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Optimization of Rhodamine B Decolorization by Adsorption and Photoelectrodegradation Combination System

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ABSTRACT

A combination of adsorption and photoelectrodegradation system was performed to reduce the concentration of Rhodamine B dye in water. The adsorption was conducted using silica and alumina activated by acid and base under various predetermined pH of Rhodamine B. The photoelectrodegradation process was performed using Ti/TiO_2 electrode as a cathode and Ti/TiO_2-NiO as an anode. TiO_2 was synthesized from titanium tetra-isopropoxide precursor (TTiP) by sol-gel method. TiO_2-NiO composite was synthesized with the same precursor with the addition of $Ni(NO_3)_2.6H_2O$. The result shows that the activation changes the amount of OH total in the adsorbent. The acid-activated adsorbent showed an optimum adsorption activity when Rhodamine B was in base condition caused by zwitter ionic structure. It reversely occured to base-activated adsorbent where an optimum absorption activity reached at acid condition. The application of base-activated silica in adsorption and photoelectrodegradation combination system decreased the concentration of Rhodamine B dye up to 98.79% using photoanode Ti/TiO_2-NiO under pH 2 at bias potential 6 V.

Keywords: adsorption, photoelectrodegradation, Rhodamine B, TiO_2-NiO

INTRODUCTION

The waste textile industry is generally derived from the coloring process using azo dyes group containing chromophore (Sen and Demirer, 2003) which is non-biodegradable that cannot be decomposed by heat and bacteria. One of the textile components are often used as a dye is Rhodamine B. Various waste treatment techniques such as filtration, coagulation, sedimentation, ion exchange and adsorption have been carried out. The adsorption method is considered an effective method of waste treatment and the process is fast. Some adsorbent that often used in adsorption are silica and alumina due to the high efficiency because of the surface area, porosity, and high mechanical properties and has good resistivity to thermal degradation (Malakootian *et al.*, 2015). Silica has active Si-OH groups called silanol and known to be effective adsorption agent when it is applied as an adsorbent as well as alumina that have O-H group. Therefore, silica and alumina can be used as an adsorbent in the adsorption of the dye Rhodamine B (Kannan *et al.,* 2008; Huang *et al.,* 2011; Alver *et al.,* 2012; Sun *et al.,* 2013).

The adsorption process is less optimal for dealing with the waste dye because it is merely quarantining adsorbed molecules and their interaction is limited to physical interactions. Research on the photodegradation by sunlight using TiO_2 catalyst shows that TiO_2 can degrade and eliminate the compound of methylene blue dye and produce the final product in the form of CO_2, SO_4^{2-}, NH_4^-, and NO_3^- (Gunlazuardi, 2001). Thus, sewage treatment of Rhodamine B dye using adsorption combined with photoelectrocatalytic degradation can transform waste into a mineral dye that is more environmentally friendly.

Titanium metal oxides reported as a semiconductor material with a higher photocatalytic activity, more stable, and non-toxic. In addition to these activities, the TiO_2 powder is obtained and produced in large quantities. However, TiO_2 has a high energy gap that is proportional to the light of 388 nm (3.23 eV), where the ultraviolet light with this amount energy is only available at 10% of the sunlight. This limitation can be overcome by modification of TiO_2 by doping it with metal ions and other oxides as well as photosensitizing such various organic and inorganic colored compounds.

One way to overcome these weaknesses is by adding a metal oxide NiO with lower bandgap energy to enhanced the photocatalytic activity of TiO_2 (Wahyuningsih *et al.,* 2014) and can extend the photo-response of TiO_2 to the area visible to be used for the degradation of organic contaminants colored and organic pollutants other (Lisenbigler *et al.,* 1995). Additionally, an electrical potential can be added to mitigate these weaknesses and to improve TiO_2 activation and degradation of organic compounds. The transfer of electrons and electrical current is expected to increase the activation of TiO_2 and the degradation of organic compounds, especially dye of Rhodamine B.

The structure of the Rhodamine B is a cationic compound and can form different structures under different pH conditions (Jain *et al.,* 2007), wherein low pH (≤ 5) Rhodamine B forms a cationic structure, and at high pH (≥ 6) Rhodamine B forms the zwitter ion structure (Motahari *et al.,* 2014) which will affect the adsorption and photoelectrocatalytic activity. Therefore, pH variation of Rhodamine B was studied to determine the optimum pH condition of the solution.

The present study explores the optimization of Rhodamine B decolorization using a combination of adsorption and photoelectrocatalytic system. Using the combination of this system, the degradation of Rhodamine B increased thus its application in the wastewater treatment will reduce the environmental pollution.

EXPERIMENTAL SECTION

Materials were used are titanium tetra-isopropoxide (TTiP) from Aldrich, Ti plate (3 cm x 10 cm) of Baoji Titanium Qixin Co.Ltd, silica, alumina, Rhodamine B dye, ethanol, acetic acid, nickel nitrate, polyvinyl alcohol (PVA), hydrochloric acid and sodium hydroxide were purchased from E. Merck (Indonesia). All reagents were analytical reagent grade quality. All solutions were prepared with double distilled water.

