

Enhancing Remazol Yellow FG Decoloration by Adsorption and Photoelectrocatalytic Degradation

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ABSTRACT

The combination of adsorption and photoelectrocatalytic degradation system for Remazol Yellow FG decolorization has been studied. The adsorption of Remazol Yellow FG was carried out using alumina and silica, which was activated using H₂SO₄ 1 M and NaOH 1 M. The adsorption results at optimum pH were then used for photoelectrocatalytic process. Photoelectrocatalytic degradation cell was built by electrode Ti/TiO₂ as a cathode and Ti/TiO₂-PbO as an anode. Material characterizations were performed by UV-Vis Spectrophotometers, X-Ray Diffraction (XRD), and Fourier Transform Infra-Red (FTIR). Activation of the adsorbent can increase Remazol Yellow FG adsorption on alumina base and silica acid that were reached 99.500% and 81.631%, respectively. The optimum condition of Remazol Yellow FG 6 adsorption by alumina acid was at pH 3, alumina base was at pH 4 and pH 5, and silica base was at pH 6 and pH 10. Degradation of Remazol Yellow FG using TiO₂-PbO electrode was 72.756% at potential cells of 7.5 Volts for 10 minutes. The combination of adsorption and photoelectrocatalytic degradation can decrease the concentration of Remazol Yellow FG achieved 99.705%.

Keywords: Adsorption, photocatalytic, Titania, dye, pH

INTRODUCTION

The textile industry was known to be one source of water pollution due to textile production that passes through several stages of the process such as dyeing; leaching, measurement, printing, and improvement that have potentially produce waste. The negative impact of textile production mainly comes from the dyeing process. The chemical structure with the aromatic ring of dye causes highly toxic waste, carcinogenic, mutagenic, allergies and dermatological diseases (Gao et al., 2013). Various waste treatments such as filtration, coagulation, sedimentation, ion exchange and adsorption have been carried out. The adsorption is one of wastewater treatment that most effective and widely used in the waste treatment process for high-efficiency, easy in operation, biodegradability, and low cost (Gupta et al., 2013; Yola et al., 2014)

Alumina and silica have high efficiency due to the large of surface area, high porosity, good mechanical properties and good resistivity to thermal degradation (Mahmoud et al., 2010; Malakootian et al., 2015). The surface area of alumina and silica were known

155 m²/g and 500 m²/g, respectively (Mahmoud, 2005; Gawade et al., 2005). The active surface silica contains silanol (Si-OH) that has an important function in the adsorption process. The behavior of alumina adsorption was caused by hydroxyl acids and bases on its surface. Based on this reason, the silica and alumina can be used as an adsorbent in the adsorption of Remazol Yellow FG. The adsorption process may only a physical interaction and sometimes have effective for waste dyes treatment. Therefore, it needs the photoelectrocatalytic waste treatment that capable to degrade organic waste to minerals compound.

The semiconductor of TiO₂ has been widely studied and used as a photocatalyst because of the high photocatalytic activity, low cost, and stable (Grimes et al., 2011; Ni et al., 2011). However, TiO₂ has a wide energy gap (3.2 eV; $\lambda_g = 388$ nm) that only able to absorb in the UV region whereas only 10 % of the sunlight. Modification TiO₂ was able to increase light absorption in the visible region. It has become one of the topics of research of photocatalyst area (Henderson et al., 2011; Rehman et al., 2012; Fujishima et al., 2008).

PbO has a low band gap that can be used as a visible light oxide semiconductor. Computational studies approaches have shown that the modified TiO₂-PbO produce valence band of TiO₂ has shifted into the visible region (Iwaszuk et al., 2008). Therefore, this composite allows for the migration of the charge and charge carrier separation photogenerated (Leelavathi et al., 2013). The use of TiO₂- PbO as photoanoda which can absorb the visible region will enhance the ability photoanode in the degradation of organic compounds.

In this report, we have studied the decolorization of Remazol Yellow FG by adsorption and photoelectrocatalytic degradation system. First, the remazol yellow was adsorbed into alumina and silica adsorbents. Then, we also do the decolorization using the system.

