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Color And COD Degradation of Procion Red Synthetic Dye Using Fenton-TiO_2 Method

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Abstract

Nowadays, environmental pollution caused by industrial wastewater is quite apprehensive. Most of textile industries used synthetic dyes. Procion red is one of the synthetic dyes that was often used in textile industries and classified as a reactive dye that is difficult to decompose in nature and contain harmful toxins. One of the colored wastewater treatment process is Fenton reagent and TiO_2 catalyst (Fenton-TiO_2) as one of the Advanced Oxidation Processes (AOPs). AOPs are based on the generation of very reactive species such as hydroxyl radicals ($OH^•$) is effective for decolourization and biodegradation of pollutants. The objectives of this research are to treat of procion red synthetic dye by using Fenton-TiO_2 method and study the effect of procion red concentration, reaction time, and the concentrations of TiO_2 catalyst on color and COD degradation. In this experiment, the concentrations of procion red were varied between 150-300 ppm, the concentrations of TiO_2 catalyst were varied from 0.05 to 0.4% (w/v) and the reaction time of 5 to 20 minutes. The optimum condition was achieved by using procion red concentration of 150 ppm with TiO_2 catalyst concentration of 0.4%, and reaction time of 20 minutes, where the maximum color and COD degradation achieved of 98.67% and 92% respectively.

Keywords: Procion red, Fenton reagent, TiO_2, color, COD, AOPs

Abstrak (Indonesian)

Saat ini, pencemaran lingkungan oleh limbah industri sudah cukup memprihatinkan. Kebanyakan industri tekstil menggunakan pewarna sintetik. Procion red merupakan salah satu dari pewarna sintetik yang sering digunakan dalam industri tekstil dan tergolong sebagai zat warna reaktif sehingga sulit terurai di alam dan mengandung zat yang berbahaya. Salah satu proses pengolahan zat warna adalah dengan menggunakan reagen Fenton dan katalis TiO_2 (Fenton-TiO_2) yang termasuk dalam teknologi *Advanced Oxidation Processes* (AOPs). AOPs didasarkan pada pembentukan spesies yang sangat reaktif seperti radikal hidroksil ($OH^•$) yang efektif untuk penghilangan warna dan biodegradasi polutan. Penelitian ini bertujuan untuk mengolah limbah sintetik procion red dengan metode Fenton-TiO_2 serta mempelajari pengaruh konsentrasi procion red, waktu reaksi dan konsentrasi katalis TiO_2 terhadap penurunan warna dan COD. Pada penelitian ini digunakan limbah sintetik procion red dengan konsentrasi 150-300 ppm, konsentrasi TiO_2 0,05-0,4% (w/v) dan proses pengolahan selama 5-20 menit. Kondisi optimum dicapai pada konsentrasi procion red 150 ppm dengan konsentrasi katalis TiO_2 0,4%, dan waktu reaksi 20 menit, dimana degradasi warna dan COD maksimum yang dicapai berturut-turut adalah 98,67% dan 92%.

Kata Kunci: Procion red, reagen Fenton, TiO_2, warna, COD, AOPs

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INTRODUCTION

Wastewaters from textile and dye industries are highly colored with large concentrations of organic matter. Many textile industries are unaware that the wastewater generated belongs to the category of B3 (hazardous and toxic materials) waste. The main source of wastewater in the textile industries is on the use of dyes [1], it is because the textile dyes may be composed of various chemicals, toxins, heavy metals, pharmaceuticals, petroleum based oils, and greases, that are difficult to decompose [2]. The textile industries use a lot of synthetic dyes such as procion, erionyl and auramin [3] because of its relatively cheap price, long-lasting color, more various color choices and easy to use compare to natural dyes [4]. However, effluent is still colorful and difficult to decompose in nature (non-biodegradable). If the textile wastewater is immediately disposed of without being processed, so the pollution in the territorial water will be difficult to avoid, because the wastewater still contains a lot of dye. Textile dyes may interfere the aesthetics, decrease incoming sunlight into the water, disrupt the balance of the photosynthesis process, and the effect of carcinogenic and mutagenic of the dye [4].

