COMBINATION OF COAGULATION-ULTRAVIOLET PHOTOCATALYTIC TREATMENT BY USING ZINC OXIDE WITH POLYARCYLAMIDE AND TANNIN FOR REMOVAL OF COLOUR

By

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ABSTRAK

Air adalah komponen yang penting dalam kehidupan seharian kita. Kehadiran bahan kimia toksik dan bakteria boleh mendedahkan hidupan kepada penyakit bawaan air yang berisiko tinggi akibat daripada penggunaan air yang tercermar. Air sisa dari industri tekstil adalah salah satu masalah alam sekitar selain dari isu-isu kecil seperti sisa pepejal dan pengurusan sumber sisa. Terdapat pelbagai jenis pewarna tiruan yang digunakan oleh industri tekstil dan pelepasan dari industri ini mempunyai jumlah air sisa yang besar dan mempunyai kepekatan warna yang tinggi. Air sisa yang mempunyai pewarna tekstil yang tinggi memberi kesan teruk kepada fungsi fotosintetis dalam tumbuhan dan memberi impak kepada kehidupan akuatik kerana penembusan cahaya yang rendah dan penggunaan oksigen. Oleh itu, air sisa tekstil harus dirawat dengan baik sebelum dilepaskan kepada persekitaran. Di dalam kajian ini, berlainan kaedah rawatan untuk merawat air sisa tekstil telah di bentangkan. Dalam kajian ini, proses penggumpalan proses fotopemangkin ultraviolet, dan gabungan pengumpalan-fotopemangkin ultraviolet telah digunakan. Kajian ini juga melibatkan pengubahsuaian zink oksida dengan polyacrylamide dan tannin sebagai komposit polimer untuk mengurangkan pewarna. Pengubahsuaian komposit polimer ini telah disediakan sebagai bahan pengental dan juga fotopemangkin untuk kedua-dua kaedah rawatan dan dicirikan dengan menggunakan kaedah Perubahan Fourier Infra-merah (FTIR). Aktiviti penggumpalan dan fotopemangkin (ZOPAT) menggunakan air sisa mentah tekstil telah dikaji dengan mengoptimumkan parameter seperti kesan nilai pH, dos pemangkin dan masa tindakbalas. Optima peratus pengurangan warna dicapai bagi kaedah UV-fotopemangkin (93.67%) di masa rawatan 24 jam manakala bagi kaedah kombinasi (93.92%) di masa rawatan 4 jam telah dicapai pada kondisi pH 10 dan 800 mg/L dos

pemangkin komposit polimer. Penyahwarnaan air sisa tekstil diharapkan apabila komoposit polimer digunakan pada kedua-dua kaedah rawatan ini.

ABSTRACT

Water is an important component in our daily lives. The presence of toxic chemicals and harmful bacteria may expose living things to waterborne diseases and has led a major health risk due to the consumption of contaminated water. Wastewater from the textile industry is one of the many environmental obstructions besides other minor issues like solid waste and resource waste management. There are many types of synthetic dyes that textile industry use and the discharge have massive amounts of highly coloured wastewater. Wastewater with excessive coloured textile sorely effects the photosynthetic function in plant and also impact aquatic lives due to low light penetration and consumption of oxygen. Hence, textile wastewater must be treated properly before being discharged to the environment. In this study, the different treatment methods to treat the textile wastewater is presented. The treatment methods discussed in this study are the coagulation and UV-photocatalytic treatment processes, where both of these methods have been investigated with a combined method. This study involves the modification of zinc oxide with polyacrylamide and tannin as a composite polymer to remove the colour. The objective of this study has been successfully achieved. The modification of composite polymer is prepared as coagulant and catalyst for both treatment methods and it is characterized using the Fourier Transform Infrared Spectroscopy (FTIR) method. The coagulation and photocatalytic activity of ZnO/Tannin/PAM (ZOPAT) using raw textile wastewater is investigated by optimizing parameters such as the effect of pH value, dosage and contact time. The optimum percentage of colour removals obtained for UV-photocatalytic method (93.67%) at 24 hours of treatment period and for combined method (93.92%) at 4 hours of treatment period were achieved at condition of pH 10 and 800 mg/L of the composite polymer dosage. The decolourization of textile wastewater is dependable on the composite polymer used for both treatment methods.