EXPERIMENTAL SECTION

The material consists of Ti plate (3 cm x 10 cm) of Baoji Titanium Qixin Co. Ltd, alumina, silica, Remazol Yellow FG, titanium tetraisopropoxide (TTIP), ethanol, acetic acid, lead nitrate, hydrochloric acid and sodium hydroxide. The materials were used without further pre-treatment.

The activation of alumina (50 g) and silica (50 g) were carried out by adding into 1 M H₂SO₄ (250 mL) and 1 M NaOH (250 mL), respectively, then stirred for 1 hour. The result was washed using distilled water to neutral conditions.

An optimum condition of adsorbent properties was carried out by adsorption of 10 ppm Remazol Yellow FG on untreated silica and alumina, and acid and base activated. Then they were stirred at 120 rpm for 60 minutes. The residual of Remazol Yellow FG was analyzed by UV-Vis spectrophotometer. Remazol Yellow FG at various pH (pH 3, 4, 5, 6, 7, 8, 9, 10, and 11) have been carried out by adsorption using activated silica and activated alumina. Each sample was stirred for 60 minutes. The residuals were also analyzed by UV-Vis spectrophotometer.

Preparation of Ti/TiO₂ electrode refers to the Wahyuningsih methods (Wahyuningsih et al., 2007a, 2014b). Titanium isopropoxide solution (TTIP) was added acetic acid at a temperature of 14 °C then it was stirred and heated to a temperature of 90 °C. The gel

obtained was heated at a temperature of 150 °C for ± 24 hours and then annealed to 400 °C at 10 °C/min. Preparation of Ti/TiO₂ electrode was done by mixing TiO₂ powder into ethanol then it was stirred and sonicated for 60 minutes. The TiO₂ suspension then was sprayed to titanium plate and heated at a temperature of 200 °C for 15 minutes. The electrodes characterization was performed by XRD.

The same treatment was done for the preparation of TiO₂-PbO composite, except for the addition of PbNO₃ (3.31 g). Preparation of Ti/TiO₂-PbO electrode was done by mixing TiO₂-PbO composite (12.5 g) into ethanol (50 mL) then it was stirred and sonicated for 60 minutes. The TiO₂-PbO solution then was sprayed to titanium plate and heated at a temperature of 200 °C for 15 minutes. The electrodes characterization was also performed by XRD.

The photoelectrocatalytic process of Remazol Yellow FG (10 ppm) has been carried out at the optimum pH condition of adsorption process. Ti/TiO₂ electrode was used as a cathode, while Ti/TiO₂-PbO electrode was used as an anode. The process was prepared using a positive potential bias of 7.5 volts for 10 minutes by batch system. Remazol Yellow FG removal in the photoelectrocatalytic process was analyzed using a UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Adsorbent activation indicates there is an OH group stretching vibration of untreated alumina, and acid and base activated at 3462.37 cm⁻¹, 3461.41 cm⁻¹, and 3459.48 cm⁻¹, respectively. While at 1630.88 cm⁻¹, 1634.74 cm⁻¹, and 1636.67 cm⁻¹ show the bending vibrations of OH groups. Absorption at 775.42 cm⁻¹, 731.05 cm⁻¹, and 732.98 cm⁻¹ was observed of the untreated alumina, and acid and base activated, respectively due to the stretching vibration Al-O group.

Figure 1 shows the % ΔT represented of the amount of OH active sites on the untreated alumina surface, and acid and base activated alumina. Those differences indicate that a change in the amount of OH active sites on the untreated activated alumina surface as well as activated alumina surface which can affect the absorption ability of the adsorbents.

