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Decomposition efficiency of some azo dyes in the systems consist of persulfate, zero-valent iron powder and UV light in water environment

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ABSTRACT

This research focused on surveying the decomposition efficiency of methyl orange, alizarin yellow and mordant black -T in the systems without and with UV light in water: alone zero-valent iron; alone persulfate; both zero-valent iron and persulfate. Results of research show that the decomposition efficiency some azo dyes are the highest in the systems of zero-valent iron/persulfate/azo dyes/UV and zero-valent iron/persulfate/azo dyes with the same reaction conditions. After 30 minutes of reaction, the decomposition efficiency of methyl orange, alizarin yellow and mordant black -T are 95.89 %, 90.99 % and 79.85 % in the zero-valent iron/persulfate/azo dyes/UV system and 73.65 %, 71.42 % and 58.94 % in the zero-valent iron/persulfate/azo dyes system. These results can be explained that persulfate has peroxide bond in molecular structure activated by zero-valent iron and UV light to generate in-situ free sulfate radical $SO_4^{-\bullet}$ (E^0=2.6 V) and free hydroxide radical $^{\bullet}OH$ (E^0=2.8 V). These radicals are very active and strong oxidation property. They are agents to oxidize those azo dyes strongly in the water environment.

Introduction

The method of treating organic polluted water by advanced oxidation processes (AOPs) have advantages comparing to traditional methods such as: fast treating time, mineralizing recalcitrant toxic organic substances. In some cases, AOPs are used as pretreatment methods for biological methods. adsorption methods [1], [4], [5].

Recent scientific announcements by scientists on the researching and application of other oxidants, such as persulfate and peroxymonopersulfate, are also suitable for wastewater treatment of persistent organic pollutant. If these oxidants are activated, they also produce free radicals which are higher oxidation activity than the original ones. Persulfate, peroxymonopersulfate are not stronger than hydrogen peroxide and ozone, but they are more durable than hydrogen peroxide and ozone in solution, better soluble in water than one [12], [16].

Specially, the process of activating the persulfate produces free radicals $SO_4^{-\bullet}$ (E^o = 2.6 V) and free radicals $^{\bullet}OH$ (E^o= 2.8 V). Persulfate exists longer in aqueous solutions, which affects positively the decomposition of organic compounds in aqueous environments [8]. Dyes are important and a long history of development in everyday life. At first, dyes were prepared from plants and insects in nature. The

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dyeing industry is development now. Dyes were mainly prepared by synthetic pathways. Azo dyes (AZOs) occupy more than 50% of the dye global trade. Some azo dyes have been found to cause cancer, mutations in genes and are banned worldwide. However, they are still produced and used on a large scale in the dyeing industry now. Because they are low production cost, easy to synthesize and some good color properties. The bonds in the azo molecules are quite stable, showing the ability to decompose and accumulate in the environment [6], [7], [14].

The textile industry consumes a large amount of clean water and also discharges a similar amount of wastewater which is complex composition and properties. This wastewater contains residual dyes from dyeing process (occupying about 10 to 15 % of the dye initial amount) and has color, temperature, content of COD, BOD and surfactants being very high [2], [11], [14].

Vietnam had a strong textile industry in recent decades, which brings many jobs and income to workers. Besides, it also releases a large amount of wastewater polluting environment [2], [11], [14].

Experimental

Chemicals used in the research experiments: Methyl orange (MO); Alizarin yellow R (AY); Mordant black-T (BT); Zero-valent iron (ZVI) powder (d< 212 μm, 99%); Sodium persulfate (PS); Sodium hydroxide; Sulfuric acid; Potassium iodide; Sodium thiosulfate. These chemicals are analytical reagent products from Merck, Germany. Acetonitrile, ethanol, methanol with cleanliness for high-performance liquid chromatography analysis, Fisher, Belgium.

Analytical method used the high-performance liquid chromatography (HPLC) to determine the concentrations of MO, AY, and BT in solution. Retention times (t_R-minute) and maximum adsorption wavelengths (λ_{max}-nm) of MO, AY and BT are 2.6 m, 430 nm; 2.5 m, 360 nm; 2.7 m, 550 nm at pH= 4.5 and t= 25 °C.

Results and discussion

The activated PS systems without UV

The ZVI/AZOs systems

Results of MO, AY and BT decomposition efficiency in ZVI/MO, ZVI/AY and ZVI/BT are shown in Fig 1. The experiments were performed under the reaction conditions: C_{ZVI}= 0.5 g/L, C_{AZOs}= 0.1 mM, pH= 4.5, t= 25 °C.