Adsorbents activation

Activation process has been done by mixing each silica (50 g) and alumina (50 g) into H_2SO_4 1 M (250 mL) and NaOH 1 M (250 mL) for an hour. A mixed solution of adsorbent in acid or base washed by water until a neutral solution obtained. Each adsorbent was analyzed by FTIR Shimadzu model 8201 PC (ratio mass of sample: KBr = 1: 200).

Adsorption Process

The optimum conditions of the adsorbent can be determined by adsorption process of Rhodamine B solution (10 ppm, 12.5 mL) using silica (0.5 g) and alumina (0.5 g) with various treatment such as without activation process, acid activated, and base activated on shaker rotary for 60 minutes. The filtered mixed solutions were then analyzed by Lambda 25 Perkin Elmer UV-Vis spectrophotometer.

The adsorption process of Rhodamine B 10 ppm (12.5 mL) at various pH condition *i.e.* 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12, was performed with addition of silica (0.5 g) and alumina (0.5 g) activated by acid and base and was shaken for 60 minutes. The filtered mixed solutions were then analyzed by Lambda 25 Perkin Elmer UV-Vis spectrophotometer. The percentage adsorbed (%) of Rhodamine B can be calculated using equation 1.

$$\%\ \text{adsorption} = \frac{Co-Cr}{10}\ x\ 100\ \% \qquad (1)$$

where C_0: Initial concentration; Cr: Concentration of residual adsorption

Synthesis and preparation of Ti/TiO$_2$ electrode

The TiO_2 film was synthesized using procedures published previously (Wahyuningsih *et al.,* 2014). 10 mL solution of TTiP was hydrolyzed in 100 mL acetic acid glacial solution and mixed under vigorous stirring in an ice waterbath (10 ºC – 15 ºC) until a clear yellow solution of TiO_2 was formed. The solution was heated at 90 ºC for 2 h until it became a gel, which was then placed in an oven at 150 ºC for 24 h to undergo an aging process. Next, the TiO_2 xerogel was calcinated in a muffle furnace at 400 ºC for 2 h at a heating rate of 10 ºC.min^{-1}. The TiO_2 powder (12.5 grams) and 1 grams of PVA was added into 50 mL of ethanol and stirred for 15 min. Then TiO_2 solution was sprayed to Ti plate. The TiO_2-coated Ti plate was then dried at 200 ºC for 15 min. The coating and drying treatments were repeated until Ti plate covered completely. Materials were characterized by XRD (Bruker D8 Advance).

Synthesis and preparation of Ti/TiO_2-NiO electrode

The TiO_2-NiO composite was synthesized using a procedure published previously (Wahyuningsih *et al.,* 2014). 1.145 grams of synthesized xerogel TiO_2 (previous procedure) was added in 0.81 grams of $NiNO_3 \cdot 6H_2O$ that has dissolved in 25 mL of distilled water. The mixed solution was stirred with a magnetic stirrer to fuse. Then, the uniform mixture was dried at 110 ºC for 3 h. To improve the crystalline TiO_2-NiO after the green suspension was formed, it was calcinated at 700 ºC for 4 h at 10 ºCmin^{-1}. The crystalline TiO_2-NiO (12.5 grams) and 1 gram PVA was added into 50 mL of ethanol and stirred for 15 min. The TiO_2-NiO solution was sprayed to Ti plate and dried at 200 ºC for 15 min. The coating and drying treatments were repeated until Ti plate covered completely. Materials were characterized by XRD (Bruker D8 Advance).

Photoelectrocatalytic (PEC) Degradation Process

PEC degradation process of Rhodamine B 10 ppm solution at optimum pH (from adsorption process) was performed by a batch method using Ti/TiO_2 as a cathode and Ti/TiO_2-NiO as an anode. The PEC degradation process was performed at voltage~~s~~ of 6 V from DC Power Supply (ATTEN TPR3005T-3C) under visible light irradiation from a 300 Watt halogen lamp (Osram 300 Watt) for 10 min. The degradation process was done in a closed black box. Rhodamine B solution after degradation was analyzed by Lambda 25 Perkin Elmer UV-Vis spectrophotometer. The percentage degradation (%) of Rhodamine B was calculated using equation 2.

$$\% \text{ degradation} = \frac{Co - Cr}{10}\ x\ 100\ \% \qquad (2)$$

where C_0: Initial concentration; Cr: Concentration of residual degradation

Residual concentration of Rhodamine B after adsorption and degradation was calculated with equation (5). In which A is the residual Rhodamine B after adsorption (equation (3)), and B is the residual Rhodamine B after degradation (equation (4)). The decreasing of Rhodamine B concentration after treatment was calculated with equation (6).

