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Chitosan-functionalized Ag nanoparticles for Degradation of Methylene Blue: Effect of Chitosan Pre-treatment

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Abstract:
Coloured wastewater discharge mainly from textile industries will affect the water source and became pollution. Methylene blue is one of common dyes exist in every textile industries. Silver is known as a photocatalyst for the removal of environmental contaminants. Due to high tendency to agglomeration happened, biomaterial was used to support the metal which is chitosan. In this research, chitosan will be treated with different condition by using different type of chemical followed by preparation of AgO/Chitosan. From FTIR study, found that existence of AgO bound with chitosan. Photocatalytic process of methylene blue clearly inllutrates that NaOH treated chitosan was very active for the photo degradation of methylene blue.

Keywords*: Photocatalytic process, Methylene blue, Chitosan, Silver nanoparticle*

1. Introduction

Nowadays, many industries release huge quantity of dyes compound that cause water pollution thus causes environmental problems due to toxicity and some of these dyes are suspected carcinogenic (Cruz-Rizo *et al*., 2016). Environmental pollutants are substance that would affect the water or the atmosphere. Usually, major contributor to water pollution by releases dyes, surfactants, heavy metal ions, electrolytes, detergents and solvent is from textile industry (V.M. Correia *et al*., 1994). There are huge number of available dyes with over 70000 tonnes of dyestuff produced annually. Methylene blue is one example of dyes that not save for living organisms such as to human beings because it is toxic substance (Sapawe et al., 2013). So, it must be removed and eliminate before discharge into water resource such as river and sea. Methylthioninium chloride or methylene blue is heterocyclic aromatic chemical compound with chemical formula $C_{16}H_{18}N_3SCl$. As a physical property, it appears as a dark green powder and change to a blue solution when dissolved in water with 319.85 g/mol of molecular weight. Colour diminish from wastes is one of the most difficult requirements, faced by the dye manufacturing, pulp and paper industries other than textile industries. Among the various types of dye, methylene blue, are used in dye, paint production and also wool dyeing. It is also used as a sensitizer in photo-oxidation of organic pollutants, surgery and diagnostics (Rahman *et al*., 2012). In term of dangerous to water resources, it can be toxic to aquatic life due to highly coloured effluents with low biochemical oxygen demand, BOD and high chemical oxygen demand, COD (A.Y. Lehi, A. Akbari, 2016). Other than that, in term of chemical structure, dyes are resistant to fading on exposure to light, water and many chemicals (Ahmad *et al*., 2002). There are a lot of method have been conducted by researchers in order to degrade, decolourize or eliminate of MB such as membrane filtration, ion exchange, coagulation, adsorption, photocatalytic and many more (K. A. Adegoke *et al*., 2014).

Thus, dye removal process must be applied with suitable method to overcome serious environmental problem. All that method could be categorized either by chemical, physical or biological treatments. Contrarily, all of these methods have advantages and disadvantage especially the treatment methods that require high cost rarely to be used in large scale dye wastewater treatments like textile and paper industries (G. Crini, 2005). In research area, many researchers intended and interested to degrade dye-containing wastewater biologically. They have studied and experimented various kinds of dye wastewater using biological process but they found that the colour of dye in wastewater could not be efficiently diminished (Ahmad *et al*., 2002). Other than that, coagulation and oxidation process studies showed that inefficient method in order to reduce colour of dye wastewater (Ahmad *et al*., 2002). Other method such as adsorption process, according to N.F.M. Salleh *et* *al*., (2014) commonly used in industries but it also gives harmful to the environment because presence of activated carbon as adsorbent in the reactor. Among degradation process, photocatalytic process promising advantages rather than other method. Photocatalytic process uses low energy cost in to do the treatment of toxic (Ksibi *et al*., 2003). By using natural sunlight or artificial light, it showed the process is available everywhere in the world (Feilizadeh *et al*., 2015). In addition, the dominance of photocatalytic removal in wastewater treatment is due to its advantages over the conventional methods, such as quick oxidation and no formation of polycyclic products (S. Muthukrishnan. *et al*., 2015). Lastly, the end products of photocatalytic treatment are uncritical products such as water and does not produce secondary product. So, photocatalysis is considered as a suitable alternative (Ksibi *et al*., 2003). Comparison table is made to compare with other method in Table 1.

