USE OF PHOTOCATALYTIC TECHNIQUE IN TREATMENT OF WASTEWATER CAUSED BY YARN DYEING PROCESS IN THE TEXTILE INDUSTRY IN BANGPAKONG, CHACHOENGSAO PROVINCE

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Abstract- Wastewater from reactive dyeing process is a primary cause to wastewater pollution. This is due to the facts that most types of dyes are organic and soluble; as a result, it is difficult to be treated. This research thus aims to discuss the use of Photocatalytic technique in the treatment of wastewater caused by the textile industry in Bangpakong, Chachoengsao, together with the absorption technique through titanium dioxide and sawdust, and to study the results of the treatment. Water wasted with reactive dye, acid dye, disperse dye, and direct dye will be treated in this study. According to SEM/EDX study, it is found that sawdust are consisted of 63.15% of carbon and 32.33% of oxygen, other minerals, for example, a small amount of potassium and calcium are detected. From SEM photographs and BET surface area analysis, it shows that when sawdust are conditioned through water and 0.1 N HCl, it will dissolve components, for example, potassium and calcium, increasing holes on the surface of absorption materials as a result. From the study, direct and reactive dye reacts satisfyingly to the Photocatalytic wastewater treatment and the absorption method while disperse dye react well to the absorption technique. However, only small amount of acid and basic colours are present in the wastewater; thus, they are not tested. The proper conditions for treating direct dye are the use of 10 g of titanium dioxide per litre for a 6-hour period and the use of 10 g of sawdust per litre for a 2-hour period. For reactive dye, 10 g of titanium dioxide per litre for a 6-hour period and 10 g of sawdust for a 2-hour period are recommended. Lastly, disperse dye wastewater requires 15 g of sawdust per litre and a 4-hour period. In conclusion, Photocatalytic in combination with absorption technique can be employed for wastewater treatment caused by the textile industry.

Index Terms- Textile Industry, Titanium Dioxide, Photocatalytic Technique.

I. INTRODUCTION

The Photocatalytic process is the technique of catalysis by using light to stimulate electrons in valence band of semiconductors in contaminated water. This could be explained as the technique that allows the light energy to pass into the systems to defeat valence band and produces electron hole pairs and absorbed species (reactants) on the surface of semiconductors. The chemical that can generate this result is titanium dioxide, which has the characteristics of catalyst in Photocatalytic process as titanium dioxide can interact effectively in sunlight; it has features on wastewater treatment and effective organic substance eradication.

The use of titanium dioxide can reduce the costs of the production in wastewater treatment system. Therefore, Photocatalytic technique with absorption process using titanium dioxide and sawdust in wastewater treatment process is used in the textile industry in Bangpakong, Chachoengsao Province.

The aim of this research is to study the results of wastewater treatment caused by dyeing process through the use of titanium dioxide and sawdust and to study the forming of sorbents from natural materials and sawdust in wastewater treatment.

II. METHODOLOGY

The reason for using titanium dioxide as a substrate in Photocatalytic for wastewater treatment caused by dyeing process in the textile industry, in Bangpakong, Chachoengsao Province, is the exceptional characteristics of titanium dioxide that can recover wastewater and eradicate volatile organic compounds effectively. Moreover, it has the proficiency to interact effectively with sunlight or solar power. The aim of this researching is to study the results of wastewater treatment for reactive dye, acid dye, disperse dye, basic dye and direct dye with the mixed use of titanium dioxide and sawdust. Sawdust is used as the sorbent; it is a by-product from factory derived from furniture making. Then the sawdust is burnt at 1,000 degrees Celsius and retrieved using cyclone dust collector and further employed in this research.

A. Preparation of Sorbents : Preparation of Sawdust Sawdust can be produced through the drying

process at 110 degrees Celsius for 3 hours. Then it is blended in the blender and filtered of which its size must be smaller than 75 micrometres using a sieve. After that, weighing the prepared 120 g of sawdust and soak in 1,000 millilitres of distilled water for 3 times until the pH of substance is stable, pH = 12.