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LIST OF ABBREVIATIONS

AOP	Advance Oxidation Process
ATR	Spectroscopy Attenuated Total Reflectance
CdS	Cadmium Sulfide
CH_3COOH	Acetic Acid
$C_3H_8O_3$	Glycerol
C_2H_5OH	Ethanol
COD	Chemical oxygen demand
DAF	Dissolve Air Flotation
FTIR	Fourier Transform Infrared Spectroscopy
H_2SO_4	Sulfuric Acid
MgO	Magnesium oxide
MB	Methylene Blue
NaOH	Sodium Hydroxide
OH•	Hydroxyl Radical
PAC	Polyaluminum chloride
PAM	Polyacrylamide
SS	Suspended Solid
TiO_2	Titanium Dioxide

UV	Ultraviolet
ZnO	Zinc Oxide
ZOPAT	Zinc Oxide/Polyacrylamide/Tannin

CHAPTER 1

INTRODUCTION

1.1 Background of study

Water is a basic requirement for human being and other living organisms. Water is fundamental for human activities such as cleaning, cooking, agriculture and drinking. One of the causes that contributes to water pollution is industrial activities. The textile industry is one of the many causes to water pollution as it is fast in discharging the wastewater into the river and negatively impact the environment. The finishing processes of textile industry is the main cause to water pollution and releases the dyes into the environment. These coloured compounds in textile effluents are usually detected in the effluent and has to be removed before discharging into water bodies since these dyeing effluents have toxic effects on the ecosystem, especially on microorganisms. Their long degradation time in the environment is a cause for concern (Zhu et al., 2012). Moreover, each of their processes produce a lot of waste that are non-biodegradable, which could affect the health of plants, aquatic animals, and people (Ismail, 2017). Therefore, in order to monitor the quality of the wastewater, photocatalytic method is one of the solutions to treat the effluent. The photocatalyst oxidizes a surface to eliminate harmful components in industrial dye wastewaters (Ismail, 2017).

1.2 Objective of the study

The objectives of the study are:

1. To determine the performance of new composite polymer (ZOPAT) as a photocatalyst for colour removal from textile wastewater.
2. To examine the combine treatment of coagulation (ZOPAT) and Ultra-Violet (UV) photocatalytic at different pH, dosage and contact time.
3. To evaluate the performance of ZOPAT as coagulant with Polyaluminum chloride (PAC), Zinc Oxide (ZnO), Polyacrylamide (PAM) and Tannin.

1.3 Problem Statement

Due to continuous population growth, the fashion industry is growing bigger. Thus the textile industry is growing faster as well in order to follow and fulfil the demand in this era (Ismail, 2017). In this case it may increase the water pollution as the effluent contain dyes. Textile effluent is characterized by high COD (150-10,000 mg/L), BOD (100-4000 mg/L), pH 96-10) and colour content (50-2500). Discharge of even a small quantity of dye is not acceptable and may produce toxic compounds by the end of treatment process (Asghar et al., 2015). Wastewater from textile industry produces coloured effluents and contain dyes. One of the dye is azo dyes which is most important class of synthetic dyes in textile industries. Since the azo dyes contain several benzene rings which make them persistent and hardly biodegradable, the effluents that release to natural water bodies causes serious hazards to the ecosystem (Jor et al., 2016). Also, discharge of colour effluents to aquatic environment limits the penetration of sunlight into the water body and can interfere the algal and aquatic plants photosynthesis. Therefore, in order to minimize the impact in the quality of water, coagulation-ultraviolet (UV) photocatalytic method is one of the solution for water treatment. The conventional method such as adsorption, chlorination, filtration, reverse osmosis and ion exchange process can only transfer from one phase to another phase for organic compounds. These methods are less efficient because dyes are stable against biological degradation which results in sludge formation, membrane fouling and incomplete mineralization (Asghar et al., 2015). However, heterogeneous photocatalysis was proven to be an effective advanced oxidation technique for the complete mineralisation of active hydroxyl free radical (OH) as a main product by irradiation of semiconductor materials (Nithya and Jothivenkatachalam, 2015). Due to photocatalysis is a great potential as a green and ecofriendly process for the elimination of persistent organic pollutants, it is increase the security of clean water (Boon et al., 2018).