$$\text{Cr (residual adsorption)} = A \qquad (3)$$

Cr (residual adsorption) x (% degradation/100) = B (4)

% degradation and adsorption (C) = $Co - \frac{A-B}{10}\ x\ 100\ \%$ (5)

% decreasing activity= (C - % degradation) (6)

RESULTS AND DISCUSSION

Acid and Base Activation of Adsorbents

Activation performed on silica affects the active site of silica because the addition of the acid-base activation which the activation of the acid will enhance the acidity of the silica due to addition of the active site of H^+ and activation of bases will improve the properties of alkalinity in silanol (Si-OH) as the active site, silanol (Si-OH) on the surface of adsorbent undergo protonation at acid activation thus the surface positively charged. Meanwhile, the activation using a base, silanol groups on the surface of the adsorbent will lose a proton to the negatively charged surface of the adsorbent (Al-Ghouti *et al.*, 2003).

$$\text{Si-OH} + H^+ \rightarrow \text{Si-OH}_2^+ \quad (7)$$

$$\text{Si-OH} \rightarrow H^+ + \text{Si-O}^- \quad (8)$$

In the FTIR spectra of non-activated silica and acid-base activated, there was no significant change in the functional group. The only change occurred in the total number of O-H due to the activation using acids and bases. FTIR spectra of the adsorbent silica non-activated and acid-base activated can be seen in Figure 1.

The FTIR spectra of un-activated silica, acid-, and base-activated silica adsorbents show the absorption functional group of O-H silanol group at wavenumber 3444.05 cm^{-1}, 3462.37 cm^{-1}, and 3441.19 cm^{-1}, respectively. Uptake of bending vibration O-H group in silanol appears at wavenumber 1631.85 cm^{-1} for acid activated silica and 1632.81 cm^{-1} for base activated silica. The stretching vibrations asymmetry of -Si-O on siloxane appear at a wavenumber of 1095.61 cm^{-1}, 1083.08 cm^{-1}, and 1101.40 cm^{-1} for un-activated, acid-, and base-activated silica adsorbents, respectively. Uptake in the area of 802.42 cm^{-1}, 801.46 cm^{-1}, and 795.67 cm^{-1} in each of the silica adsorbents showed symmetry stretching vibration of -Si-O. In the wavenumber of 975.06 cm^{-1}, 967.34 cm^{-1}, and 954.80 cm^{-1} showed stretching vibration -Si-O group in silanol for each non-activated silica and acid-base activated silica. The bending vibrations from the group siloxane Si-O-Si in each of the silica adsorbents were shown by the respective absorption at wavenumber 456.18 cm^{-1}, 468.72 cm^{-1}, and 472.58 cm^{-1} (Silverstein, 1991). There are differences of O-H amount (ΔT) on silica adsorbents without activation, acid activated and base activated respectively 18.1%, 12.2%, and 25.8%.

Base-activated silica contains more O-H functional group due to silica can absorbs H_2O with maximum in the base condition, so it is possible activation silica with base formed Si-OH and Si-O$^{\bullet}$. Percentage ΔT of the total content of O-H on the higher base silica will affect silica adsorption activity with Rhodamine B.

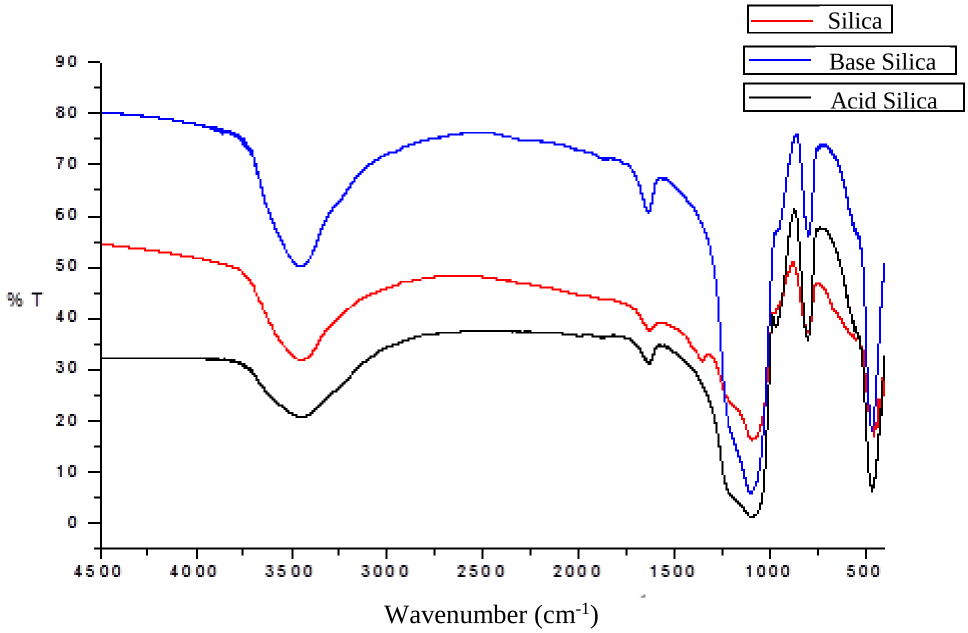
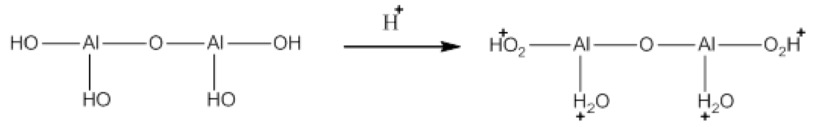