Then dry the sawdust at 110 degrees Celsius and blend the sawdust in the blender. Select the sawdust of which its size is smaller than 75 micrometres by using a sieve and collect the sawdust for the research.

B. Preparation of Sorbents : Preparation of Conditioning Sawdust with 0.1 NH_2SO_4

Weigh 110 g of prepared sawdust from 1.1, soak in 1,000 millilitres of NH_2SO_4 solution, stir constantly for 1 hour and then use 1,000 millilitres of distilled water to clean the sawdust for 3 times until the pH of substance is stable (pH = 11). Dry the substance at 110 degrees Celsius and blend the sawdust in the blender. Select the sawdust of which its size smaller than 75 micrometres using a sieve and collect the sawdust for the research.

C. Preparation of Sulphuric Acid 0.1 N Concentration Solution

Pipette 34.63 millilitres of 65% Sulphuric acid in 250 millilitres volumetric flask and adjust the volume using deionised water in 250 millilitres volumetric flask until it reaches the required volume.

D. Synthesis of Titanium Dioxide

Prepare titanium dioxide through sol-gel technique, by dissolving $C_{12}H_{28}O_4Ti$ in 2-butanol in a 1:10 ratio. Stir the substance for 15 minutes at the room temperature while also releasing Nitrogen throughout the experiment. Add HCL 4M and stir the substance for 70 minutes and leave the solution until it turns into gel. Bake the gel at 110 degrees Celsius until it crystalises and burn the crystalised gel at 540 degrees Celsius to produce titanium dioxide.

E. Analysis of Dye Intensity in Untreated Wastewater

Prepare 1% of wastewater for experiments and proceeds it in the dyeing process. After that, analyse the intensity of dye in untreated wastewater. The details are as follow.

- **Preparation of Direct Dye Water**

Prepare direct dye water with concentration of 2%. Add sodium sulphate at 20 g/l and acetic acid with concentration equivalent to the weight of fabric used in this research (acid dye only). After that, process the liquid through dyeing process through the automatic dyeing machine. The details of dye used in this research are as follow. Trade name: Direct Fast Scarlet 4BS, Characteristic of Dye: Bright Red, C.I. Number: C.I. Direct Red 23, Structure: Diazo, Highest Wavelength: 496.5 nm.

- **Preparation of Reactive Dye Water**

Prepare dye water with concentration of 2%. Add sodium sulphate at 52 g/l and sodium carbonate with concentration of 17 g/l. After that, process the liquid to dyeing process through the automatic dyeing machine. The details of dye used in this research are as follow. Trade name: Begative Scarlet HD3G, Characteristic of Dye: Bright Bluish Red, C.I. Number: C.I. Reactive Red 21, Structure: Monoaza, Highest Wavelength: 508.5 nm.

- **Preparation of Acid Dye Water**

Prepare dye water with concentration of 2%, Add acetic acid with concentration equivalent to the weight of fabric used in this research. After that, process the liquid to dyeing process using the automatic dyeing machine. The dyeing process is similar to direct dyeing process. The details of dye used in this research are as follow. Trade name: Polynyl red MBN, Characteristic of Dye: Bright Red, C.I. Number: C.I. Acid Red

- **Preparation of Disperse Dye**

Prepare dye water with concentration of 2%. Add acetic acid with concentration of 2 g/l and 6.5 g/l of dispersants. After that, process the liquid to dyeing process through the automatic dyeing machine. The details of dye used in this research are as follow. Trade name: Lonspersel Red S5-BL, Characteristic of Dye: Bluish Red, C.I. Number: C.I. Disperse Red 167, Structure: Azo, Highest Wavelength: 467.0 nm.

- **Preparation of Basic Dye Water**

Basic dye is water-soluble and produces positive ions when dissolved and disintegrated. Basic dye is commonly used in acrylic fabric. The condition of basic dyeing process is acidic and could be prepared by adding dye auxiliary such as acetic acid, which has concentration equivalent to the weight of fabric used in this research, to adjust the dye water for suitable dyeing condition. The general structure is aromatic such as triarylmethane, methines and xanthenes. The dyeing process is similar to direct dye process. The details of dye used in this research are as follow. Trade name: Cationic Red GTL 200%, Characteristic of Dye: Dull Red, C.I. Number: C.I. Basic Red 18, Structure: Monoazo, Highest Wavelength: 488.0 nm.