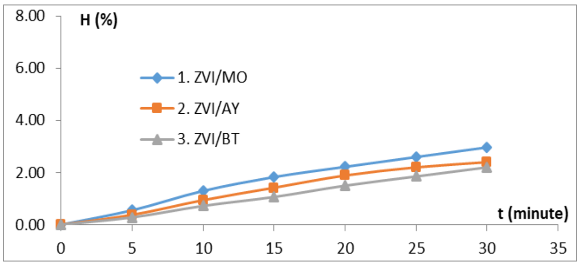

Figure 1: The decomposition efficiency of MO, AY and BT in systems: 1. ZVI/MO, 2. ZVI/AY and 3. ZVI/BT

From Fig 1 found in the ZVI/AZOs system, there is an increase in the decomposition of AZOs over the survey time. However, the degradation efficiency of AZOs is very low. After 30 minutes of reaction, the decomposition efficiency of dyes reached: $H_{ZVI/MO}$= 2.95 %, $H_{ZVI/AY}$ = 2.39 %, $H_{ZVI/BT}$= 2.20 %. The decomposition of AZOs in the ZVI/AZOs system can be explained in the following way: ZVI in water environment with pH = 4.5 is capable of decomposing organic substances according to the documents [3], [5], [13], [15]. In water environment ZVI is corrupted and converted to Fe^{2+}:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad \text{(acidic environment)} \qquad (1)$$

$$Fe^0 + 2H_2O + 1/2O_2 \rightarrow Fe(OH)_3 + 1/2H_2 \qquad (2)$$

The process of shaking the flask was stirring and also increasing the solubility of oxygen. In the acidic environment, Fe^{2+} is newly form with high chemical activity, then a small amount of H_2O_2 was formed by the following

$$2Fe^{2+} + O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O_2 \qquad (3)$$

ZVI powder in acidic solution was slowly and continuously corrosive and was a regular supply source of Fe^{2+}. According to Fenton, when there is simultaneous presence of Fe^{2+} and H_2O_2 in the solution forming free hydroxyl radicals •OH.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (4)$$

$${}^{\bullet}OH + AZOs \rightarrow Products \qquad (5)$$

Free radicals •OH has a strong oxidizing activity ($E_{\bullet OH}$ = 2.8 V) and reacts strongly with organic substances. In this case, free radicals •OH decomposes to AZOs. However, the pH = 4.5 is not the optimal pH according to Fenton (according to Fenton, the optimal pH= 2.5÷3.5) and the reaction time is short, causing the amount of H_2O_2 produced is very small and leading to the amount of free radicals •OH is also very low, so the degradation efficiency of AZOs is low. This is also consistent with the research results in documents [3], [20] which use only ZVI powder and air oxygen to decompose some organic substances. The AZOs have different decomposition efficiency in ZVI/AZOs. according to Fig 1 the decomposition efficiency of AZOs is arranged in order: ZVI/MO> ZVI/AY> ZVI/BT.

The PS/AZOs systems

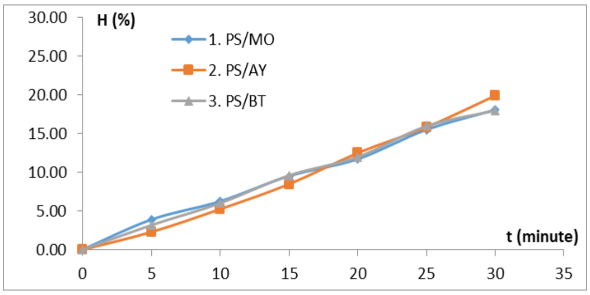

Figure 2: The decomposition efficiency of MO, AY and BT in systems: 1. PS/MO, 2. PS/AY and 3. PS/BT

Results of MO, AY and BT decomposition efficiency in systems: PS/MO, PS/AY and PS/BT are shown in Fig 2, experiments were performed under the reaction condition: C_{PS}= 1.0 mM, C_{AZOs}= 0.1 mM, pH= 4.5, t= 25 °C. According to the results of Fig 2 show that the systems are present in PS, the decomposition of AZOs are better than that of ZVI/AZOs. The decomposition efficiency of MO, AY and BT in systems: PS/MO, PS/AY and PS/BT was nearly the same during the all survey period. After 30 minutes of reaction, the decomposition efficiency of MO, AY and BT reached: $H_{PS/MO}$= 18.05 %, $H_{PS/AY}$= 19.88 %, $H_{PS/BT}$= 18.02 %. The cause of this similarity may be due to the oxidation of AZOs by PS being quite similar. Persulfate is a powerful oxidizer with a high standard redox potential (E^0= 2.1 V). Therefore, in this case the AZOs are decomposed by the usual oxidation reaction as equation (6).