Chemical wastewater treatment method is relatively more effective compared to the wastewater treatment method by physical and biological processes, one of them is Advanced Oxidation Processes (AOPs). The processes are economic because it can save space and energy, low cost investment, simple and safe. The process is also fast, effective and capable of degrading harmful, toxic and non-biodegradable compound in the wastewater through the oxidation process [5]. The Fenton reagents involve the application of ferrous ions (Fe^{2+}) to react with hydrogen peroxide (H_2O_2) producing hydroxyl radicals ($OH^•$) with the powerful oxidizing ability to degrade organic pollutants in wastewater [6] otherwise there is no energy needed in terms of activating hydrogen peroxide because the reaction takes place at room temperature and atmospheric pressure [7].

Fenton’s reagent is a solution of hydrogen peroxide with dissolved ferrous iron as a catalyst. It is used to oxidize organic contaminant found in industrial wastewaters [8]. Fenton's reagent is most commonly used to destroy organic compounds that are resistant to other wastewater treatment techniques such as biological treatment or carbon adsorption. Typical application is the destruction of organic solvents that are resistant to biological oxidation such as phenols, formaldehyde, methylene chloride and chlorinated solvents [9]. In this research also used reagent Fenton which is combined with TiO_2 catalysts. TiO_2 is a semiconductor photocatalysis [10] that easy to obtain and having low cost manufacturing is relatively low. It also has advantages such as high photocatalytic activity, nontoxic, corrosion resistant and insoluble in water [11].

The research using AOPs technology based on the production of hydroxyl radicals ($OH^•$) with various combinations of the process to treat wastewater containing dyes has been widely practiced [12], such as by Fenton method, photo-Fenton (UV-Fenton), photo-Fenton-catalytic (UV-Fenton-TiO_2) and photocatalytic (sunlight-TiO_2) [4]. All these processes produce hydroxyl radicals ($OH^•$) to oxidize the contaminant in the wastewater [13]. However, the effective, efficient and economical methods should be chosen to degrade organic waste pollutants. Therefore, it is necessary to conduct the research on the treatment of procion red synthetic dye by using Fenton-TiO_2 method to know the effect of procion red concentration, TiO_2 concentration, and reaction time on color and COD degradation.

MATERIALS AND METHODS

Materials

The procion red dye obtained from Fajar Setia Dyestuff in Jakarta and used without further purification. The other chemicals were supplied from Merck and Sigma Aldrich such as hydrogen peroxide (H_2O_2 30% w/v), ferrous sulfate ($FeSO_4.7H_2O$), titanium dioxide (TiO_2), sodium thiosulfate ($Na_2S_2O_3$), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4).

Methods

The treatment of procion red synthetic dye was carried out by using Fenton-TiO_2 in a stirred tank reactor. The procion red concentration of 150-300 ppm and TiO_2 concentration of 0.05-0.4% (w/v) were used in this study. Firstly, a 150 ppm of procion red was made by weighing a certain amount of procion red and dissolve in distillation water. The initial absorbance and COD value were measured. The Fenton reagent of 1 : 80 molar ratio and TiO_2 concentration of 0.05 (w/v) were utilized. Place the synthetic dye, reagent Fenton and the catalyst in the reactor. Stirred speed of 500 rpm was applied. During the oxidation process, samples were taken at 5, 10, 15, and 20 minutes, then add the solution of $Na_2S_2O_3$ to each sample immediately. After that measure the final absorbance and COD value. Repeat the procedures by using different concentration of procion red and catalyst.