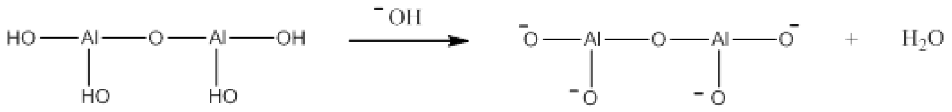
Figure 1. FTIR spectra of silica adsorbents without activation, acid activated and base activated.

Activation of alumina using acid or base caused alumina as cation and anion exchanger in accordance with conditions of activation using acid or base. The alumina had a high affinity for cationic species when it was activated using bases; whereas it has a high affinity for anionic species when it was activated using acid (Mahmoud *et al.*, 2010). Activation using acid and base affecting active sites on the surface of alumina, which can act as Bronsted acid and base.



(9)

Bronsted acid



(10)

Bronsted base

Figure 2 showed alumina FTIR spectra of non-activated alumina and acid-base activated alumina. The FTIR spectra of respective un-activated alumina, acid- and base-activated alumina reveal O-H stretching vibration which each appears at the wavelength of

3462.37 cm^{-1}, 3461.41 cm^{-1}, and 3459.48 cm^{-1} and the O-H bending vibration which each appears at the wavelength of 1630.88 cm^{-1}, 1634.74 cm^{-1}, and 1636.67 cm^{-1}. The vibration activated functional group Al-O of each alumina without activation, acid activation, and base activation appear at the wavelength of 775.42 cm^{-1}, 731.05 cm^{-1}, and 732.98 cm^{-1}. FTIR spectra results showed that no change of functional groups on the adsorbent alumina. However, the acid or base activation on alumina caused changes in the total number of O-H active sites on alumina which affect the adsorption ability to dye Rhodamine B (Motahari *et al.*, 2014). The O-H content changes were indicated by the changes of percentages of ΔT (Δ transmittance) of the adsorbent alumina without activation, acid activation, and base activation as = 61.2, 41.8, and 63.7%, respectively. The ΔT percentage of the total content of O-H of the base activation alumina is higher than that of alumina without activation and acid activation. Acid-base activation in silica and alumina adsorbents can cause the change in the intensity of the vibration of O-H.

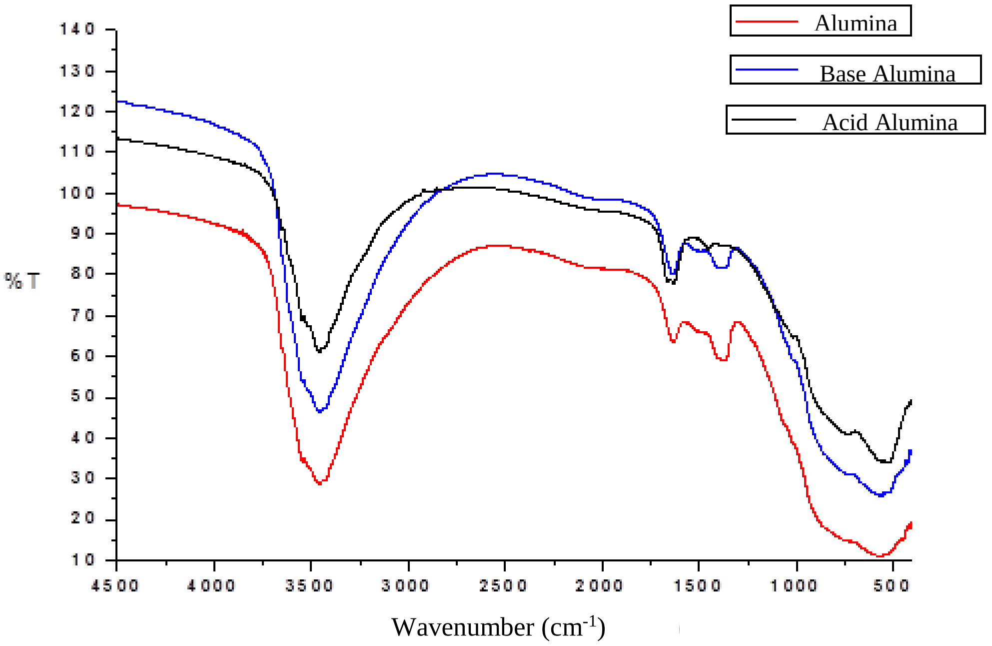


Figure 2. FTIR spectra of alumina adsorbents without activation, acid activated and base activated.

