of 15°-80° with a phase of 0.02°, the XRD patterns were noted.
3. To measure the crystallite size of the powder, the Scherrer-Debye equation was applied.
4. Inside this matrix, the sum of rutile crystals was determined using the Spurr equation:

$$\%\mathrm{rutile} = \frac{100}{1} + 0.8\left(\frac{\mathrm{I_A}}{\mathrm{I_R}}\right)$$

Where:

$\mathrm{I_A}$= Integrated main peak intensities of anatase

$\mathrm{I_R}$= Integrated main peak intensities of rutile

5. Pawley XRD pattern fitting was done using the GSAS-II software.

2.2.4 Morphology of the Materials

The field emission scanning electron microscopy machine analyzed the morphology of such materials collected under various conditions. Figure 2 shows the JEOL JSM-7600F FESEM.

Figure 2: JEOL JSM-7600F FESEM

The result was obtained by:

1. To research the elemental compositions, SEM was combined with Energy-dispersive X-ray spectroscopy (EDX).
2. To investigate the particle size and distribution, transmission electron microscopy is included.
3. The surface area of Brunauer-Emmett-Teller (BET) as well as the porosity measurements of the samples were determined by the nitrogen gas adsorption-desorption instrument (Micrometrics ASAP 2020) as shown in Figure 3.
4. At 250°C, samples were degasified for 2 hours before measurements were made.

Figure 3: Micrometrics ASAP 2020

2.2.5 Bonding Patterns

In order to test the bonding pattern of such synthesized materials using the FTIR Spectrometer, Fourier transform infrared spectroscopy has been used for analysis. In order to characterize the presence of particular chemical groups in materials, FTIR spectroscopy is used. With FTIR spectroscopy, the structure of chemical reactions as well as the identification of unstable compounds are studied. Figure 4 shows the Perkin Elmer 100 Series FTIR spectroscopy

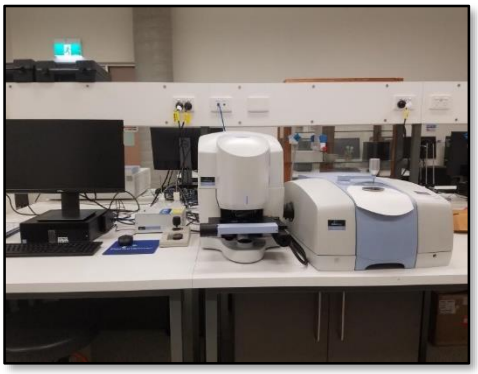

Figure 4: Perkin Elmer 100 Series FTIR spectroscopy

The result was obtained by:

1. The IR spectrometer was fitted with a detector for DTGS KB.
2. In the range of 400-4000cm^{-1}, the aggregate of 64 scans via an optical velocity of 0.6334cm^{-1} and a wavenumber resolution of 4cm^{-1} is generated.

2.1 Photocatalytic Test

Photocatalytic test was conducted with the presence of ultraviolet (UV) light in order to accelerate the chemical reaction. In water treatment purpose, it is a developing technology for the reduction of toxic metals which destroying pollutants or transforming them into less toxic forms. The performance of the beads is examined via photocatalytic test. Ti02 and Si02 which act as photocatalysts were added in the beads as to enhance the photocatalytic performance of the beads.

3. Results and Discussion

The analysis of titanium dioxide and silicon dioxide, as well as the efficiency of Photocatalytic action, will be addressed in this section. And as per the previous study, experiment, and journal, the result is obtained. Numerous findings can also be correlated thanks to the experimental substance and treatment.

3.1 Comparison of TiO2-SiO2 from Different Synthesis Method

Table 1: General Comparison on Different Techniques of Composite for TiO2-SiO2 Synthesis

Authors and years	Routes	Level of purity
(Alotaibi et al., 2018)	Chemical vapour deposition	High
.(Karbassi et al., 2018)	Micro emulsion	Medium
(Zikriya et al., 2019)	Chemical precipitation	Medium
(Chen et al., 2018)	Hydrothermal crystallization	High
(Atout et al., 2017)	Sol–gel methods	High

There are various different methods that have been used to synthesize the titania-silica composites. As reported in previous work and present in Table 1, several technique to synthesis tio2-sio2 nanoparticle that normally used were chemical vapour deposition (CVD), micro emulsion, chemical precipitation, hydrothermal crystallization and sol gel method. Among this technique hydrothermal, sol gel and chemical vapour deposition have shown better or high output value of the targeted silica-titania composite. This may be due to all these technique involves the used on controlled parameter such as temperature, pressure, high concentration chemical substances etc. Even all these 3 techniques able to produce the composite structure of particles synthesis but some technique involves with high chemical substances, high vapour pressure and temperature, that need high energy consumption and involves with complex processing technique.