In order to perform the photocatalytic process, photocatalyst with unique properties must be presence in order to increase the efficiency. Photocatalysis usually use photocatalyst semiconductor, noble and magnetic in order to remove pollutant. There are a lot of several photocatalyst have been used such as TiO_2, ZnO, SnO, and noble metals. Hence, in the present work, TiO_2 is among of the semiconductors that has great abilities for degradation. However, based on study, interaction factor on TiO_2 photocatalysis are limited which is high photogenerated electron-hole recombination rate (Choquette-Labbé *et al*., 2014). Among those photocatalyst, researchers have been investigated that silver Ag in nanoscale has excellent potential to remove organic contaminants from waste water. (Mondal, 2015). Nanotechnology is one of the recent and modern technology in modern era of material science. Besides that, according to Sergeev and Shabatina (2008) about nanoscience is an entire knowledge on fundamental properties of objects that have nano size. The prefix 'nano' indicates 10^{-9} units and based on willams's (2008) study, it is believed that nanoparticles are cluster of atoms. Furthermore, Ag as noble metal is classified as inorganic nanoparticle same as magnetic and semiconducter nanoparticle (Kathiresan K. and Asmathunisha N., 2013). A significant body of research has focused recently on the development and characterization of nanoparticles (NPs) based on noble metals such has Ag, Au, Pt and Pd because of their excellent characteristics compared to bulk metals (Reicha *et al*., 2012). Moreover, nanoparticle has a unique property in term of size, distribution and morphology and it also contribute to several applications such as in catalysis, microelectronics, sensors, biomaterials, therapeutics and antimicrobial (Bin Ahmad *et al*., 2011). Among the noble metal, silver also be a better due to its high stability, excellent electrical and thermal conductivity, and lower cost (Feilizadeh *et al*., 2015).

Thus, various methods have been studied by researchers to prepare noble metals-based nanoparticle in term of physical and chemical approach. Evaporation-condensation is examples of physical approach while chemical reduction by electrolysis and microemulsion are examples for chemical approach (Kholoud M. M., 2010). Evaporation-condensation technique could be performed using a tube furnace at atmospheric pressure. This method has several disadvantages such as need big space because of tube furnace, consume high energy to raise the temperature around the source material and take a lot of time to stabilize the temperature. However, evaporation-condensation technique is suitable as calibration device for nanomaterial measurement equipment (Kholoud M. M., 2010). Next, microemulsion is production of Ag nanoparticle in two immiscible phases in the presence of surfactant. According to W. Zhang *et al*. (2006), one advantage of this method is it allows the synthesis of metal-based material producing high surface area and high catalytic activity in the range of nano size. Although, it could produce good quality but it consumes large amount of surfactant and organic solvent, so it is expensive method (K.M.M. Abou El-Nour *et al*. 2010). Lastly is chemical reduction by electrochemical technique. This method is rapid, attractive, simple for the synthesis of AgNPs and also widely used. Electrochemical uses ionic liquid (ILs) as a reaction media or electrolyte that have a lot of charge-carrying ions and stable in nature (Reicha *et al*., 2012). Moreover, the end product which is nanoparticle is in high purity and also no need expensive equipment to adjust the current density in order to control the particle size. As a result, this technique is low cost (Khaydarov R. *et al*., 2008).