F. Creating Standard Curve

Prepare standard solution of sample dyes concentration of 100 ppm, by weighing 0.100 g of sample dyes (4 decimal places) and dissolve in water and adjust the volume until it reaches 1,000 millilitres in the volumetric flask. Then prepare standard solution of sample dyes concentrations of 25.00, 20.00 15.00, 5.00 and 2.00 millig/l respectively. Pipetting standard solution of sample dyes concentrations of 100.00 millig/l for 12.50, 10.00, 7.50, 5.00, 2.50 and 1.00 millilitres respectively into six of 50 millilitres volumetric flasks and diluted in distilled water until it reaches expected levels. After, measure an absorbance at 544 nanometres wavelength using spectrophotometer and process the results in developing standard curve to present the relation between absorbance and concentration of sample dyes.

III. PHOTOCATALYTIC PROCESS AND ABSORPTION

The study can be divided into 6 steps as follow

Step 1 Measuring suitable concentration of titanium dioxide

- Bring the sample dye from dyeing process, which is not added by titanium dioxide, to UV-Box for 6 hours and collect the sample for measuring absorbance and pH.
- Repeat step 1.1 but adjust the concentrations of titanium dioxide to 5, 10 and 15 g/l.
- Repeat step 1.1 and 1.2, but change sample dye to active dye, acid dye, disperse dye and basic dye. Afterwards, compare saturation of each solution.
- Select the most suitable concentration of titanium dioxide for further steps.

Step 2 Measuring the relation of titanium dioxide

- Use the most suitable concentration of titanium dioxide for experiment derived from step 1 to find the appropriate time of titanium dioxide for dye wastewater treatment.
- Add the sample of dye with titanium dioxide concentration of 10 g in 1 litre of direct dye, bring into UV-Box for 2 hours and collect the samples every 3 hours. Then measure absorbance and pH of collected dye samples. Repeat the step but adjust the duration in UV-Box to 4, 6 and 8 hours.
- Repeat step 2 but change the dye sample to active dye, acid dye, disperse dye and basic dye. Compare saturation of each solution and use the results of dye wastewater treatment of titanium dioxide to find the appropriate duration in the next steps.

Step 3 Measuring the characteristics and features of sawdust

Measure sawdust conditioned with 0.1 NH2SO4 using the scanning electron microscope(SEM/EDX), the Fourier transform infrared spectrophotometer (FTIR), and the surface area analyser. The details of experiments are as follow.

- Analyse sawdust conditioned with 0.1 NH_2SO_4 and processed through drying process by scanning through Scanning Electron Microscope (SEM/EDX) at different scale. For structure analysis, dried sawdust needs to be coated with carbon before performing the analysis.
- Paste the sawdust conditioned with 0.1 NH_2SO_4 and mix with KBr in a 1:100 ratio before processing the analysis through Fourier transform infrared spectrophotometer (FTIR).
- Dry the sawdust conditioned with 0.1 NH_2SO_4 and store in sample containers before proceeding to BET Surface area analysis.

Step 4 Measuring characteristics of acidity and basicity on sawdust surface.

The details are as follow.

- 1 Measure acidity characteristics on sawdust surface by washing sawdust in water. Treat sawdust with 0.1 NH_2SO_4 for 1 hour and treat sawdust with 0.1 NH_2SO_4 for 24 hours. Put the 0.2000 g of processed sawdust into the flask with 25.00 millilitre of Sodium Hydroxide (NaOH) concentration 0.1 N solution inside. Then, stir the solution at 150 rpm at 30 degrees Celsius for 24 hours. After that, strain the solution using grade 5 filter paper and titrate the solution by Hydrochloric acid concentration 0.1 N solution.
- Measure basicity characteristics on sawdust surface by washing sawdust in water. Treat sawdust with 0.1 NH_2SO_4 for 1 hour, and treat sawdust with 0.1 NH_2SO_4 for 24 hours. Put the 0.2000 g of processed sawdust into the flask with 25.00 millilitre of Sodium Hydroxide (NaOH) concentration 0.1 N solution inside. Then, stir the solution at 150 rpm at 30 degrees Celsius for 24 hours. After that, strain the solution using grade 5 filter paper and titrate the solution by Sodium Hydroxide concentration 0.1 N solution.