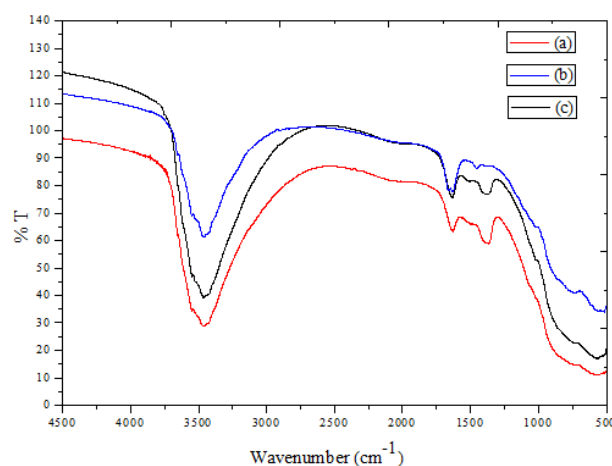


Figure 1. FT-IR spectras of the alumina (a) untreated ; (b) acid activation; (c) base activation

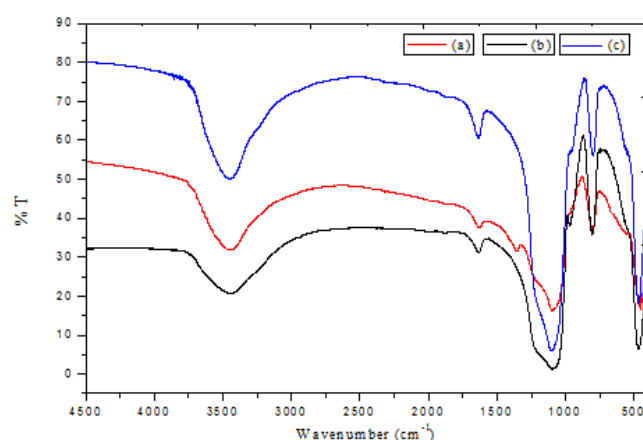


Figure 2. FT-IR spectras of the silica (a) untreated; (b) acid activation; (c) base activation

Whereas on the untreated silica and acid and base activated silica (**Figure 2**) shows the -OH stretching vibration of silanol at 3444.05 cm^{-1} , 3462.37 cm^{-1} , and 34401.19 cm^{-1} . While at 1632.81 cm^{-1} was base activated silica and at 1631.85 cm^{-1} was untreated silica as well as acid activated by bending vibration -OH of silanol. Absorption at 1095.61 cm^{-1} , 1083.08 cm^{-1} , and 1101.40 cm^{-1} are asymmetric stretching vibration -Si-O of -Si-O-Si- (siloxane group). Bending vibrations of Si-O-Si was shown at 560.18 cm^{-1} , $468,72\text{ cm}^{-1}$, and 472.58 cm^{-1} . The differences of OH active sites on the untreated silica surface as well as activated silica surface may also affect the ability of adsorption.

In untreated, acid and base activated alumina, adsorption Remazol Yellow FG obtained the decolorizations about 75.51%, 99.50% and 78.05%, respectively (**Figure 3a**). Remazol Yellow FG adsorption with acid activated alumina is highest. Alumina has been known a high affinity for anionic species on acid activation.

Remazol Yellow FG adsorption with untreated, acid and base activated silica, adsorption Remazol Yellow FG obtained the decolorization 73.93%, 77.12%, and 81.63%, respectively (**Figure 3b**). Remazol Yellow FG adsorption using base activated silica is highest due to the effective interaction of -Si-O- and H₂O formed positive site of lewis acid silica that will interact with anionic sites of Remazol Yellow FG.

Furthermore, the pH effect was also investigated. Adsorption study with base activated alumina was optimum at pH 10 about 77.87% and at pH 4 about 76.87% (**Figure 4a**). Adsorption with base activated silica optimum at pH 10 about 82.62% and at pH 6 about 81.96% (**Figure 4b**). Under alkaline conditions, it may structural transformation of Remazol Yellow FG form a vinyl sulfone group. Under acidic conditions it also probably generates structural transformation forming vinyl sulfone group because of the protonation by H⁺. The vinyl sulfonic group was further interacting with adsorbent.