Rhodamine B adsorption activity of silica and alumina adsorbents

Adsorption of 10 ppm Rhodamine B dye solution was conducted to determine the adsorption activity of the adsorbent silica and alumina to Rhodamine B dye. Various pH conditions of Rhodamine B also affect the adsorption activity of the adsorbent for the adsorbate. The pH conditions can form some structure of Rhodamine B. At the low pH conditions (pH ≤5) Rhodamine B tends to form the cationic structure that positively charged on $=N^+(Et)_2$ group. At high pH conditions (pH ≥6), Rhodamine B tends to form a zwitter ionic structure (Motahari *et al.,* 2014).

Rhodamine B adsorption

Figure 3 shows the optimum adsorption activity of Rhodamine B to the acid-activated silica is 97.15 ± 0.113%. The active site of silica (silanol) have more H^+ ions from the acid solution so can reacted with Rhodamine B which have negative charge ($-COO^-$) form zwitter ionic structure. However, the interaction between Rhodamine B with silica is more likely through a cation exchange mechanism in chemisorption (Long *et al.*, 2016).

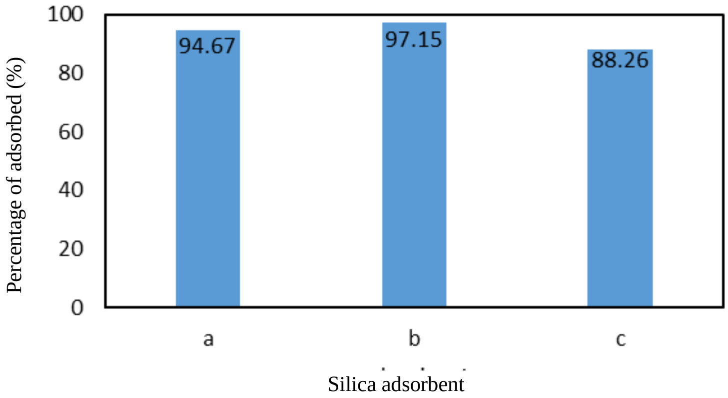


Figure 3. Decreasing the concentration of Rhodamine B dye after going through the process of adsorption using silica adsorbent (a) without activation, (b) acid activated, and (c) base activated.

No significant difference on Rhodamine B dye adsorption activity to un-activated alumina and acid-, and base- activated adsorbent was observed. This is consistent with the results of FTIR spectra of the activated alumina and without activation showed the amount of O-H did not differ significantly. The optimum activity of base- activated alumina to adsorb Rhodamine B was 86.86 ± 0.371% as shown in Figure 4.

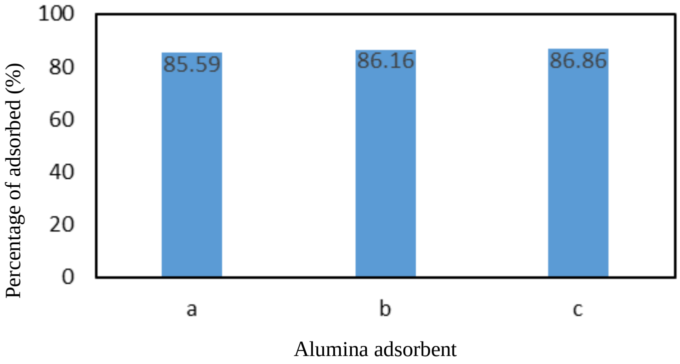


Figure 4. Decreasing the concentration of Rhodamine B dye after going through the process of adsorption using alumina adsorbent (a) without activation, (b) acid activated, and (c) base activated.

Rhodamine B adsorption at various pH conditions using acid and base activated silica.

Figure 5 shows the optimum Rhodamine B dye adsorption using an acid-activated silica at pH 9 reached 83.35±0.408%, which in these conditions Rhodamine B dye tends to form structures zwitter ion (Motahari *et al*., 2014) which has a negative charge thus the interaction with silica is much more powerful than the acidic form's Rhodamine B structure while in acidic conditions it forms cationic structure. In contrast, at the highly acidic conditions (pH 2), Rhodamine B was adsorbed up to 81.91 ± 8.175% using base activated silica adsorbent~~s~~. Interaction of cationic form of Rhodamine B and base activated silica that has more dominant O-H group in the silanol active site provides an effective role to quarantine the Rhodamine B molecule.