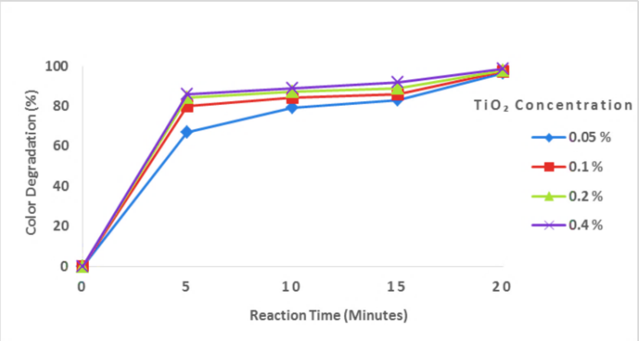
Analysis Data

The samples were taken periodically for analysis of color and COD degradation. Color degradation was determined using Thermo Scientific Spectrophotometer UV-Visible Genesys^{TM}20 while COD degradation was determined by titrimetric method.

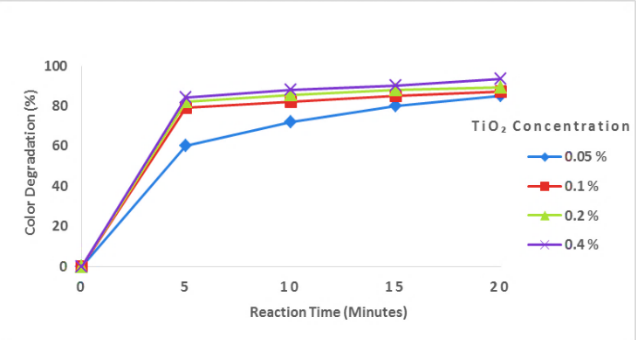
RESULT AND DISCUSSION

Effect of reaction time and TiO_2 concentration on color degradation

The oxidation process was examined for 20 minutes with TiO_2 concentrations from 0.05% to 0.4%. The effect of reaction time and TiO_2 concentration on color degradation can be seen in Figure 1.



(a)



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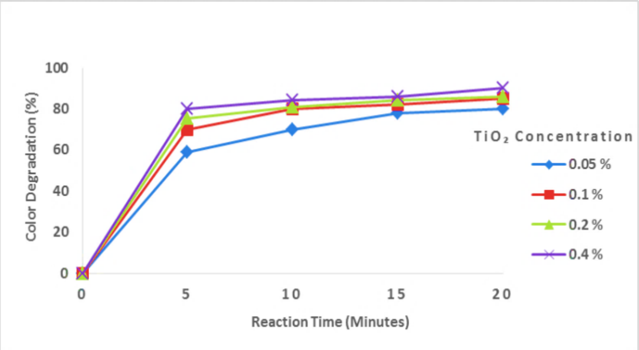

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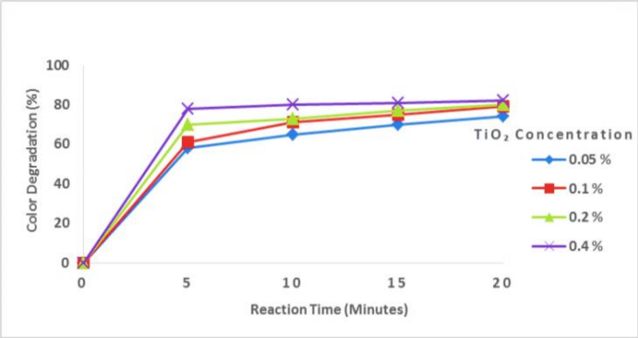


(d)

Figure 1. Effect of reaction time and TiO_2 concentration on color degradation at various procion red concentration of (a) 150 ppm, (b) 200 ppm, (c) 250 ppm, (d) 300 ppm