$$PS + AZOs \rightarrow Products \tag{6}$$

But the decomposition efficiency of AZOs in PS/AZOs systems are moderate which compared to the decomposition efficiency of AZOs in ZVI/PS/AZOs systems (Fig 3).

The ZVI/PS/AZOs systems

Results of MO, AY and BT decomposition efficiency in the systems: ZVI/PS/MO, ZVI/PS/AY and ZVI/PS/BT are shown in Fig 3, experiments were performed in the reaction condition: C_{ZVI}= 0.5 g/L, C_{PS}= 1.0 mM, C_{AZOs}= 0.1 mM, pH= 4.5, t= 25 °C.

From the results of Fig 3 show the decomposition of AZOs in ZVI/PS/AZOs being quite highly. The decomposition efficiency of AZOs in ZVI/ PS/AZOs is much higher than the total decomposition efficiency of AZOs in ZVI/AZOs and PS/AZOs combined.

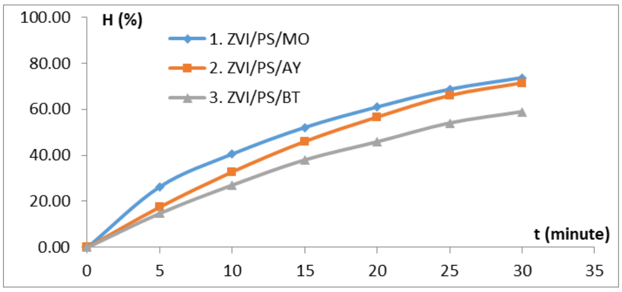

Figure 3: The decomposition efficiency of MO, AY and BT in systems: 1. ZVI/PS/MO, 2. ZVI/PS/AY and 3. ZVI/PS/BT

After 30 minutes of reaction, the decomposition efficiency of MO, AY and BT is: $H_{ZVI/PS/MO}$= 73.65 %, $H_{ZVI/PS/AY}$= 71.42 %, $H_{ZVI/PS/BT}$= 58.94 %.

The cause of the decomposition efficiency of AZOs increased sharply in the ZVI/PS/AZOs systems compared with the PS/AZOs and ZVI/AZOs systems which may be explained as follows: In the ZVI/PS/AZOs system, the dual oxidation effects have appeared. ZVI activates PS to create free radicals $SO_4^{-\bullet}$ and $^\bullet OH$. Free radical $SO_4^{-\bullet}$ is a strong oxidizing agent (E^0=2.6 V) [19], [20], [22] with a strong ability to decompose organic compounds. The formation of Fe^{2+} in PS/ZVI/AZOs systems can be in the form of reactions:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{7}$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \tag{8}$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{9}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \tag{10}$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \tag{11}$$

Like the Fenton process, Fe^{2+} activates directly $S_2O_8^{2-}$ to form free radicals $SO_4^{-\bullet}$ and Fe^{3+} is newly form to react with Fe^0 to form Fe^{2+} [13]:

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-\bullet} \tag{12a}$$

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + {}^\bullet OH \tag{12b}$$

$$SO_4^{-\bullet} + AZOs \rightarrow Products \tag{13a}$$

$$^\bullet OH + AZOs \rightarrow Products \tag{13b}$$

The role of ZVI is a gradual, stable, continuous supply source of Fe^{2+} ions for the reaction (12a). When ZVI interacts with water, oxygen and the presence of organic matter, it also produces hydroxyl radicals $^\bullet OH$ as mentioned in the ZVI/AZOs system. In addition, at pH= 4.5, there is an interaction between $SO_4^{-\bullet}$ with water to form $^\bullet OH$ according to reaction (12b). Thus, in the PS/ZVI/AZOs system, there are two free radicals •OH and $SO_4^{-•}$ with strong oxidation activity, which accelerates greatly the decomposition of AZOs.

According to Fig 3, the decomposition efficiency of MO, AY and BT in the ZVI/PS/AZOs is ordered: ZVI/PS/MO> ZVI/PS/AY> ZVI/PS/BT.