Coagulation treatment is widely used due to its low capital cost and simple operation for removal of dyes. Coagulation is a process of destabilizing the dye solution systems to form agglomerates by adding the inorganic coagulants and synthetic or natural polymers in wastewater (Liang et al., 2014). One of the disadvantages of coagulation treatment is it is challenging in selecting suitable coagulant due to the large number of dyes which have complex structures (Liang et al., 2014). In order to overcome the limitations of biological processes, physical-chemical treatments have been envisaged as promising alternatives to efficiently remove organic matter, suspended solid and turbidity (Yasmina et al., 2014). Whereas for solar driven photocatalytic method prove that it is an efficient way to treat wastewater from textile industry that it can be transform and mineralize the organic pollutant to inorganic matter (Nithya and Jothivenkatachalam, 2015). Furthermore, by using photocatalytic method also can be produce to readily biodegradable organic matters. Since this process does not require the addition of hydrogen peroxide to treat wastewater to remove various persistent organic and inorganic micro-pollutants and uses solar light, it can be developed as an economically feasible and environmentally friendly method to decolorize or treat the water using sunlight (Zhu et al., 2012). This method is low cost as the catalyst could be reused based on the stability for the decolourization of wastewater (Ismail, 2017). In this study also used combined method of coagulation process and photocatalytic process in order to gain a better results and may show potential to meet standard regulation other than use single process.

In this ultraviolet photocatalytic activity, Zinc Oxide (ZnO), Tannin, and Polyacrylamide are involved as composite polymer. Firstly, ZnO is in the form of white powder that is insoluble water. The greatest advantage of ZnO is its ability to absorb a wide range of solar spectrum and more light quanta compared to some semiconducting metal oxides, while its major drawback include its wide band gap energy and photocorrosion (Ismail, 2017). Thus, with the wide band gap of semiconductor of ZnO, the electron mobility is higher as well along the strength of its metal oxides. Furthermore, other advantages of ZnO is its good gas sensing property, photocatalytic activity, antibacterial activity, good optical property and also low cost (Nithya and Jothivenkatachalam, 2015). Therefore, ZnO also need to mix with other polymers as a support catalyst to gain good effectiveness in removal of colour.

Tannin is a natural polymer and an inexpensive material. Tannins are extracted from biomass, leaves, bark, roots, seed, wood and fruits as it is the most generous compounds (Bacelo et al., 2016). For cationic dye removal, the tannin molecular has shown that the adsorbent capacity is very strong and it is also evident that the excellent of chelating affinity towards a lot of metal ions by owing to the large amount of multiple adjacent phenolic hydroxyls (Pei et al., 2016).

Polyacrylamide (PAM) has gel-like properties, the polymer is hydrophilic and it is very high concentration in aqueous solutions form. Hence, due to the properties, the solutions can utilize as flocculants for treatment of sewage and industrial effluents in the removal of suspended particles. The chemical molecular structure of PAM is unusual, the adsorption materials of PAM is one of the most adaptable to use in order to remove dye for wastewater treatments (Zhou et al., 2014).

Thus, in promoting a sustainable way by using photocatalytic treatment process, the source of UV light can be used from natural sunlight. However, as the investigation run in the laboratory, it is crucial to apply natural sunlight in this process to determine the photocatalytic activity effectiveness of removing the desired pollutants. Thus, the applying UV light by commercial lamp which is 360 nanometer for photocatalytic process to treat wastewater from textile industry is investigated.

1.4 Scope of the study

The main concern is the colour removal from textile wastewater by using ZnO/PAM/Tannin (ZOPAT) a composite polymer as hybrid catalyst and coagulant. There are three parts that make up this research which are methodology, the synthesis of catalyst and the characterization of the composite polymer and analysis by using FTIR. Moreover, the effect of composition and dosage of the catalyst ZnO, Tannin and PAM used for coagulation and photocatalytic method is studied. Next, coagulation and photocatalytic methods have been applied individually and combined by proceeding with the treatment by sequence to investigate the efficiency of the process in removing colour of wastewater.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water is a basic requirement for daily activities such as drinking, cooking, and cleaning. The availability of clean water is disrupted by human activities which include the usage and the process of purification. In any country, the industrial activity grows as the development increases as it is playing an important role. Water pollution occurs because industries releases the wastewater directly into the water bodies. The water pollution from various industries cause several harmful effects to humans and nature as it contains organic pollutants.

