

Removal of Textile Waste Dye Agent by Photodegradation Catalysed by Iron Oxide Intercalated Bentonite

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Abstract - Liquid textile waste contains noxious chemicals including dye agents that are notoriously hard to remove, putting them as potential aquatic pollutants. Photodegradation is theoretically capable of breaking these pollutants down into simpler-harmless molecules that are safe to discharge. Photodegradation requires photocatalyst to increase the rate. In this paper, iron oxide intercalated bentonite is reported to be used as the photocatalyst in the photodegradation of liquid textile waste containing blue dye. The photodegradation was conducted with UV light under optimized pH, irradiating duration, and photocatalyst mass. The samples were analyzed to determine the decreases in the dye absorbances, BOD, COD, and TOC by the photodegradation process. The results suggest that the photodegradation effectively remove the pollutants as shown by 84.34 + 1.2% decrease in the dye absorbance, 94.4 + 1.6% in BOD, 88.9 + 1.1% in COD, and 90.5 + 1.4% in TOC. Furthermore, both BOD and COD values of the degraded waste fulfil the maximum concentrations allowed by the Indonesian government guideline.

INTRODUCTION

Textile liquid waste contains many different chemicals including coloring compounds which can potentially pollute the aquatic environment if discarded untreated. Coloring compounds which are used in textile industries usually consists of chromophore and auxochrome and are stable [1] and non-biodegradable. When liquid waste containing these compounds is discharged into water catchment, they will mix with other chemicals and make it even harder to degrade due to its matrix complexity. Adsorption and sedimentation which are usually applied to treat them cannot effectively rid the pollutants [2,3]. Amongst other researchers, Vinuth et al [3] claimed that adsorption using Iron (III)-montmorillonite can rapidly remove dye agents from aqueous solution. While it might be true that the dye agents disappear from the aqueous solution, it does not remove the molecules. Instead, it only traps them in the adsorbent materials which, in turn, require further treatment. Photodegradation, on the other hand, can solve this pollution problem [1] since the persistent organic pollutants including dye compounds will be broken down into simpler and less toxic molecules.

Photodegradation mechanism is initiated by absorption of photon by the photocatalyst materials causing the excitation of electrons from the valence bands to the conduction bands, leaving positive holes in the valence bands. These electron deficient bands will attract electrons from water molecules or hydroxide ions in the suspension and produce hydroxyl radicals (and protons). Meanwhile, the excited electrons in the conduction bands react with the protons or peroxide if present, producing more radicals. These free radicals in turn react with the pollutants such as dye compounds resulting in smaller molecules such as carbon dioxide, water, and ammonia [4-9, 11-12]. Semiconductors widely used as the photocatalysts including titanium oxide and iron oxide. The latter is magnetic that can easily be separated from the suspension after used and recycled [5]. Unfortunately, the adsorption capacity of iron oxide is very low that when used as a photocatalyst the limited contact with the pollutant molecules reduces its catalysis ability. Scientists have been trying to modify the iron oxide using many different techniques including making composite with adsorbent materials. Adsorbent which is abundant, easily obtained at low cost, with high adsorption capacity, is ideal for this. Natural bentonite has been widely used due to its characteristics: large surface area, layered, and expandable [2-5, 7-11]. In this work, Iron oxide supported by bentonite was applied as photocatalyst in the photodegradation of textile dye liquid waste under UV light.

EXPERIMENTAL

2.1. Materials

The materials used in this study included commercial Na bentonite, liquid textile waste containing rhemazol brilliant blue (RBB), analytical grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AgNO_3 , NaOH , HCl from Sigma, demineralized water, and distilled water.

2.2. Apparatus.

Apart from the usual laboratory glass wares and equipment, we used irradiation boxes with UV lamp (259 nm), 106 μm sieves. The instruments were UV-Vis spectrophotometer, LIBS, SEM, and XRD.

2.3. Procedure

The experiment consists of three steps namely synthesis of the composite, optimization of the photodegradation conditions (pH, photocatalyst mass, and irradiation time), and photodegradation of the liquid waste. The synthesis of the photocatalyst was carried out as described in Suprihatin *et al* [13]. Likewise, the determination of the optimum pH and photocatalyst mass, but in this study liquid waste was used in place of Remazol brilliant blue solution. For the optimum irradiation time we used 2 hours as obtained in the previous work [13].

The degradation percentage was measured to determine the photodegradation capacity. The experiment was conducted as reported in [13] using 25 mL liquid waste under the optimum conditions. The parameters measured before and after photodegradation were the absorbances, BOD, COD, and TOC. The degradation percentage (D) was obtained by the following equation:

$$D (\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

Where, C_0 = the initial parameter measured (A, BOD, COD, or TOC)

C_t = the measured parameters after irradiation

RESULTS AND DISCUSSIONS

3.1. The insertion of Fe in the bentonite

LIBS spectra (Figure 3.1) show that Fe is detected in the composite (Fe-bentonite) in the forms of atomic Fe and Fe(III). This suggests that the synthesis has resulted the intercalation of iron in the bentonite. This fact is supported by the Xray diffractogram (Figure 3.2) and the EDX image (Figure 3.3). The diffraction of Fe_2O_3 is shown at 2θ 20.960° and 36.635° [11].