Step 5 Finding suitable amount of sawdust

- Use the results of dye wastewater treatment by titanium dioxide and suitable time for further experiment to find the suitable quantity of sawdust for dye wastewater treatment.
- Use treated direct dye wastewater by titanium dioxide to measure the suitable amount of sawdust for wastewater treatment. This could be done by gradually increasing the amount of sawdust for 2 hours and collect the samples to measure saturation and pH. Repeat the step by changing the amount of sawdust to 8, 16, and 24 g.
- Repeat the step 5.2 by changing the dye to reactive dye, acetic dye, disperse dye, and basic dye respectively. Then measure the saturation of each dye and compare the results for each concentration.
- Choose the most suitable amount of sawdust for further experiment.

Step 6 Finding the relationship between the right quantity of sawdust and suitable duration

- Use the results from step 5.4 to find the suitable duration for dye wastewater treatment by determining the amount of sawdust at 8 g/l.
- Add 0.7 g of sawdust into 120 millilitre of direct dye and leave for 1 hour. Then collect the sample to measure absorbance and pH. Repeat the step by changing type of dye to active dye,acetic dye, disperse dye, and basic dye respectively. After that, measure the absorbance of each type of dye on an hourly basis.

II. MEASURING SATURATION IN TREATED WASTEWATER SAMPLES

Measure the saturation of dye using UV-VIS Spectrophotometer, model UV-160A.

$$\text{Change of saturation (\%)} = \frac{[C]2 - [C]i}{[C]0} \times 100$$

When [C]i = initial saturation (%w/v)

[C]0 = saturation at specific time (%w/v)

III. DEVELOPMENT OF SORBENTS FROM NATURAL MATERIALS AND SAWDUST FOR WASTEWATER TREATMENT

In this research, sorbents from natural materials and sawdust are developed by boiling palm leaves with sodium hydroxide concentration of 28 g/l for 4 hours at 120 degrees Celsius, mixed with polyvinyl alcohol (PVA) at 2 g/l, and sawdust at 8, 16 and 24 g/l. Then, heat the mixture at 120 degrees Celsius and use for dye wastewater treatment experiment in step 5 and step 6.

IV. RESULTS AND ANALYSIS

1) Measuring the results of wastewater treatment by Photocatalytic Technique

The saturation of direct dye before treatment is 0.0017 %w/v. When compared to the amount of titanium dioxide used in treatment at 5, 10, 15 g/l, it can be seen that the increase in amount of titanium dioxide can enhance the decrease in direct dye saturation. For the treatment duration that is increased to 2, 4, 6 and 8 hours, the results show that the increase in the treatment duration can enhance the decrease in direct dye saturation. Therefore, the duration of treatment directly impacts the change of saturation as well. Moreover, the increase in amount of titanium dioxide used can increase the surface area for dye absorption. Furthermore, the duration of using light as a catalyst for treatment by Photocatalytic can decrease the saturation of dye after the treatment. This is due to the Photocatalytic process that uses light energy as a catalyst; this leads to better results for treatment which its effectiveness vary based on the duration of the treatment.

When the titanium dioxide received the light power that is higher than the band gap, electrons in titanium dioxide will be stimulated and move from valence band to conduction band. In addition, a hole will be formed at the valence band; these are called electron-hole pair (e-/h+ pairs). There will be 2 types of electron movements. The first one, electrons will move from conduction band to electron acceptor in the solution and create reduction reaction. In the second one, electrons will move from electron generator to the hole in valence band, creating oxidation reaction and produce hydroxyl radicals (OH*) and superoxide anion (O2*). This reaction also creates volatile organic compounds (VOCs) and it will change the formation to carbon dioxide and water at the room temperature, by hydrogen radicals, which will react with hydrogen, becoming water. Moreover, superoxide anion will react with carbon in organic substance and create carbon dioxide. Therefore, the results of wastewater treatment study indicate that the researcher should use titanium dioxide concentration at 10 g/l for 6 hours as initial substance for treatment in next steps.