Hydrothermal normally used very low temperature and pressure. In addition, the mixture can be directly mixed before exposed to the low temperature and pressure. As reported previously(Chen et al., 2018) , the composite of titania-siliza can be produced by an indirect way by adding premade titania nanoparticles into a silica support at a pH of around 3 until 4. At that pH, the titania and silica have opposite charges so that the titania and silica will have electrical attraction. The solution was heated at 110ºC in distilled water and subsequently calcinated. Among this technique hydrothermal may offer an easy and better step with low energy usage.

3.2 Specific Comparison of Hydrothermal Method

As shown in Table 2, most of the works that used hydrothermal in synthesizing titanium dioxide have used temperature as controlled parameter. From (Dong et al., 2016) and (Bo et al., 2017), the researchers only use two controlled parameter which is temperature and reduction of medium that indicate the efficiency of nanoparticles is moderate towards the experiments (Fauzi et al., 2020), (Fu et al., 2020) and (Palhares et al., 2020) had maximize his results by adapting almost all controlled parameter which are temperature, reduction of medium and mode precipitation through the hydrothermal treatment. Catalyst also had been used in the experiments to act as an agent of reduction for the nanoparticles. There were controlled parameter that less been choose which is mode of precipitate because it involves high cost of overall experiment.

Table 2: Controlled parameters of hydrothermal treatment

Authors and years	Temperatures	Reaction\Reduction of medium	Mode precipitation\ Agitation
(Fauzi et al., 2020)	/	/	/
(Fu et al., 2020)	/	/	/
(Palhares et al., 2020)	/	/	/
(Dong et al., 2016)	/	/	
(Bo et al., 2017)	/	/	

Table 3 presents the method of Hydrothermal Method which explains briefly about the parameters, characteristic including performance. Each author has their own reaction or reduction medium used for their very own experiments.

Table 3: Hydrothermal methods: Parameters/Characteristic/Performance

Research	Vary Parameters (Significant)		Characteristic		Performance
Author/ Year	**Calcination Temperature, ⁰C**	**Reaction/ Reduction medium**	**Level of Purity**	**Particle morphology**	**Band Gap**
(Fauzi et al., 2020)	550	1-Butanol and tetraethyl orthosilicate (TEOS).	High	✓	✓
(Fu et al., 2020)	450	Titanium (IV) isopropoxide (TTIP), tetraethyl orthosilicate (TEOS).	High	✓	✓
(Palhares et al., 2020)	700	Titanium tetra-isopropoxide (TTIP), Hydrochloric acid (HCI) and ethanol(C_2H_5OH).	High	✓	✓
(Dong et al., 2016)	700	Tetrabutyltitanate, tetraethoxysilane, HCl and ethanol.	High	✓	✓
(Bo et al., 2017)	900	Tetrabutyltitanate, tetraethoxysilane, Cyclohexane and ethanol.	High	✓	✓

3.3 Discussion Regarding Catalyst by Different Author

The main objectives of this research conducted by those scientists have always been the synthesization of new resources and the change of an explanation of the synthesis method. Moreover, it is obvious that all of five authors have different opinion and method of conducting their experiments to indicate the best results in synthesis of TiO2-SiO2 nanocomposite for monitoring photocatalytic activity by degradation of methylene blue (MB) solution. All authors had their own specimen that had been testing to achieve the best photocatalysis activity that had been proved success in their own experiments.

Furthermore, each author had their own strength and weakness regarding the synthesis of TiO2-SiO2 nanocomposite in their own particular experiments. As a result, in a review, the comparison of each author's finest specimen would be differentiated according to the evidence that backs up that statement. Table 4 shows the specimen for each of the author's finest catalyst products.

Table 4: Finest Catalyst Products by each Authors

Author and Year	Calcination Temperature	Finest Catalyst Products	Band Gap Energy (eV)
(Fauzi et al., 2020)	550	FST	2.92
(Fu et al., 2020)	450	Ti/Si= 1:5	2.58
(Palhares et al., 2020)	700	SH-Ti 700	2.95
(Dong et al., 2016)	700	TS-30	3.02
(Bo et al., 2017)	900	TS1100	3.20

For the finest catalyst product by calcination temperature 550°C (Fauzi et al., 2020) , In the experiments, FST was successfully synthesized via hydrothermal method. The potential of the synthesized FST were evaluated towards photocatalytic degradation of MB under visible light for 2 hours. The band gap energy is 2.92 eV that shown the value is lower than commercial TiO2 .It was proven that FST exhibited higher photodegradation percentage of MB than commercial TiO2 which were 99.9% and 94.6% respectively. This was due to the unique morphology, narrow band gap, existing of interaction of Si-O-Ti that acts as an active site and large surface area obtained by FST.