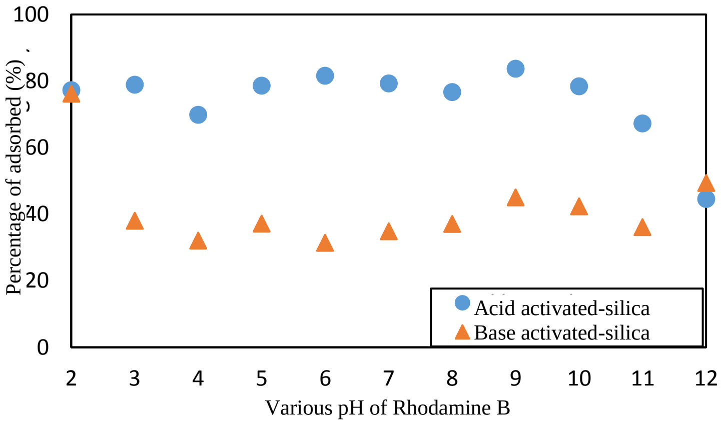


Figure 5. The percentage of adsorption at a various pH with acid- and base-activated silica as adsorbent.

Rhodamine B adsorption at various pH conditions using acid and base activated alumina.

The optimum of Rhodamine B adsorption activity using an acid-activated alumina at pH 8 was 74.73 ± 10.109% as shown in Figure 6. It is due to the structure of Rhodamine B in the base condition can form zwitter ionic which interacted with active groups of acid-activated alumina. The adsorption activity of base-activated alumina has similar to the adsorption activity of base-activated silica adsorbent, where in pH 2 the Rhodamine B (cationic structure) adsorption activity with base-activated silica adsorbent was 69.20% ± 21.285. The interaction of adsorbent and Rhodamine B can form cationic and zwitter ion because of several bonds, such as hydrogen bonds, ionic bonds, or cation exchange interactions of adsorbents with Rhodamine B (Jain *et al*., 2007).

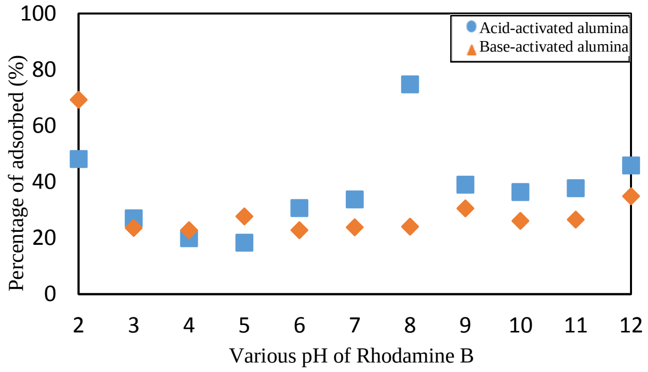


Figure 6. The percentage of adsorption at a various pH of Rhodamine B solution.

Characterization of Ti/TiO$_2$ and Ti/TiO$_2$-NiO electrode

The electrode of Ti/TiO$_2$ was prepared by coating TiO$_2$ on plate of titanium. The diffractogram of Ti/TiO$_2$ is shown in Figure 7, which all peaks are belong to the characteristic of crystalline TiO$_2$ (anatase). The peaks appears in the 2θ= 25° (d$_{101}$= 3.4967 Å), 2θ= 37° (d$_{004}$= 2.3679 Å), 2θ= 48° (d$_{200}$ = 1.8874 Å), 2θ= 54° (d$_{105}$ = 1.6931 Å), and 2θ = 62° (d$_{211}$= 1.6674 Å) according to the JCPDS standard No. 78-2486.

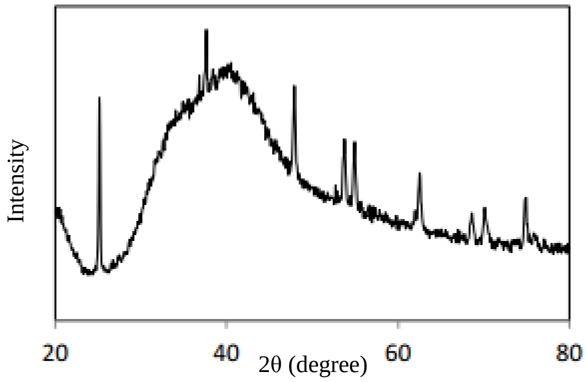


Figure 7. Diffractogram of Ti/TiO$_2$ electrode.

The diffractogram of Ti/TiO$_2$-NiO electrode shown in Figure 8 presents the peaks of TiO$_2$-NiO composite at 2θ= 25° (d$_{012}$= 3.4768 Å), 2θ= 27° (d$_{110}$= 2.340 Å), 2θ= 38° (d$_{110}$= 2.3540 Å), 2θ= 40° (d$_{102}$ = 2.2441 Å), 2θ= 54° (d$_{018}$ = 1.6895 Å), and 2θ= 70° (d$_{103}$ = 1.3330 Å) according to the JCPDS standard No. 33-0960.