However different shapes of nanoparticle can be easily synthesized by controlling the reaction conditions but the resulting particle tend to aggregate and grow to become large particle, so it need to avoid (Zhang W. *et al*., 2007). In this case biomaterial seem to be promising alternative such as gelatine, polyethylene glycol (PEG) and chitosan. Thus, suitable biomaterial must be used to perform the degradation process. Noble metal-based polymer of nanoparticle is becoming unique compound in order to treat wastewater. Usually, biomaterials are made from natural polymer, inorganic or organic material (Bin Ahmad *et al*., 2011). Among the biomaterial, chitosan showed promising material due to several advantages such as low cost, abundant (Vega-Baundrit J. 2014) and renewable marine polymer (Motawie *et al*., 2014). Chitosan is also widely used in many different fields other than in chemical engineering such as medicine, food, pharmaceuticals, nutrition, and agriculture (Wei *et al*., 2009). The marine polymer for production of chitosan are cuticles of several crustaceans such as crabs and shrimps (Younes *et al*., 2012). Huge amounts of shrimp shells have been named as wastes by worldwide seafood companies. In addition, Nouri *et al*., 2016 also stated that the shrimp waste is a major environmental safety due to insoluble and resistant material, so this problem was proposed to change the waste to useful product. Thus, by using shrimp shell waste will lead to renewable wastes (Teli and Sheikh, 2012).

Additionally, chitosan properties are remarkable such as non-toxicity, biodegradability, and biocompatibility and also has high ability to chelate metal ions including silver ion (Reicha *et al*., 2012). Recently, researcher showed biopolymer derived from polypolysaccharide is suitable supported materials for metal nanoparticles, providing them chemical stability and a suitable environment for use in biological systems. Several studies have demonstrated that chitosan–silver nanocomposites could be applied in wastewater treatment (Murugadoss *et al*., 2009).

2. Materials and Methods

2.1. Materials

Silver and platinum plate is purchased from Nilico, Japan. Shrimps are bought from supermarket around Kuantan. Methylene blue dye solution, sodium hydroxide (NaOH), hydrochloric acid (HCl) and 1-Ethyl-3-methylimidazolium ethylsulfate purchased from merck.

2.2. Pre-treatment process

2.2.1. Chitosan pre-treatment process

Chitosan is prepared by 3 different of method which are by using 0.1 M HCl, 0.1 M NaOH and distilled water. 0.1 of HCl is diluted into 1L of deionized water and also apply same quantity to 0.1 NaOH and lastly for 1L of distilled water. After that, put 5 g of shrimp into each solution and stir for 3 hours. After it finished, let the shrimp immersed in solution for 12 hours. Lastly, clean the shrimp with water until the pH turn neutral and grind the shrimp using grinding machine into smaller form and then dry all the shrimp into the air oven at temperature 100 °C (L. Pranee *et al*., 2002).

2.2.2. AgO/Chitosan nanoparticle preparation

The synthesis will be performed in a one-compartment cell equipped with a magnetic stirring bar a two-electrode configuration. Silver plate (2 cm x 2 cm) anode and a platinum plate (2 cm x 2 cm) cathode will be cleaned using 1 M HCl and followed by distilled water. 2 electrodes will be inserted in parallel with a distance 2 cm into 15 mL into ionic liquid solution with a volume ration of imidazole to water of 1:1. The current will be used in the electrolysis at a constant current of 60 mA/cm^2 and 0 °C under air atmosphere. The prepared chitosan will be added to the electrolysis product mixture and will be immersed at 80 °C in an oil bath before dry overnight at 110 °C (Jusoh *et al*., 2014).

2.3. Characterization of Silver nanoparticles

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

The chemical components in the catalyst will be identified by using FTIR spectra on material for different type of pre-treatment. The range used is at 500-4000 c/m (Jusoh *et al*., 2014).