The highest color degradation percentage of 98.67% was reached when using the procion red concentration of 150 ppm, TiO_2 concentration of 0.4%, and reaction time of 20 minutes as can be seen in Figure 1 (a). When using procion red concentration of 200 ppm (Figure 1b) the percentage of color degradation achieved decreased when compared to the procion red concentration of 150 ppm, where the highest color degradation was only 93.59%. At the same condition when the procion red concentration of 250 ppm and 300 ppm applied, the highest color degradation achieved were 90.16% and 81.84%, respectively, as shown in Figure 1 (c) – (d). The percentage of color degradation decreased with increasing concentration of procion red. Because the increased concentration of procion red, the number of dye molecules contained in the wastewater is higher the smaller of procion red concentration used, the number of dye molecules contained in the wastewater is lower, so the percentage of color degradation produced is higher. This is because the procion red molecule has been oxidized, where high color degradation occurs due to oxidation of procion red by hydrogen peroxide (H_2O_2) which forms hydroxyl radical ($OH^{\bullet}$) [14] assisted by iron catalyst (Fe^{2+}). The formed hydroxyl radicals will break the double bond on the procion red into a simpler compound and so the color will degrade in the wastewater, which was originally red to became clear [15].

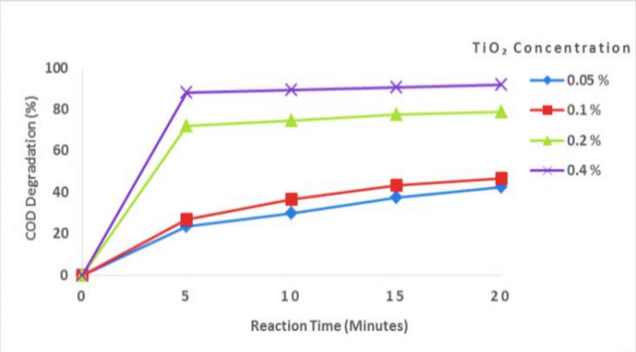
In addition, it can be seen also the effect of TiO_2 concentration occurring at various concentrations of procion red as illustrated in Figure 1 (a) – (d), where the color degradation process at all procion red concentrations occurred starting from TiO_2 concentration of 0.05% - 0.2% then continued to increase until TiO_2 concentration of 0.4%. In Figure 1

(a) – (d), it is clear that overall color degradation increasing with the addition of the amount of TiO_2 catalyst used. The greater of TiO_2 concentration then the higher color degradation obtained. Increase the number of TiO_2 catalysts will increase the number of active side [16] of the catalysts, so increase the formation of hydroxyl radical ($OH^{\bullet}$), which will oxidize the molecules of procion red.

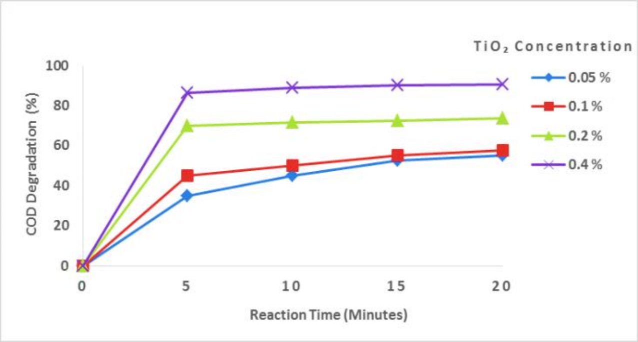
Not only procion red and TiO_2 concentration, but reaction time also affects the color degradation as demonstrated in Figure 1 (a) – (d), where the maximum of color degradation was achieved at reaction time of 20 minutes which occurred by using procion red concentration of 150 ppm and TiO_2 concentration of 0.4%. Generally, the color degradation process at all procion red and TiO_2 concentration occurred at reaction time of 20 minutes. Because the longer reaction time, the greater the degradation of the resulting color, because the longer reaction time, the more the hydroxyl radical ($OH^{\bullet}$) produced. The increasing time will provide more opportunities for the degradation of organic compounds or pollutant present in the wastewater. The results of this study are in accordance with research conducted by Agustina and Ang [17] which states that the time of oxidation will affect the efficiency of color removal. The Fenton-TiO_2 process shows that the length of reaction time causes the higher efficiency produced, so that the greater percentage of color degradation achieved. It can be concluded that the optimum conditions of color degradation occurred when using procion red concentration of 150 ppm, TiO_2 concentration of 0.4% and reaction time of 20 minutes.