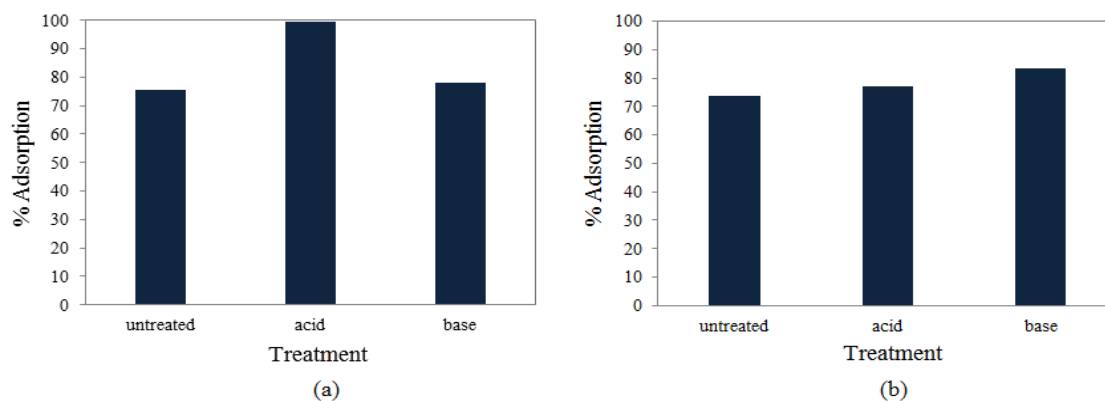


Figure 3. The effect of acid and base activation toward Remazol Yellow FG adsorption at pH 6,8 (a) alumina; and (b) silica

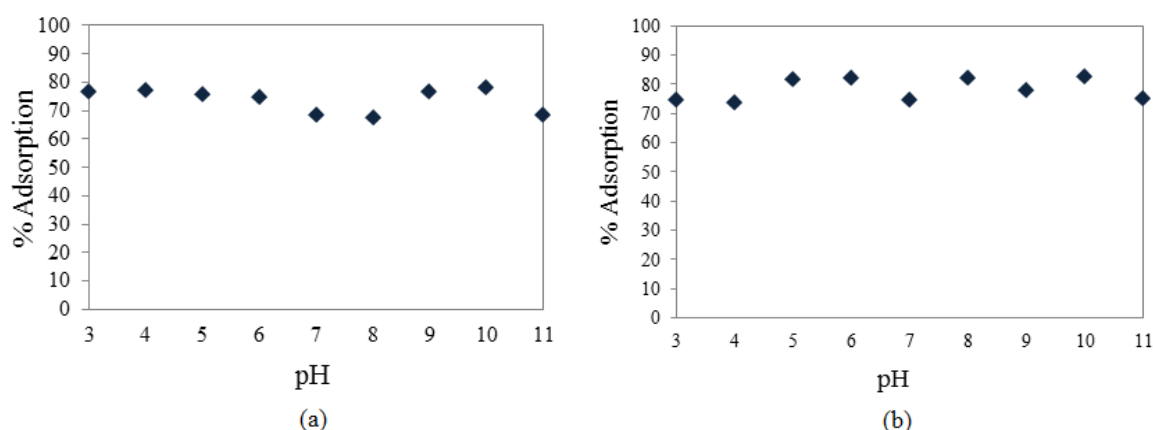


Figure 4. The effect of pH toward Remazol Yellow FG adsorption using (a) base alumina; and (b) base silica

Adsorption Remazol Yellow FG with acid activated alumina was optimum at pH 3 about 98.90% (**Figure 5a**). Remazol Yellow FG structure is a cationic acceptor, which will react with H^+ ions from the alumina, because of the cations exchange between H^+ and Na^+ from Remazol Yellow FG. In the acid activated silica, adsorption Remazol Yellow FG occurs at pH 7 about 78.72% (**Figure 5b**). This due to alumina is more acidic Brønsted, compared with silica acid so that it produces a high adsorption.