The processing operations of textile industry uses higher consumption of water as it has different phases of process which makes the textile industry a major creator of effluent wastewater. Chemicals that are contained in these effluent wastewater are acids, alkalis, dyes, hydrogen peroxide, starch, surfactants dispersing agents and metals soaps (Holkar et al., 2016). Thus, this will lead to environmental impact and lead to human diseases. The average water consumption rate of fabric processed per day by textiles mills is about 200 L per kg (Holkar et al., 2016). The problem worsens as the effluent released from mills usually high temperature and pH. There are several types of pollutant dyes such as azo dyes, anthraquinone dyes, acridine dye, triarylmethane dye, and nitro dye (Ismail, 2017).

2.2 Various wastewater treatment techniques

Water contamination occurs from dye pollutants that are produced from textile industries. The problem becomes serious as it occurs when the colour produced in effluent by the amount of dyes when they contemplate to study the affect the quality of water and unpleasant state of sight. This will give a big impact to the environment especially to the aquatic life and also water resources. Therefore, the coloured compound has to be removed before the wastewater directly discharge into water bodies.

The colour produced by minute amounts of dyes in water poses a very serious problem as they have a considerable effect on the water environment and is visually unpleasant. These substances include powders, chemicals, metal ions, oil, organics and others, and pose a threat to the environment, especially aquatic life and water resources. (Ismail, 2017). Thus, in order to treat the wastewater, there are different types that could be used from the conventional method such as advance oxidation process, adsorption process, biological treatment process and others. Table 2.1 gives the list of the advantages and disadvantages of different kind of wastewater treatment.

Table 2.1: The advantages and disadvantages of different kind of wastewater treatment

Techniques/ Method	Advantages	Disadvantages	Author
Advance Oxidation Process (AOP)	Reaction rate is fast	Removal of organic material only	(Krzemińska et al., 2015)
	Excess of materials will not produce such as chemical sludge	Expensive for a complete mineralization	
	Toxicity reduce		
Adsorption process	Promising in practical application as it is easily separated from aquatic system	Expensive	(Zhang et al., 2015)
		The process only transfer the pollutants from one phase to another	
Biological process	Cost effective	Inconvenience for cleaning because have some limitations with degrading toxic	(Ganzenko et al., 2014)
	Modified easily according to local needs		

2.3 Textile Industry Wastewater Treatment

Among all of industries, textile production industry is one of the complex industries. The wastewater from textile industry produced during the production steps of manufacturing yarns and fabrics during finishing contains a various range of dyes and chemicals Textile mills and their wastewater have been increasing followed with the high demand for textile products which caused a major problem of pollution. The chemical in textile industry wastewater cause both environmental and health problems. Therefore, wastewater treatment is very important for textiles production. Figure 2.1 shows the flow of textile industry wastewater treatment and Table 2.2 shows the characteristic of the sample wastewater from textile industry.

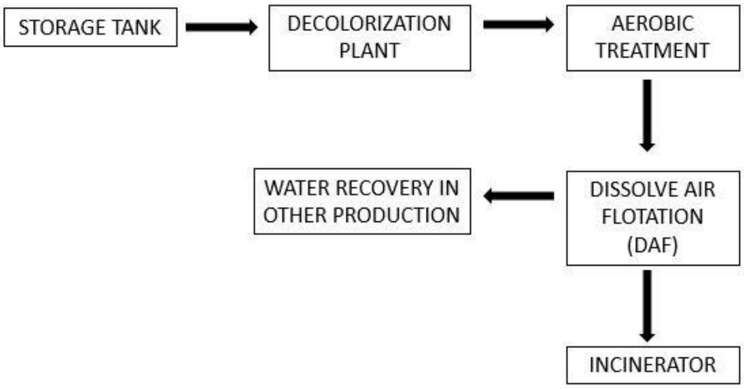

Figure 2.1: Flow of textile industry wastewater treatment (Penfabric, 2019)

Table 2.2: Characteristic of the sample wastewater from textile industry (Hayat et al., 2015)