Effect of reaction time and TiO_2 concentration on COD degradation

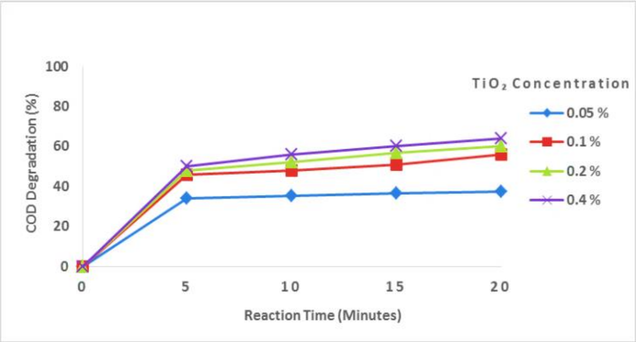
The effect of reaction time and TiO_2 concentration on COD degradation can be seen in Figure below.



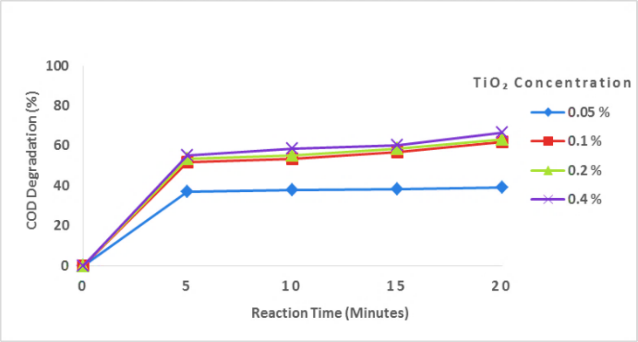
(a)



(b)



(c)



(d)

Figure 2. Effect of reaction time and TiO_2 concentration on COD degradation at various procion red concentration of (a) 150 ppm, (b) 200 ppm, (c) 250 ppm, (d) 300 ppm

Figure 2 shows the effect of reaction time and TiO_2 concentration on COD degradation at various concentrations of procion red. From Figure 2 (a) – (d), it can be seen that the highest COD percentage degradation of 92% occurs by using procion red concentration of 150 ppm at reaction time of 20 minutes (Figure 2a). The percentage of COD degradation indicates that the smaller of the procion red concentration, the greater percentage of COD degradation results. This happens because the smaller of the procion red concentration, the less of the

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number of dye molecules contained in the wastewater. The little amount of the existing dyestuff makes the hydroxyl radical ($OH^{\bullet}$) formed through the oxidation process capable of degrading the dyestuff, so that the greater percentage of COD decrease is achieved. In addition, from Figure 2 (a) – (d) it can be seen that in the use of lower TiO_2 concentrations of 0.05%, the percentage of COD degradation resulted is relatively small when compared to the higher concentration of TiO_2. The percentage of COD degradation increases with the addition of TiO_2. The highest COD degradation of 92% was reached by using the highest concentration of 0.04% TiO_2 used in this study. This happens because in the larger concentration of TiO_2, the surface area of the TiO_2 catalyst will become larger, so the hydroxyl radical ($OH^{\bullet}$) is more produced. The amount of hydroxyl radical ($OH^{\bullet}$) that are formed will oxidize more of the procion red molecules to become a simpler compounds that eventually become CO_2 and H_2O [18]. So, the more oxidized procion red molecules will more decrease the COD value. The highest COD degradation of 92% was achieved at the reaction time of 20 minutes by using 150 ppm of procion red concentration and TiO_2 concentration of 0.4%.

CONCLUSION

The Fenton-TiO_2 method can be used for the treating of procion red synthetic dye. The results show the occurrence of color and COD degradation on all concentration of TiO_2 and procion red used in this study. The optimum condition was achieved by using procion red concentration of 150 ppm, TiO_2 concentration of 0.4%, and reaction time of 20 minutes, which the maximum color and COD degradation of 98.67% and 92% were achieved respectively.

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