The intensity of reactive dye before treatment is 0.0054 %w/v and it can be seen that changing intensity trend of reactive dye is similar to direct dye. There is over 80% decrease in dye intensity change based on the results of wastewater treatment. Therefore, the treatment by using titanium dioxide concentration at 10 g/l for 6 hours is selected for the treatment in further steps.

The intensity of disperse dye before treatment is 0.0166 %w/v and the trend of changing intensity of disperse dye is similar to direct dye and reactive dye. However, the percentage of intensity change is less than 50%. Furthermore, the results show that Photocatalytic technique is not suitable for disperse dye treatment. Thus, based on the results of the treatments for 3 types of dye including direct dye, reactive dye, and disperse dye, it can be summarised that the features of direct dye are dissolving in water and the intensity change of dye is 76.50%. For the reactive dye and disperse dye, it features are dissolving in water and the intensity change of dye is 72.35% and 42.89% respectively.

The results of dye intensity measurement and percentage of intensity change by using titanium dioxide concentration at 10 g/l for 6 hours for the treatment are different. When 2 types of dyes are categorised, water soluble dye (direct dye and reactive dye) and non-water soluble(disperse dye), there is a decrease in intensity change of water dissolvable dye over 70%. For the non-water soluble dye, the results show that the decrease in intensity change is less than 50%. Therefore, the water-soluble dye has the percentage of dye intensity change greater than non-water soluble dye. The is because the molecules of non-water soluble dyes do not dissolve and this impacts the electron of titanium dioxide making it unable to attach to the structure of dye in solution; this leads to less effective results of treatment comparing to the treatment results of water soluble dye. Therefore, the results of treatment by using titanium dioxide from sol-gel technique for dye wastewater treatment is suitable for water soluble dyes.

2) Evaluation of Wastewater Treatment by Absorption Technique

The aim of this research is to find the suitable amount of sawdust for dye wastewater after being treated by titanium dioxide. The results show that the amount of sawdust and the duration of treatment have impacts on direct dye intensity. Using 5 g/l of sawdust for 1 hour can change 50% of dye intensity and enhance an effectiveness of treatment when increasing the duration of treatment and amount of sawdust. In this research, the optimal amount of sawdust and duration of treatment are 5 g/l and 2 hours respectively.

According to the results, the amount of sawdust and duration for treatment can impact the intensity of

reactive dye as well as direct dye. The use of sawdust at 5 g/l for 1 hour can change the intensity of dye for 20%, as an initial intensity of reactive dye is greater than the initial intensity of direct dye. However, the results of wastewater treatment can be improved by increasing the amount of sawdust and duration. In this research, the optimal amount of sawdust and time for wastewater treatment are 10 g/l and 2 hours respectively.

Moreover, the results also show that the amount of sawdust and duration can impact directly on the intensity of reactive dye as well as direct dye. The use of sawdust at 5 g/l for 1 hour can change the intensity of dye for 25%. The reason is the initial intensity of reactive dye is greater than the initial intensity of direct dye. However, the results of wastewater treatment can be improved by increasing the amount of sawdust and duration. In this research, the optimal amount of sawdust and time for wastewater treatment are 10 g/l and 2 hours respectively. In addition, the amount of sawdust and time used for treatment impact the intensity of dye in the same way while the results of treatment essentially depend on the amount of sawdust used. The reason is the disperse dye is non-water soluble; thus, the molecular of dye can get into the holes in the molecular of sawdust. The result of treatment will be constant or slightly increase when holes of the molecular are completely replaced by the molecular of dye. Therefore, using 5 g/l and 10 g/l of sawdust is equivalent to increasing the area to absorb the molecular of dye as well as enhancing absorption when the duration of treatment at different concentration of solution are the same. The results of treatment also vary on the time increased. In this research, the optimal amount of sawdust and time used for disperse dye wastewater treatment are 15 g/l and 4 hours respectively. Thus, once analysed combining results of dye wastewater treatment by Photocatalytic technique with absorption technique, the results show that using both treatment techniques are suitable for direct dye and reactive dye. The disperse dye is not suitable for treatment by Photocatalytic Technique but it suitable for treatment by absorbents.