The use of Ti / TiO_2 -PbO composites as electrodes is proven to degrade Remazol Yellow FG. The excitation of electrons from the valence band to the conduction band will leave the hole in the valence band. The electrons in the resulting TiO_2 conduction band may trigger the reaction with O_2 resulting in a superoxide anion radical ($O_2^{\cdot -}$). The holes form will react with H_2O to produce a hydroxyl radical (OH^{\cdot}). Superoxide anion

radicals ($O_2^{\cdot -}$) and hydroxyl radicals (OH^{\cdot}) will degrade Remazol Yellow FG dye through redox reactions.

The electrons in the conduction band can return to the valence band. The addition of oxide is capable of suppressing electron-hole recombination by electron trapping on metal sites where electrons will migrate toward metal and trapped in metal. This results in the hole freely diffusing onto the semiconductor surface and effectively enhances the photocatalytic effectiveness in degrading the Remazol Yellow FG dye.

Positive potential through photoanode will attract electrons to the cathode then minimize electron-hole pair recombination and accelerate the oxidation process of organic compounds (EPA, 2003). Also, the addition of positive potentials will cause excited electrons split and holes to be accelerated (Hu et al., 2003).

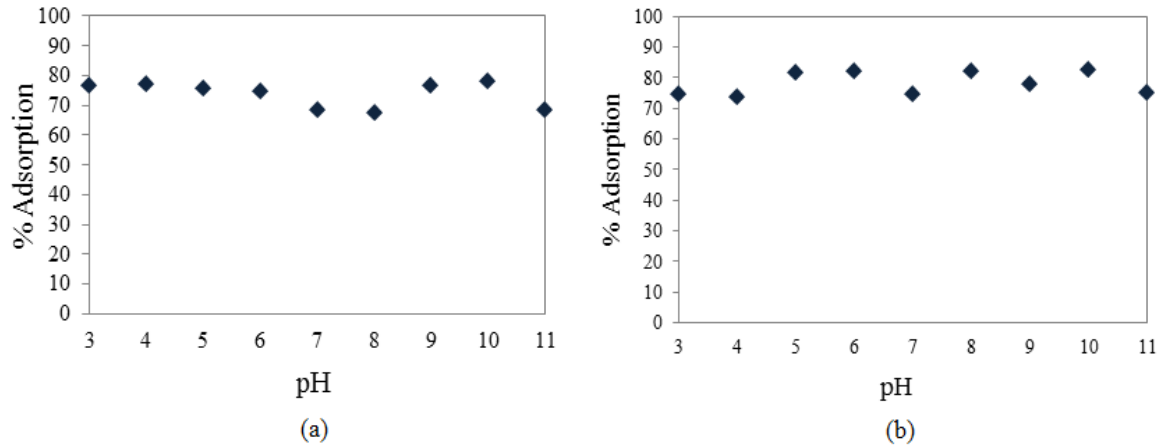
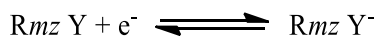
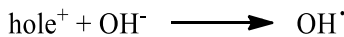
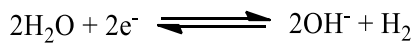
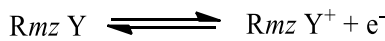


Figure 5. The effect of pH toward Remazol Yellow FG adsorption using (a) acid alumina; and (b) acid silica

Possible reactions that can occur in electrodegradation cells are as follows:



Photoelectrocatalytic degradation of Remazol Yellow FG using Ti/TiO₂-PbO electrode as anode and Ti/TiO₂ electrode as cathode can degrade Remazol Yellow FG. The preparation procedure of electrode materials will be published in a separate report. Degradation

using photoanode Ti / TiO₂-PbO on Remazol Yellow FG reached 62.06%.

The optimum degradation occurs in the initial solution pH 3 Remazol Yellow FG, about 72.756%. **Figure 6** shows that differences in the pH of the initial solution Remazol Yellow FG influenced degradation. This is due, acid solution Remazol Yellow FG already protonated form a positive charge. Thus affinity to the reaction of hydroxyl radicals (OH[•]) and superoxide anion radicals (O₂^{•-}) is higher. Addition of HCl also affects the degradation Remazol Yellow FG. The Cl can be oxidized to generate the ClO³⁻ species. These species turn out to be powerful oxidizing agents, which together with the hydroxyl radicals can degrade the dye thus at pH 3 the degradation Remazol Yellow FG becomes higher (Cerventes et al., 2012).