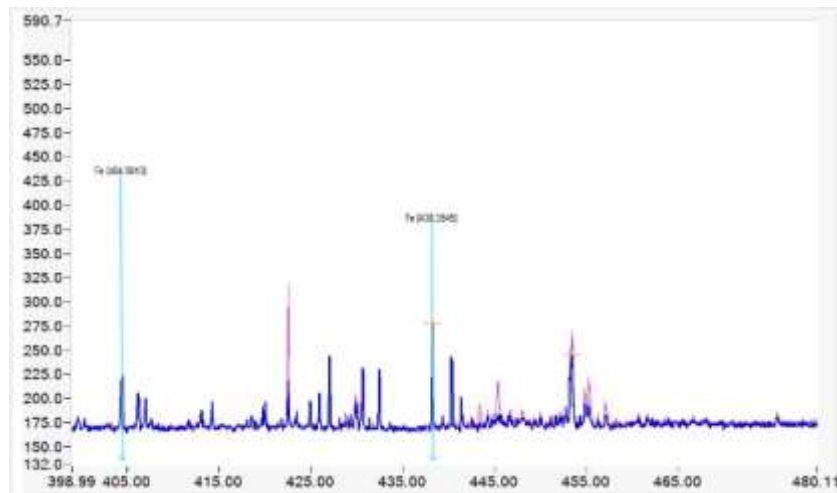


Figure 3.1. LIBS spectra of Fe-bentonite

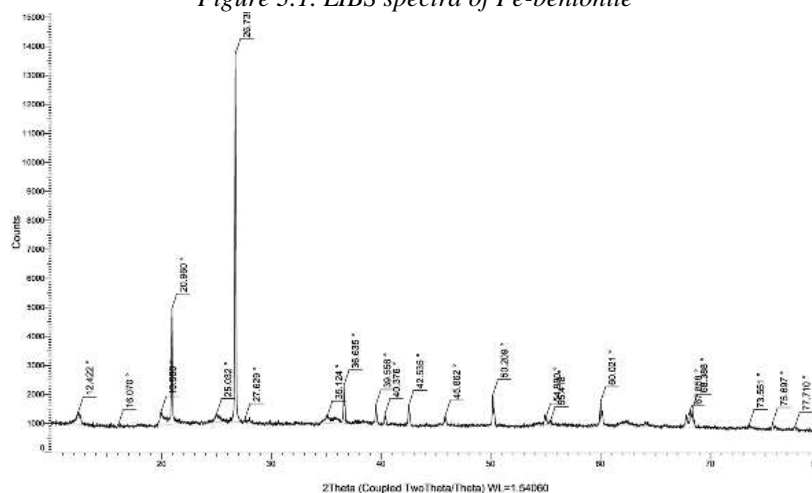


Figure 3.2. The Xray diffractogram of Fe-bentonite

The image in Figure 3.3 shows the Fe (purple) in the Fe-Bentonite composite which, as presented in Table 3.1, contributes 5.45% to the atomic surfacial contents of the Fe-bentonite.

Table 3.1. The atomic composition of Fe-bentonite analyzed using SEM-EDX

Element Name	Atomic Conc.(%)	Weight Conc.(%)
Oxygen	46.64	40.01
Carbon	32.75	21.09
Iron	5.45	16.33
Silicon	9.07	13.66
Aluminium	5.44	7.87
Potassium	0.26	0.55
Magnesium	0.39	0.50

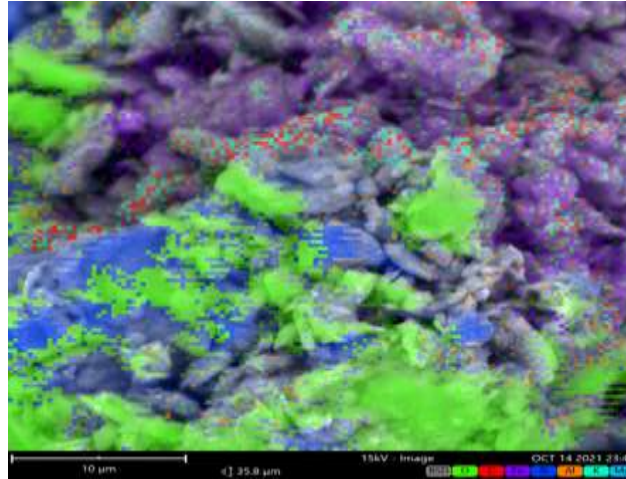


Figure 3.3. EDX image of Fe-bentonite. Iron is represented by the purple structures.

3.2. The optimum photocatalyst mass.

Figure 3.4 shows the degradation percentages of the dye waste at various mass of photocatalyst used. The data reveals that the optimum mass for the degradation of 25 mL liquid waste is 150 mg. This is slightly higher than the mass required by the aqueous solution of Remazol brilliant blue (RBB) [13]. This is reasonable because the liquid waste contains RBB and many different unknown pollutants. The complexity of the liquid waste matrix and its contents may have caused the extra mass required to degrade the waste.