Parameter	Unit	Concentration
pH	-	7.7 ± 0.115
DO	mg/L	0.3 ± 0
Temperature	°C	25.7 ± 0
Conductivity	µs	145 ± 1.01
Turbidity	NTU	188.6 ± 0.57
Total solids	mg/L	1731.6 ± 8
Total dissolved solids	mg/L	86.7 ± 0.28
Total suspended solids	mg/L	1697 ± 7
COD	mg/L	2.6 ± 2.5

2.4 Zinc Oxide/Polyacrylamide/Tannin as a composite polymer

Zinc Oxide/Polyacrylamide/Tannin or namely as ZOPAT works as a composite polymer for coagulation-photocatalytic process to treat wastewater from textile industry. Not only that, for organic pollutants degradation, a study have proved that ZnO can be used as a very promising photocatalyst as the ZnO is a semiconductor with exceptional physicochemical and optical properties, wide band gap, also low cost, stability in environment and nontoxicity (Lam et al., 2018). Zinc Oxide (ZnO) nanoparticles were synthesized from Zinc Chloride ($ZnCl_2$) by using glycerol ratio (Z. Wang et al., 2018). ZnO nanoparticles that has already synthesized which have a suitable nanostructure of ZnO will allow higher efficiency of process and amplify the photocatalyst recovery during post treatment stage (Boon et al., 2018). Treatment of photocatalysis is a known choice, as it can absorb more pollutants easily and can achieve higher rate of degradation as the nanoparticles provide a high surface areas (Boon et al., 2018). Table 2.3 shows method used to synthesize zinc oxide whereas Table 2.4 shows the list of advantages and disadvantages of different ZnO nanostructures to operate in photocatalytic applications.

Table 2.3: Method used to synthesize zinc oxide

Method	Parameter	Authors
Precipitation	Solution reacting with polyethylene glycol for 2 hours at room temperature, wash the precipitates and filter with ammonia solution with pH 9 and anhydrous ethanol for several times, then dry under vacuum for 12 hours. Finally, calcined the precursors in an oven at 450 °C for 3 hours and milled.	(Ismail, 2017)
Sol-gel	Using zinc acetate and sodium hydroxide precursors. 50ml of 0.12M Zinc acetate was added into 50ml of 0.5M sodium hydroxide solution under constant stirring at room temperature for 2 hours. The white precipitation obtain dried at 80°C for 5 hours.	(Nithya and Jothivenkatachalam, 2015)
Precipitation	To fabricate ZnO colloidal nanoparticle, the as-prepared solution was agitated by a magnetron for 30 min at 60 ◦C. The 10 nm ZnO powders were collected from the solution by centrifuge and dried at 60 ◦C without washed.	(H. Wang et al., 2007)
Precipitation	The solution was separated using centrifudge for 10 minutes at 4000rpm to remove the supernatant. The precipitate ZnO nanoparticle were wash with ethanol and distilled water twice. Dried in the oven at 80°C before grind to powder form.	(Z. Wang et al., 2018)
Reflux	The mixture was then slowly added into NaOH (0.1 M) solution under magnetic stirring. Adjusted the final pH value of solution to 12.12. Then, the mixed suspensions were heated and refluxed at	(Lam et al., 2018)

	60°C for 8 h. Next, filtered and washed with distilled water and ethanol for several times and finally dried at room temperature.	

Table 2.4: List of advantages and disadvantages of different ZnO nanostructures to operate in photocatalytic applications (Boon et al., 2018)

ZnO nanostructures	**Advantages**	**Disadvantages**
Nanoparticles	Suspended in solution easily	Form agglomerates in solution easily
	The large surface areas give an outstanding performance	Required post-treatment for catalyst removal
		Difficult to complete recovery of catalyst
Nanowires	The growth could be easily carried out on most substrates	Conditions of growth highly restricted
	Large surface area compare to nano-thin films	The surface area is lower than nanoparticles
	Not required post-treatment to remove catalyst	
	Crystallinity is low and more defects	
Nano-thin films	Can be coated on certain substrates	Small surface area cause restricted performance
	Not required post-treatment to remove catalyst	

Polyacrylamide (PAM) is one of the synthetic organic polymers which has been used for wastewater treatment plant with its high molecular weight and excellent performance in coagulation treatment regardless of it being non-biodegradable and hazardous to living organisms (Aisyah et al., 2014). Furthermore, for tannin which is natural polymer that is suitable to be used and have reasonable approach to treat wastewater treatment in order to replace the contained of toxic material. Various types of natural organic polymers studied by previous researchers such as morringa oleifera, grape seeds and tannin as plant based meantime for animal based is chitosan (Aisyah et al., 2014). Therefore, natural organic polymer from tannin can be considered as an alternative to PAM.