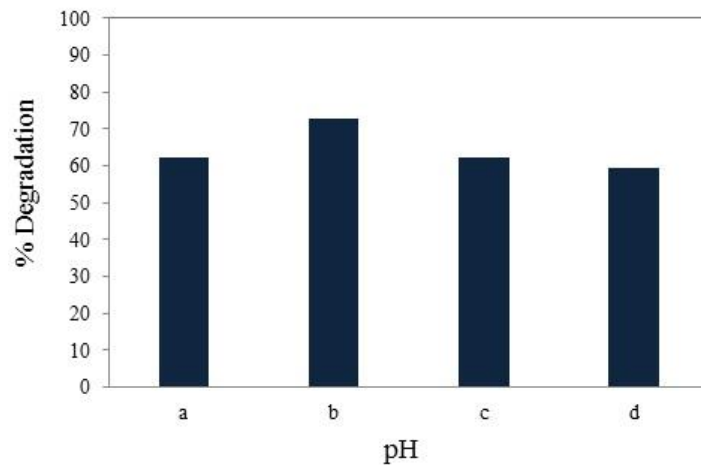


Figure 6. Degradation of Remazol Yellow FG after photoelectrocatalytic degradation process with applied bias potential 7.5 V for 10 min at various pH (a) RY neutral (at pH 6,8); (b) RY at pH 3; (c) RY at pH 7; and (d) RY at pH 10

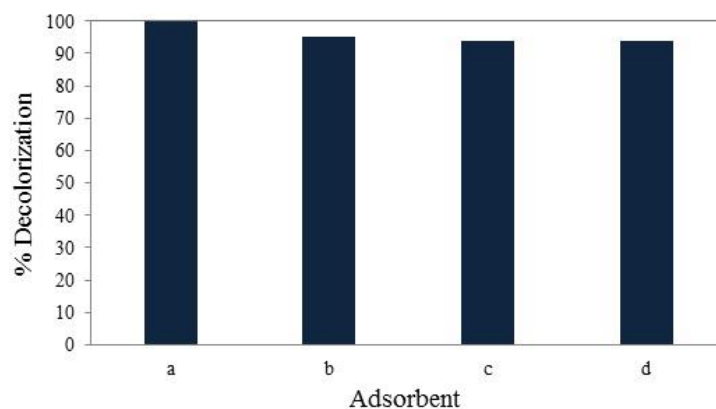


Figure 7. Decolorization of *Remazol Yellow FG* with adsorption and photoelectrocatalytic degradation process using (a) acid alumina; (b) base alumina; (c) acid silica; and (d) base silica. Photoelectrocatalytic degradation process was conducted at potential cells of 7.5 V for 10 minutes.

The decolorization of Remazol Yellow FG using a combination of adsorption and photoelectrodegradation, about 99.70% and 95.30% for acid and base activated alumina, respectively. While, for acid and base activated silica, about 94.01 %, and 94.02%, respectively (**Figure 7**).

Hydrated alumina tends electron-withdrawing than silica, due to Lewis acid sites (Kannan et al., 2008). Activated alumina is more Brønsted acid. Thus the interaction between the active site acid alumina with a negative charge (SO^{3-} group) of Remazol Yellow FG became more powerful, it may increase the adsorption Remazol Yellow FG.

CONCLUSION

The difference of active sites each adsorbent, causing differences in adsorption Remazol Yellow FG, where the alumina has a high adsorption capability. Adsorption using alumina and silica acid activation, optimum at low pH (pH 3 and pH 7), whereas activation of base alumina and silica optimum at low pH and high pH (pH 4, pH 6 and pH 10). The photoanode $\text{Ti/TiO}_2\text{-PbO}$ can be used for photoelectrocatalytic degradation of Remazol Yellow FG, about 72.75% at pH 3. The combination of adsorption and photoelectrocatalytic degradation system effective for decolorization of Remazol Yellow FG, about 99.70%.

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