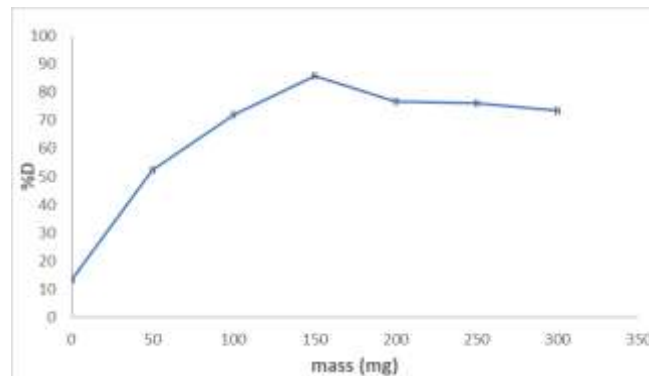


Figure 3.4. The degradation percentages at various photocatalyst masses

3.3. The optimum pH

As in the photodegradation of aqueous RBB solution, the optimum pH for the photodegradation of the liquid waste is shown to be 5 (Figure 3.5), which is good for the environment since it does not need so much alteration of the pH to be safely discarded. The high degradation percentages at pH 4 to 5 indicate that the bentonite has high adsorption capacity under the pH range, which was also reported by Hernandez *et al* [2]. The degradation in the acidic condition suggests that the photocatalysis occurs by the interaction of the H^+ with the O_2^{\bullet} resulted from the reaction between O_2 with the electrons in the conductance band [1,8]. The interaction produces OOH^{\bullet} which in turn reacts with the pollutants resulting in the degradation [1]

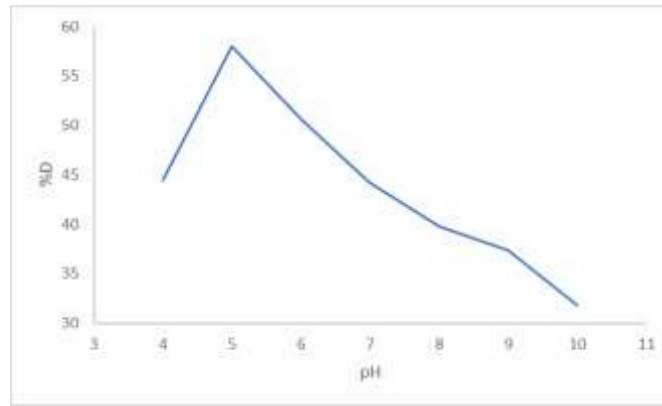


Figure 3.5. The degradation percentages with varied pH

3.4. The photodegradation effectiveness

Compared to the degradation of the aqueous RBB solution, the photodegradation of the liquid waste in this work resulted lower degradation percentages. Table 3.2 shows the differences between them, and between the catalysts used. Fe-Bentonite clearly shows higher capability than the unmodified bentonite, suggesting that the intercalation of Fe improves the capacity of the bentonite from merely adsorbent to photocatalyst.

The degradation of the pollutant molecules in the liquid waste is proven further by the decreases in BOD, COD, and TOC resulted by the photodegradation process. As known, these parameters indicate the organic and inorganic large compounds contents in a liquid sample. The more pollutants there are in the sample, the higher the values are. Furthermore, decreases in the parameter values suggest the reduction in the compounds concentrations due to their break down to smaller molecules that do not require further oxidation. The decreases in the parameter values are presented in Table 3.3.

Table 3.2. The comparison of degradation percentages of aqueous RBB and liquid waste

Photocat.	Degradation percentage (%)	
	liquid waste	RBB [13]
Bentonite	30.92 ± 2.51	46.52 ± 0.06
Fe-Bentonite	84.34 ± 1.2	98.20 ± 0.07

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Table 3.3. The degradation of pollutants indicated by the decreases in BOD, COD, and TOC

parameter	before degradation (mg/L)	after degradati-on (mg/L)	decrease (%)
BOD (Winkler)	824.22 ± 6	46.15 ± 0.6	94.4 ± 1.6
COD	1423.52 ± 11	160.28 ± 2	88.9 ± 1.1
TOC	2232.15 ± 16	211.52 ± 2	90.5 ± 1.4

As seen in the table, all three parameters investigated decrease significantly with the photodegradation process. This shows that the process did remove the compounds in the waste by degrading them into small molecules

CONCLUSION

The research has produced Fe-bentonite that is applicable as a photocatalyst with a high capability to assist photodegradation of pollutants including dye agent in liquid textile dyeing waste. Further investigation is required if the photocatalyst is to be applied in the photodegradation of liquid waste in a waste treatment process.

ACKNOWLEDGMENTS

We would like to express our gratitude to The Ministry of Education, Research, and Technology of The Republic of Indonesia for funding this and further research under the contract No. B/136-24/UN14.4.A/ PT.01.05/2021

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