Through the results shown in Fig 1, Fig 2 and Fig 3, it recognizes that there is always a rule that the decomposition efficiency of AZOs dyes in the systems is increasing: ZVI/AZOs<PS/AZOs <ZVI/PS/AZOs.

Thus, the decomposition of AZOs in the ZVI/PS/AZOs system is not merely an addition of the decomposition efficiency of AZOs under the effect of ZVI and PS separately. This proves that in ZVI/PS/AZOs, beside AZOs in direct decomposition by PS and ZVI, are also decomposed by the effects of free radicals •OH and $SO_4^{-•}$ generated by ZVI activated PS [9], [15].

The activated PS systems with UV

The ZVI/AZOs/UV systems

The decomposition results of AZOs in the ZVI/AZOs/UV system are shown in Fig 4. Experiments were performed under the reaction conditions: C_{ZVI} = 0.5 g/L, C_{AZOs}= 0.1 mM, pH= 4.5, t= 25 ºC, I= 785 Lux, λ= 254 nm.

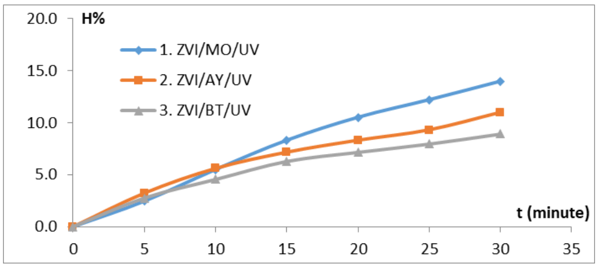

Figure 4: The decomposition efficiency of MO, AY and BT in systems: 1. ZVI/MO/UV, 2. ZVI/AY/UV and 3. ZVI/BT/UV

From the results of Fig 4, the decomposition efficiency of AZOs in the systems with ZVI and UV is much higher than that of the systems with ZVI alone. The first 10 minutes, the decomposition efficiency of AZOs is almost the same, after 20 minutes the decomposition efficiency of AZOs is significantly different. After 30 minutes, the decomposition efficiency of MO, AY and BT in the ZVI/AZOs/UV systems reached: $H_{ZVI/MO/UV}$= 13.96 %, $H_{ZVI/AY/UV}$= 10.97 %, $H_{ZVI/BT/UV}$= 8.93 %. The reasons for the above differences can be explained: As mentioned above, the ZVI/AZOs at pH = 4.5 will produce Fe^{2+}, H_2O_2 and •OH (very small amounts) according to the reaction (1) to (5). When ZVI/AZOs system combines with UV (ZVI/AZOs/UV system), UV plays a role in activating H_2O_2 to form free radicals •OH. At the first time (10 minutes), the amount of ZVI began to erode, so the amount of Fe^{2+} was very small, so the decomposition efficiency of AZOs was almost the same. After that (last 20 minutes), the decomposition efficiency of AZOs were different: $H_{ZVI/MO/UV}$ > $H_{ZVI/AY/UV}$ > $H_{ZVI/BT/UV}$. This can be explained by the quantum structure of BT are more durable than AY and MO.

The PS/AZOs/UV systems

Results of the decomposition of AZOs in the PS/AZOs/UV are shown in Fig 3.5. Experiments were performed under the reaction conditions: C_{PS}= 1.0 mM, C_{AZOs}= 0.1 mM, pH= 4.5, t= 25 ºC, I= 785 Lux, λ= 254 nm.

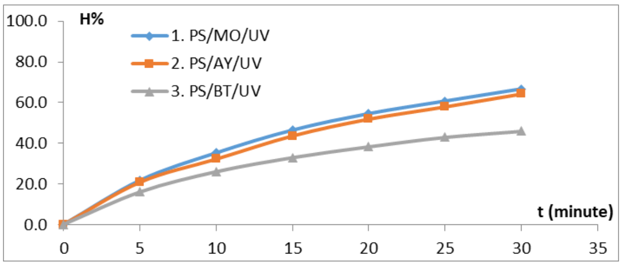

Figure 5: The decomposition efficiency of MO, AY and BT in systems: 1. PS/MO/UV, 2. PS/AY/UV and 3. PS/BT/UV

The decomposition efficiency of AZOs in the PS/AZOs/UV system is much higher than that of the PS/AZOs systems. After 30 minutes of reaction, the decomposition efficiency of MO, AY and BT in the PS/AZOs/UV systems reached: $H_{PS/MO/UV}$= 66.80 %, $H_{PS/AY/UV}$= 69.45 %, $H_{PS/BT/UV}$= 45.91 %. The decomposition efficiency of AZOs increases in this case because UV is the activation agent of PS to form free radicals $SO_4^{-•}$ [9].

$$S_2O_8^{2-} + UV \rightarrow 2SO_4^{-•} \qquad (14)$$

Oxidative free radicals $SO_4^{-•}$ decompose the AZOs well, the decomposition efficiency of AZOs increase fastly.