2.3.2. Photocatalytic activity

An amount of catalyst and methylene blue solution will be added in a Pyrex batch photoreactor and stir for 3 hours in the dark to achieve adsorption-desorption equilibrium with a certain rate. Philips TL 20W/52 fluorescent lamp within quartz glass housing (emission spectrum 350–600 nm) with a peak emission at 430 nm will be used as a light source. The process will be run at 30 °C and initial pH of solution at 5 will be proceed for another 3 hours. During the reaction, certain amount of solution will be taken at 15 min interval and centrifuge in a Hettich Zentrifugen Micro 120 at 75,000 rpm for 10 min before analysis by a double-beam UV–Vis spectrophotometer (Cary 60 UV–Vis Agilent) at 665 nm (Jusoh *et al*., 2015). The percentage removal could be calculated by using following formula:

$$Dye\ degradation\ (\%) = \left[\frac{(C_0 - C_t)}{C_t}\right] \times 100 \qquad (1)$$

Where C_0 is the initial concentration of the methylene blue solution and C_t is the concentration of the dye solution after t hours of exposure in light sources.

3. Result and Discussion

3.1. Characterization

3.1.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to indicate an infrared spectrum of absorption of different matter. FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR measurement was carried out to identify the possible biomolecules which is chitosan responsible for capping on AgO.

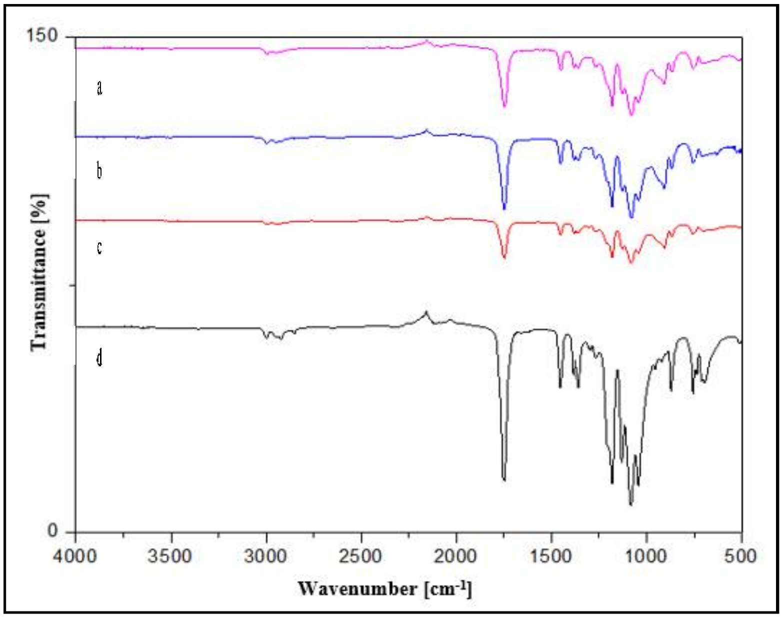

Figure 1: FTIR analysis of photocatalyst (a) AgO/Chitosan$_{NaOH}$, (b) Chitosan only, (c) AgO/Chitosan$_{HCl}$, (d) AgO/Chitosan$_{H2O}$

The medium intense band at 1690 cm^{-1} arises from the C=O stretching mode in amine group which is commonly found in the protein, indicating the presence of proteins as capping agent for AgO which increases the stability of the nanoparticles synthesized (Figure 1). Protein capability to bonded with silver nanoparticles either through free amine groups or cysteine residues (Huang *et al*., 2015). These results were summarized in Table 1.

Pretreatment	Wavenumber (cm^{-1})	Mode of vibration	Functional group
AgO/Chitosan$_{NaOH}$	1690	C=O	Amine
	1385	C=C	Aromatic amine
	1077	C=O	Carbonyl
	3104	C-H	Aromatic
AgO/Chitosan$_{HCl}$	1690	C=O	Amine
	1385	C=C	Aromatic amine
AgO/Chitosan$_{H2O}$	1690	C=O	Amine
Chitosan only	1632	N=H	Amino

Table 1: Identification of functional group

3.2. Photocatalytic activity of AgO/Chitosan

3.2.1. Effect of pre-treatment of Chitosan$_{NaOH}$, Chitosan$_{HCl}$, Chitosan$_{H2O}$

Photocatalytic activity of the AgO/chitosan nanoparticles was evaluated by degradation of methylene blue under light source. The colour of dye gradually change from blue to light blue that indicate of degradation process happened. The characteristic absorption peak for methylene blue was noticed at 665 nm (Roy K. *et al*., 2014). The degradation of the dye in presence of AgO/chitosan nanoparticles was verified by the decrease of the colour during 3 h of exposure in light but with different of chitosan pre-treatment. AgO nanoparticle formation was conducted using electrolysis process.