2.7 Coagulant treatment process

Coagulant known as the process which destabilization of a specific colloidal suspension or solution is taking place. In this processes, in order to destabilize colloidal material, inorganic coagulants and synthetic or natural polymers are added to wastewater, this will cause the aggregation of small particles into larger size so it is more easily to form the flocks (Freitas et al., 2015). Coagulation is also of one of the processes that are is for removal of colour. The function of coagulation is to overcome the factors that encourage the stability of a given system, it is achieved with the use of appropriate chemicals, usually aluminium or iron salts, the so-called coagulant agents (Z. Wang et al., 2018). There are numerous types that has been developed including inorganic-organic, inorganic-natural polymer, organic-organic and organic-natural all through the years (Aisyah et al., 2014). Coagulation of dye solutions is a process of destabilizing the dye solution systems to form agglomerates or flocs (Mahajan et al., 2017). The application of physical and chemical pre-treatment processes, such as coagulation and sedimentation may be considered for removal of colloidal and solid materials of textile wastewater (Jor et al., 2016). Thus in this study ZOPAT which is the combination of inorganic polymer, natural and synthetic organic polymer were used as coagulant for jar test.

2.8 Ultraviolet (UV) photocatalytic treatment process

The combination of photochemistry and catalysis results in the term photocatalysis. Photocatalyst can be defined as “acceleration of photoreaction in the presence of a catalyst”. Just by applying the light radiation the substance can modify the acceleration of the rate of reaction. Furthermore, photocatalyst can be describe as a material which is capable of absorbing light, enable for chemical transformations of the reaction participants by producing electron-hole pairs, and after each cycle of such interactions it can be restore the chemical composition (Ismail, 2017).

There are two processes that can be classified in photocatalytic activities which are homogeneous or heterogeneous processes. The processes depends on whether they occur in single phase or the apply the use of heterogeneous catalyst like metal supported catalysts, carbon materials, or semiconductors such as TiO_2, ZnO, and CdS (Aiin, 2017). Whereas, for homogeneous process depending on the interactions between chemical reagents and target compounds which characterized by chemical changes (Aiin, 2017). The basic principle of semiconductor photocatalyst is based on the excitation by light which are UV or visible, thus under the movement of photons, the semiconductor or catalyst assemble highly oxidizing free radicals which enable the destruction of compounds adsorbed on its surface (Yasmina et al., 2014). Based on study the optimum percentage of degradation of methylene blue, MB for photocatalyst of with zinc oxide/chitosan 1g as catalyst in 10 ppm of MB at pH 7 was reported to be 71% at a reaction of time 1.25/min (Ismail, 2017). In this study ZOPAT will be used as composite polymer for UV photocatalytic process.

2.9 Coagulation and UV-photocatalytic treatment processes

In this study, coagulation and UV photocatalytic treatment process undergo individually and combined to gain and assess the best condition to degrade the removal of colour by real textile wastewater. The combined method process followed by sequent which started with coagulation and followed by photocatalysis. Hence, for removal of solid materials and colloids of textile wastewater, the coagulation was used. Next, the photocatalytic activity for destruction of residual recalcitrant organic pollutant (Lam et al., 2018). A real textile wastewater used to evaluate the efficiency of sequencing coagulation-photocatalytic processes based on the optimum operational parameters obtained during the removal of Acid Rate 73, AR73. The operational conditions included coagulation with rapid mix (150 rpm) for 1 minute, gentile mix (15 rpm) for 15 minutes, sedimentation time is 30 minutes, catalyst dosage is 200 mg/L and pH 6, next followed by photocatalytic degradation used magnesium oxide, MgO with 0.8 g/L, pH 5 and reaction time 60 minutes (Jor et al., 2016). Table 2.5 shows the advantages and disadvantages of coagulation and UV photocatalytic treatment process.

Table 2.5: Advantages and disadvantages of coagulation and UV photocatalytic treatment process.