The calcination temperature 450°C for the finest catalyst product by (Fu et al., 2020), a molar ratio of 1:5 of TiO2-SiO2 had the highest photocatalytic activity of 99.2% after 120 minutes of UV light photodegradation towards methylene blue (MB) solution. The value of its band gap energy had been reduced to 2.58 eV to increase the photocatalytic activity of nanocomposites. Therefore, a proper molar ratio of Ti/Si both enhanced the thermal stability and increased the surface area and surface acidity. At the meantime, higher surface area and mesoporous structure provided more adsorption sites and photocatalytic reaction centers, which can enhance the photocatalytic reaction of phenol and MB.

From (Palhares et al., 2020), the finest catalyst product at calcination temperature 700°C is SH-Ti 700 because the heat treatment improved the photocatalytic performance of the TiO2–SiO2 nanocomposites. The band gap energy was the least compare to other specimen in the experiments which is 2.95 eV. The behaviour can be related to the limitation of crystallite growth and anatase-to rutile transformation, which also contributed to the maintenance of specific surface areas even after the heat treatment. This result is related to the fact that the higher the catalyst loading, the larger the number of sites available for adsorption and photocatalysis.

At the calcination temperature 700°C, the finest catalyst product from (Dong et al., 2016) is TS-30 because the increase in the specific surface area of TS-30 is slight as compared with that of pure TiO2 microspheres, the increases in pore volume and average pore diameter indicate the photocatalytic activity of nanocomposite. The band gap energy was reduced to 3.02 eV to increase the efficiency of photocatalytic activity towards the degradation of methylene blue (MB) solution in this experiment.

The finest catalyst product from (Bo et al., 2017) at the calcination temperature is 900°C is TS1100 because it possess a strong photocatalytic degradation power to methylene blue (MB) solution in this experiments. When the higher the SiO2 concentration, the faster the methylene blue decolorization rate. Moreover, the high temperature calcination also results in a higher crystallinity and lower energy band gap which are beneficial for an enhanced interaction between TiO2 and SiO2 which increases the photocatalytically active center of catalyst.

Finally, the best finest catalyst product from all five authors for my research is Ti/Si= 1:5 from (Fu et al., 2020) at the calcination temperature is 450°C whereas it has the lowest band gap energy which is 2.58 eV compare to other specimen from different experiments. The lower band gap energy will increase the efficiency of photocatalytic activity of its nanocomposite. The Ti/Si molar ratios of 5 : 1 had the highest photocatalytic activity of 99.4% towards phenol and 99.2% towards MB, which showed higher photocatalytic efficiency with the addition of 0.25 g/L photocatalyts compared with the other reported TiO2- SiO2 composites.

4. Conclusion

The experimental study can be concluded that the objective of this thesis has been achieved where review efficiency of the Titanium dioxide and silica oxide nanocomposite in purifying process for wastewater treatment compared to others metal oxide nanoparticles, to review and investigate the ability Titanium dioxide and silica oxide nanoparticles towards photocatalytic activity and to review and compare the synthesis of Titanium dioxide nanoparticles via different method such as chemical vapour deposition (CVD), micro emulsion, chemical precipitation, hydrothermal crystallization and sol gel method.

The hydrothermal treatment method was success to review by all five researchers in producing the best TiO2-SiO2 nanocomposite due to the properties such as unique morphology, narrow band gap, existing of interaction of Si-O-Ti that acts as an active site and large surface area. Hydrothermal treatment method also offer an easy and better step with low energy usage. The high photocatalytic efficiency of TiO2/SiO2 nanocomposite for the decomposition of methylene blue is mainly attributed to the novel microstructure which leads to an enhanced adsorption capacity and thus an increase in the capture efficiency of surface-bonded hydroxyl radicals. This is due to the simultaneous effects of the photocatalytic activity of TiO2 and adsorption capacity of SiO2. It was observed that the incorporation of silica on the surface of nanocrystalline titania increased the thermal stability of the composite, inhibiting the anatase-to-rutile transformation and decreasing the crystallite growth during the heat treatment.

Moreover, the presence of silica also contributed to the stabilization of the composite pore structure because its specific surface area and pore volume were less affected by the heat treatment than TiO2. The heat treatment in the nanocomposite materials was beneficial and necessary for promoting the controlled segregation of silica and titania phases, leading to the combined effect of enhanced adsorption and photocatalytic activity of the nanocomposite towards the field of degradation of dyes in textile and wastewater treatment.

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