The ZVI/PS/AZOs/UV systems

The results of AZOs decomposition in the ZVI/PS/AZOs/UV systems are shown in Fig 6. Experiments were performed under the reaction conditions: C_{ZVI} = 0.5 g/L, C_{PS}= 1.0 mM, C_{AZOs}= 0.1 mM, pH= 4.5, t= 25 ºC, I= 785 Lux, λ= 254 nm. From Fig 6. it is found that the decomposition efficiency of AZOs in the ZVI/PS/AZOs/UV systems increases sharply

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compared to previous systems. After 30 minutes of reaction, the decomposition efficiency of MO, AY and BT were very high: $H_{ZVI/PS/MO/UV}$= 95.89 %; $H_{ZVI/PS/AY/UV}$= 90.99 %; $H_{ZVI/PS/BT/UV}$= 79.85 %. This can be explained in the ZVI/PS/AZOs/UV system which have two activation agents ZVI and UV.

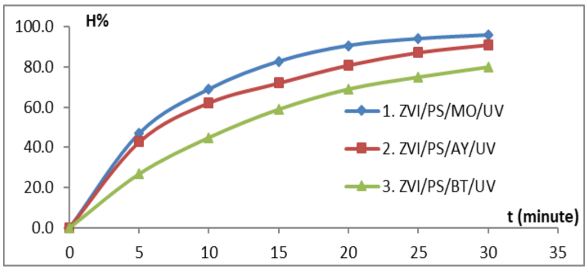

Figure 6: The composition efficiency of MO, AY and BT in systems: 1. ZVI/PS/MO/UV, 2. ZVI/PS/AY/UV and 3. ZVI/PS/BT/UV

The ZVI/PS/AZOs/UV systems is activated by UV shown reactions (3.14), (3.15). In addition, UV catalyzes the process to recover Fe^{2+} from Fe^{3+} [10].

$$H_2O_2 + UV \rightarrow 2HO^{\bullet} \qquad (15)$$

$$Fe^{3+} + UV + 1e \rightarrow Fe^{2+} \qquad (16)$$

Therefore, the amount of free radicals $^{\bullet}OH$ and $SO_4^{-\bullet}$ produced in the ZVI/PS/AZOs/UV system is higher than the other systems.

Parameters of these researchs were carried out in bath form. The amount of ZVI and concentration of PS decreased gradually over the reaction time due to forming Fe^{2+}, Fe^{3+} ions and $^{\bullet}OH$, $SO_4^{-\bullet}$ radicals. The lifetime of these radicals are very short, the half-life of $^{\bullet}OH$ is $t_{1/2}$ = 10 µs, the one of $SO_4^{-\bullet}$ is 30 ÷ 40 µs [15]. They are formed continuously in reaction (*in-situ*). So, when the reaction in a continuous form, it is necessary to add ZVI and PS to ensure the efficient decomposition of AZOs.

Conclusion

Summing up the results of the study on the composition of substances present in the system and comparing the decomposition efficiency of AZOs in the without UV and with UV systems draw the following conclusions: In the PS activation systems by ZVI without UV and with UV (ZVI/PS/AZOs and ZVI/PS/AZOs/UV) result in AZOs decomposition being far superior than other systems. This confirms that in these systems (ZVI/PS/AZOs, ZVI/PS/AZOs/UV), there are strong oxidizing agents with higher oxidation potential than PS (E^0= 2.1 V). They are free radicals $HO^{\bullet}$ (E^0= 2.6 V) and $SO_4^{-\bullet}$ (E^0= 2.8 V) are formed in-situ during activated PS by ZVI, UV. These free radicals are the key factors of improving the degradation efficiency of AZOs in the system. Thus, the results show that ZVI activated persulfate without and with UV has potential in treating organic compounds in water and applying in wastewater treatment technology.

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