Treatment	Advantages	Disadvantages	Author
Coagulation	Low capital cost	Ineffective for some soluble dyes	(Liang et al., 2014)
	Simple operation	Due to the large number of existing dyes which have complex structures it is challenging in selecting suitable coagulant	
	Destabilizing dye solution systems in order to form agglomerates or flocs.		
UV-photocatalytic	Does not require extra recovery steps	Less studies about stability of polymer membrane	(Boon et al., 2018)
	Stable flux and low flux-decline rate	Less relation of kinetic models and mass transfer limitations	
	Enhanced the absorption of photons and reactants	Not recommended to investigate the treatment with synthetic proxies	
	High efficiency in degrading persistent organic pollutants		

2.9.1 Effect of pH value

The characteristics of textile wastewater that contain dyes, pH plays an important role which is one of the most major parameters that may influence the photo-oxidation processes (Zhu et al., 2012). Based on study, by using zinc oxide under the conditions tested, the highest degradation was achieved at pH 5-7. At this pH range, most of the phenol remains undissociated. Hence, the maximum numbers of phenol molecules are adsorbed on the zinc oxide surface and consequently resulted in enhanced photo-degradation (Harife, 2012). The interpretation of the effect of pH on the photocatalytic process is complicated due to its multiple roles which are electrostatic interactions between the semiconductor surface, solvent molecules and substrate, and charged radicals formed during the reaction process (Ismail, 2017). Moreover, the changes of solution's pH by the surface charge property of metal oxide thin films causes by the amphoteric behaviour of semiconductor. The zero charge of the surface nearly achieved at basic pHs as the nanosized In_2O_3, the pH zero point charge (pHzpc) is known to be 8.64 (Ismail, 2017). In other word, the dye adsorption at basic pHs of surface has not been saturated and remained fresh and accessible for dye molecules. The amount of hydroxide radicals, •OH produced by UV irradiation is greatly affected by the pH and as a result effective dye decolourization rate is highly dependent on the pH of the solution (Harife, 2012). Study also stated that ZnO reacts with acids to produce the corresponding salt and with bases to form complexes at acidic pH and alkali pH, respectively. It should be noted that the solution pH significantly changed during the period of decolourization without controlling pH at various initial solution pH values (Harife, 2012). Experiments were conducted at different initial pH values in order to investigate the effect of pH on the decolourization kinetics. Table 2.6 tabulates the effect of pHs on the decolourization efficiency.

Table 2.6: Effect of pH value on the decolourization efficiency (Zhu et al., 2012)

pH value	**Percent of decolourization**
2	99.8%
6	50.7%
12	28.2%

2.9.2 Effect of initial catalyst dosage

The amount of the photocatalyst dosage and the high amounts of catalyst particles may influenced the dye degradation in wastewater treatment. The production of active sites for photocatalytic reaction increases as has large surface area due to the increasing of the photocatalyst dosage and also give the efficiency of adsorption by the catalyst. Therefore, the generation of more •OH may take place for the photocatalytic degradation of the target pollutant (Jor et al., 2016). However, at a certain amount of catalyst as the solution become turbid, the UV radiation may be block to proceed the reaction which the degradation could be limit (Ismail, 2017). Based on a study, as the dye concentration increases, rate of degradation decrease due to the catalyst surface area is fixed. Limited number of dye molecules attach at the active site of the catalyst. The remaining dye molecules persist in solution until earlier attached molecules are degraded. The number of active sites of catalyst also decreases due to less availability of photons for excitation of catalyst molecules (Harife, 2012). The effect of the catalyst dosage on the photodegradation efficiency by using zinc oxide is tabulated in Table 2.7.

Table 2.7: The effect of the catalyst dosage on the photodegradation efficiency (Harife, 2012)

Dosage (mg/L)	**Percent of degradation (%)**
500	71
600	73
800	84
900	97
1000	99.9

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter discusses the materials, processes, and method used in this study. The method to synthesis the ZnO/PAM/Tannin photocatalyst is described. The content of this chapter includes the details of experimental work which are coagulation method and photocatalytic activities to investigate the efficiency removal of colour by using wastewater sample from textile industry. Next, the design of the experiment is described with the sample preparation and the characterization of the ZnO/PAM/Tannin a composite polymer that used as a catalyst.