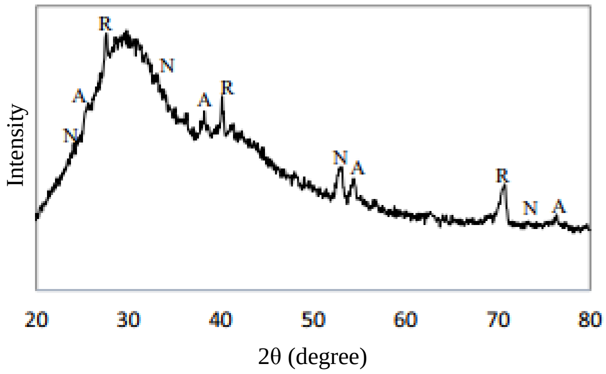


Figure 8. The diffractogram of Ti/TiO_2-NiO electrode (N=$NiTiO_3$; A=TiO_2 (anatase); R=TiO_2 (rutile)).

Photoelectrocatalityc degradation of Rhodamine B

The photoelectrodegradation process was also studied to optimize the concentration decrease of Rhodamine B. The degradation of 10 ppm Rhodamine B was done by a photoelectrocatalityc reactor in the batch system using 300 Watt halogen lamp as a source of photon energy. The voltage applied to a working electrode was set at 6 volts using a potentiostat. The measurements were made using a single electrode system where Ti/TiO_2-NiO and Ti/TiO_2 were used as photoanode a photocathode, respectively.

The experimental measurements were performed on 10 ppm Rhodamine B dye in various pH conditions. The pH conditions applied were derived from optimum pH conditions obtained in the adsorption studies using various types of adsorbents at the pH conditions of 2, 8, and 9 and a neutral pH. Figure 9 shows the optimum photoelectrodegradation activity under acidic conditions (pH 2) of Rhodamine B of 90.76 ± 0.046%. This is because of the cationic structure of Rhodamine B able to interact with radical $OH^{\bullet}$ and $O_2^{\bullet}$ that formed by photoanode. The form of zwitterionic structure of Rhodamine B less degraded than the cationic form (Wahyuningsih *et al.*, 2013).

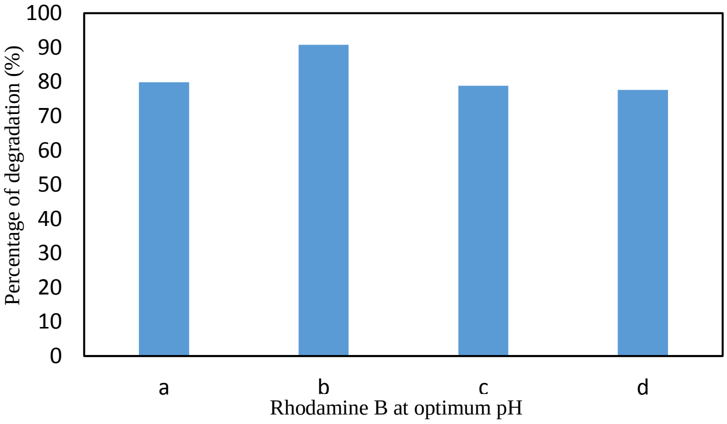


Figure 9. The percentage of degradation after photoelectrodegradation at (a) a neutral pH, (b) pH = 2, (c) pH = 8, and (d) pH = 9.

Combined Systems of Adsorption and Photoelectrodegradation to Optimize~~d~~ the concentration decrease of Rhodamine B

The results of adsorption and photoelectrodegradation systems can be combined in order to know the value of concentration decrease of Rhodamine B after both processes. Figure 10 shows the optimum combined system of adsorption and photoelectrodegradation system reached at 98.79% concentration decrease of Rhodamine B using base activated silica and Rhodamine B pH condition at highly acid (pH 2).

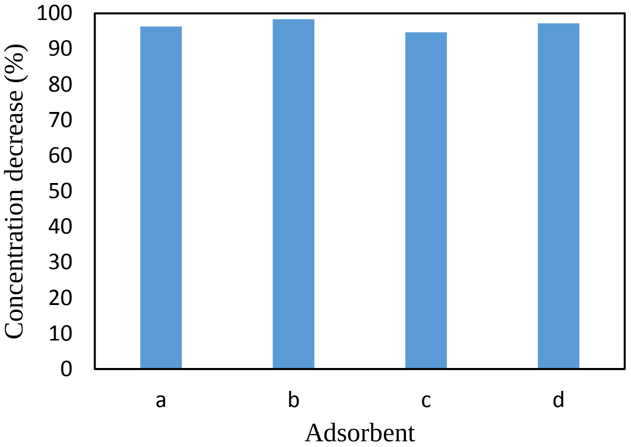


Figure 10. Decreasing of Rhodamine B concentration after treatment in the combination of adsorption and photoelectrodegradation using adsorbent (a) silica acid, (b) silica base, (c) alumina acid, and (d) alumina base.

The percentage of degraded Rhodamine B has an average increase which equals to 12.11 ± 6.04% after the adsorption process using an adsorbent of acid- and base-activated silica and acid- and base-activated alumina. This increase shows that the degradation of Rhodamine B using a combination of adsorption and photoelectrodegradation systems provided a better result than using a photoelectrodegradation system~~s~~ only.