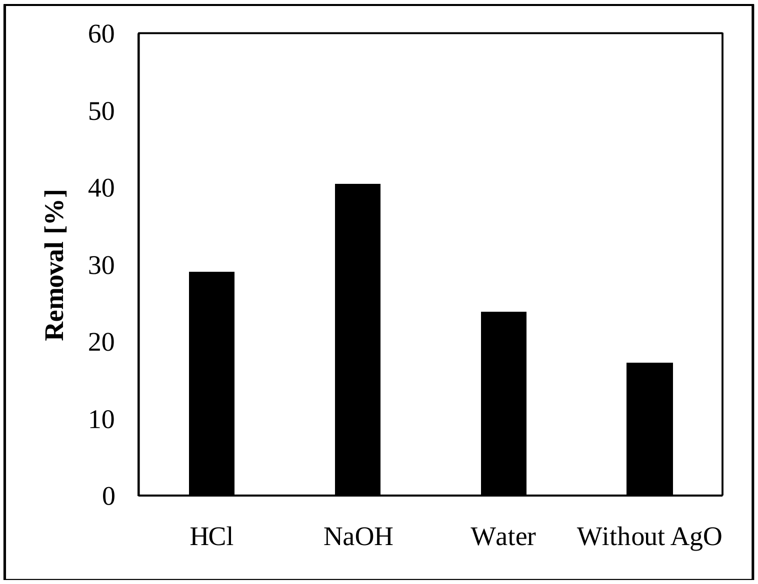

Figure 2: The photcalatys performances of MB using Chitosan$_{HCl}$, Chitosan$_{NaOH}$. Chitosan$_{H2O}$ and without AgO. [pH 5; photocatalyst dosage 35 mg L^{-1}; initial concentration 10 mg L^{-1}; stirring speed 1000 rpm].

Figure 2 shown the result of percent removal when different of chitosan pre-treatment with of presence of AgO. All dye concentrations were measured by taking the value of absorbance at 665 nm in the UV–Vis spectra as the concentration is directly proportional to the absorbance value. It showed AgO/Chitosan by using NaOH with high percentage of removal of dye or decrease in concentration about 40.45% compared with other treatment with lowest than that.

According to L. Pranee *et al*. (2002) NaOH gave more efficient removal of protein and coloured matter compared with HCl. By using 0.1 M of HCl coloured matter and protein still remained bound to the solid matrix of shrimp exoskeleton. Supposedly, incomplete reduction of protein increases the amount of minerals that remains bounded. In order to complete reduce of protein, shrimp needs to further treatment using NaOH. Aside from that, ash content also need to be reduced in order to get chitosan material from shrimp. So, concentration of NaOH during treatment resulted in a degradation in the ash content. The result showed treatment of shrimp by using NaOH give more efficient removal protein, coloured matter and ash content thus give high percentage of chitosan compared with using HCl and water only. Thus, it can be said that, high percentage of chitosan could be supported on AgO to prevent it from agglomeration and remain high surface area.

4. Conclusion

The photocatalytic degradation study was carried out in the presence of visible light. The degradation of MB dye in aqueous solution by an AgO supported by chitosan photocatalytic process under light was found to be technically feasible under optimum experimental conditions. Methylene blue degraded by more than 72% with optimum condition. By using NaoH to treat exoskeleton of shrimp in order to get the chitosan thus be able to support the AgO to perform photocatalytic process as photocatalyst. The photocatalysis was proved to be as attractive method to remove of pollutants from industrial wastewaters which convert to nontoxic compounds.

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