3.2 Materials and Chemicals

The synthesis of ZnO/Tannin/PAM is used as sample in this experiment to treat wastewater. Therefore, the materials used in this research are zinc chloride ($ZnCl_2$), zinc oxide (ZnO), acetic acid (CH_3COOH), sodium hydroxide (NaOH), Tannin, Polyacrylamide (PAM), glycerol ($C_3H_8O_3$), and ethanol (C_2H_5OH). Table 3.1 shows the list of the general information of materials throughout this experiment.

Table 3.1: The general information of materials throughout this experiment

Material	Manufacturer	Function
Zinc Chloride ($ZnCl_2$)	R&M Chemicals	Catalyst
Acetic Acid (CH_3COOH)	QReC	Solvent
Sodium Hydroxide (NaOH)	QReC	Solvent

Tannin	R&M Chemicals	Support Catalyst
Polyacrylamide (PAM)	R&M Chemicals	Support Catalyst
Glycerol ($C_3H_8O_3$)	ChemAR	Stabilizer
Ethanol (C_2H_5OH)	ChemAR	Remove impurities

Furthermore, wastewater sample is taken from one of the textile industry which is located at Perai, Pulau Pinang. The sample of the textile wastewater was taken from the storage tank which is stored after the final process of textile production. After the final process in textile, the effluent of the wastewater will be stored in storage tank. After that, pH of the wastewater adjusted which have sulfuric acid tank to make sure the effluent followed the pH requirement. Next, the wastewater will undergo the step of decolourization plant by using coagulation process to reduce the colour in order to comply with standard regulation and followed by aerobic treatment. This treatment also has Dissolve Air Flotation (DAF) system to allow to eliminate the content of oil, grease and other surfactants. Lastly, this treated water is suitable for water recovery system which can be used in production in the future. Figure 3.1 shows the decolourization plant of the textile industry. The textile wastewater will undergo the decolourization plant from the storage tank.

Figure 3.1: Decolourization Plant (Penfabric, 2019)

The wastewater sample was taken two times from the storage tank of the textile industry which is on 22nd January and 19th February 2019. The wastewater taken on each days with 20 L bottle of sample. The sample was test on site with YSI multi-probe system and brought to the laboratory to test the characteristics of the raw sample textile wastewater. The characteristics that are tested for the raw sample are pH value, turbidity, suspended solid (SS), chemical oxygen demand (COD) and also colour.

3.3 Equipment

The equipment that are used for the characteristics of the sample is to determine the turbidity, colour, SS, COD and pH value of the textile wastewater. The multi-probe system YSI was used on site for a direct test on characteristics of sample. Whereas in laboratory, to determine the characteristics of sample wastewater turbidity meter, spectrophotometer and pH meter was used. For ZnO nanoparticle preparation, centrifuge was used. FTIR was used for characterization analysis. Table 3.2 shows the list of equipment along with the usage of equipment.

Table 3.2: The equipment used along with the usage of the equipment

Equipment	Usage
Fourier Transform Infrared Spectrocospy (FTIR)	Determine photocatalyst functional group
Turbidity meter (TB400)	Measure turbidity
Spectrophotometer DR2800	True colour testing and determine suspended solid and chemical oxygen demand
pH meter	Measure pH
Multi-Probe System (YSI 556 MPS)	Measure temperature, pH and any other parameters on site

3.4 Design of experiment and parameter studied

The production of zinc oxide/polyacrylamide/tannin (ZOPAT) solution which is composite polymer used ex-situ method will be explained the along the experimental procedures and parameter studied in this section. First objective of this study is to determine the new composite polymer, ZOPAT. Therefore, at first stage of the experiment is to synthesis the ZnO from ZnCl. Each of the polymers need to be in form of solution before prepare the composite polymer. After the formation of ZOPAT, the experiment can proceed with wastewater treatments. Next, the second objective of the study is to examine the UV-photocatalytic process, coagulation process and combined treatment processes by using ZOPAT as a catalyst and coagulant to treat the wastewater sample. There are a few parameters were investigated that effect the treatment processes which are pH value, catalyst dosage and contact time by using wastewater sample from textile for the decolourization. The third objective is to evaluate ZOPAT as coagulant with the comparison using different type of polymer which are PAC, ZnO, PAM and Tannin for jar test. Lastly, to characterize the composite polymer by using FTIR. Figure 3.2 shows the overall flow of the procedures in completing the experiment.