3) The results of dye wastewater treatment by using natural sorbents and sawdust

Natural sorbent are developed by boiling palm leaves in sodium hydroxide concentration at 24 g/l for 3 hours, at 100 degrees Celsius and mixed with 1 gram/litre of polyvinyl alcohol (PVA) and 5 and 10 g/l of sawdust. After that, dry the substance at 100 degrees Celsius. It can be seen that sawdust can be shaped when it is mixed with palm leaves and polyvinyl alcohol concentration at 5 g/l. However, when increasing the concentration of solution to 10 g/l and 15 g/l, the substance cannot be shaped by direct mixing technique as the sorbents are divided in different pieces. After that, using sawdust concentration at 5 g/l for the experiment and compared the results.

Moreover, the results show that the capacity for wastewater treatment by using sawdust as absorbent is better than using shaped absorbents. The reason is the shaped sorbents are created through the mixture of many initial substances; this leads to transition of molecular of substances into the holes of sawdust before the wastewater treatment. Therefore, the molecular of wastewater were unable to get into the holes of sawdust. The recommendation for further research is, in case forming absorbents using sawdust is required, the sawdust should be mixed with polyvinyl alcohol or any other substances that can attach the molecular of sawdust firmly. It will then be unnecessary to use other absorbents.

CONCLUSION

The study of using Photocatalytic technique with absorption technique through the use of sawdust for wastewater in the textile industry in Bangpakong, Chachoengsao Province, aims to study the results of dye wastewater treatment by titanium dioxide and sawdust. Furthermore, it is to study the development of absorbents from natural materials and sawdust for wastewater treatment. The structure of dyes used in this research is azo dye; when analysing the intensity of processed dye, it can be seen that the fabric can completely absorb acetic dye and basic dye during the dyeing process. Therefore, with diverse intensity, the research excludes this from the scope of study. This research uses Photocatalytic technique by titanium dioxide, which was prepared through sol-gel technique for dye wastewater treatment. The objective is synthesising titanium dioxide using sol-gel technique. The quantity of titanium dioxide used for treatment are 0, 5, 10 and 15 g/l while the time used are 0, 2, 4, 6, and 8 hours respectively. The results show that direct dye and active dye are suitable with treatment by Photocatalytic technique and the titanium used for treatment is 10 g/l for 6 hours. Also, the experiment indicates that the significant variables for treatment are initial intensity, saturation, and quantity of catalyst. Moreover, the results showed that disperse dye is not suitable for treatment by Photocatalytic technique as its ability to decrease dye intensity is less than 50%. The effectiveness of treatment by Photocatalytic technique for 3 types of dye are as follows; direct dye > reactive dye > disperse dye. For the absorption using sawdust as the main sorbent to absorb dye in the solution, the quantity of sawdust used in this research are 0, 5, 10 and 15 g/l while the time used are 0, 2, 4, 6 and 8 hours. Similar to the Photocatalytic technique, the results show that the disperse dye produced the best result as disperse dye is non-water soluble dye. The molecular of dye can

directly pass into the holes of sawdust. Furthermore, variables that impact the results of treatment are solubility of dye in the solution, initial intensity, quantity of sawdust and duration of treatment. The effectiveness of treatment by absorption technique for 3 types of dye are as follows; disperse dye > direct dye > reactive dye. For treatment by using of sorbent from natural materials and sawdust , this technique has less effectiveness than using sawdust as a single sorbent. Therefore, using Photocatalytic technique together with absorption process can be used for dye wastewater treatment and the results of treatment depend on main type of dye.

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