CONCLUSIONS

The acid and base activation to silica and alumina adsorbent changed the total amount of -OH group in the adsorbent. The optimum adsorption reached when the acid-activated adsorbent adsorb Rhodamine B under base condition, due to the formation of zwitter ionic structure. Meanwhile, base-activated adsorbent has an optimum adsorption activity when Rhodamine B in a highly acid condition that formed cationic structure. Adsorption and photoelectrodegradation combination system using photoanode Ti/TiO_2-NiO at a bias potential of 6 V cause a decrease of Rhodamine B dye concentration of 98.79% using base-activated silica at highly acid pH condition (pH 2).

REFERENCES

Alver, E., Metin, A. U., 2012. Anionic Dye Removal from Aqueous Solutions Using Modified Zeolite: Adsorption Kinetics and Isotherm Studies. *Chemical Engineering Journal* 200-202, 59-67.

Al-Ghouti, M.A., Khraisheh, M.A.M., Allen, S.J., Ahmad, M.N., 2003. The Removal of Dyes from Textile Wastewater: A Study of The Physical Characteristics and Adsorption Mechanisms of Diatomaceous Earth. *Journal of Environmental Management* 69 (3), 229-238.

Gunlazuardi, J., 2001. *Fotokatalisis pada Permukaan TiO_2: Aspek Fundamental dan Aplikasinya*. Seminar Nasional Kimia Fisika II. Universitas Indonesia, Jakarta

Huang, C.H., Chang, K.P., Ou, H.D., Chiang, Y.C., Wang, C.F., 2011. Adsorption of Cationic Dyes onto Mesoporous Silica. *Microporous and Mesoporous Materials* 141, 102-109.

Jain, R., Mathur, M., Sikarwar, S., Mittal, A., 2007. Removal of The Hazardous Dye Rhodamine B Through Photocatalytic and Adsorption Treatments. *Journal of Environmental Management* 85, 956-964.

Kannan, C., Sundaram, T., Palvannan, T., 2008. The Environmentally Stable Adsorbent of Tetrahedral Silica and Non-Tetrahedral Alumina for Removal and Recovery of Malachite Green Dye from Aqueous Solution. *Journal of Hazardous Materials* 157, 137-145.

Long, Z., Xu, W., Lu, Y., Qiu, H., 2016. Nanosilica-Based Molecularly Imprinted Polymer Nanoshell for Specific Recognition and Determination of Rhodamine B in Red Wine and Beverages. *Journal of Chromatography*. *B, Analytical Technologies in The Biomedical and Life Sciences* 1029-1030, 230-238.

Mahmoud, M.E., Osman, M.M., Hafez, O.F., Hegazi, A.H., Elmelegy, E., 2010. Removal and Preconcentration of Lead (II) and Other Heavy Metals from Water by Alumina Adsorbents Developed by Surface-Adsorbed-Dithizone. *Desalination* 251 (1-3), 123-130.

Malakootian, M., Mansoorian, H.J., Hosseini, A., Khanjani, N., 2015. Evaluating The Efficacy of Alumina/Carbon Nanotube Hybrid Adsorbents in Removing Azo Reactive Red 198 and Blue 19 Dyes from Aqueous Solutions. *Process Safety and Environmental Protection* 96, 125-137.

Motahari, F., Mozdianfard, M.R., Salavati-Niasari, M., 2014. Synthesis and Adsorption Studies of NiO Nanoparticles in Presence of H_2acacen Ligand for Removing Rhodamine B in Wastewater Treatment. *Process Safety and Environment Protection* 93, 282-292.

Silverstein, R.M, Bassler, G.C, Morril, T.C., 1991. *Spectrometric Identification of Organic Compounds 4th Edition*. John Wiley and Sons Inc., New York.

Sen, S., and Demirer, G. N., 2003. Anaerobic Treatment of Real Textile Wastewater with A Fluidized Bed Reactor. *Water Research* 37, 1868–1878.

Sun, D., Zhang, Z., Wang, M., Wu, Y., 2013, Adsorption of Reactive Dyes on Activated Carbon Developed from Enteromorpha prolifera. American. *Journal of Analytical Chemistry* 4, 17-26.

Wahyuningsih, S., Purnawan, C., Kartikasari, P.A., Praistia, N., 2013. Visible Light Photoelectrocatalytic Degradation of Rhodamine B Using A Dye-Sensitized TiO_2 Electrode. *Chemical Paper* 68(9), 1248-1256.

Wahyuningsih, S., Purnawan, C., Saraswati, T. E., Pramono, E., Ramelan, A. H., Pramono, S., Wisnugroho, A., 2014. Visible Light Photoelectrocatalytic Degradation of Rhodamine B Using Ti/TiO_2-NiO Photoanode. *Journal of Environmental Protection* 5, 1630-1640.