染色廃水に対するフェントン様処理における触媒金属の影響

Fenton-like treatment for dyes degradation: Effect of metal catalyst

○Guntur Adisurya Ismail*, Hiroshi Sakai*
＊：東京都立大学　都市環境学部

論文要旨

染色廃水からの色度の除去は重要な問題であり、沈殿や生物処理などの従来の方法には課題がある。フェントン様処理は色度成分の分解に有効であることが示されているが、様々な染料に対して、その効果を比較した研究は乏しい。そこで本研究では、複数の染料に対して触媒の効果を比較した。その結果、硫酸ラジカルの方が OH ラジカルよりも色度の除去に対して効果的であること、また触媒金属を比較したところ、硫酸ラジカル分解系に説いて銅触媒を用いることが TOC 除去の観点で最適であることを見出した。

The removal of color from textile wastewater is a crucial issue, and traditional methods such as sedimentation and biological processes are not effective. Fenton-based processes have been shown to be effective in degrading color, but there is a lack of direct comparison between different Fenton-based processes on various textile dyes. Our results suggest that sulfate radical is generally more effective than hydroxyl-radical, and copper catalyst in sulfate system has the best performance in removing total organic carbon.

キーワード: Industrial waste water, color, advanced oxidation process.

１．Introduction

Fenton process for pollutant degradation has been investigated since 1876 and has further developed into various Fenton-based process and has seen actual implementation, and even considered the best technology to remove emerging pollutants [1]. Fenton-based processes also find its application in textile wastewater treatment. Textile wastewater usually contains high chemical oxygen demand (COD), total solids (TS), and more importantly, offensive color [2]. In actual textile wastewater treatment plant, removal of TS and COD can be done by employing sedimentation and biological process, respectively. However, those processes are not capable to remove color up to acceptable level. The issue become much more important with the inclusion of color as effluent standard, urging the needs of alternative process that could safely and efficiently degrade color [3]. Color removal is usually done via coagulation-flocculation, which take place after biological process. However, this process will produce high amount of sediment which requires further handling.

Possibilities of Fenton-based process application on textile color degradation have been studied extensively with mostly positive results [4]. However, research on the direct comparison of various Fenton-based process on different textile dyes is still uncommon. Moreover, comparison study on combination between various catalyst, radical agent in homogenous Fenton-based system is, as far as writer knows, not yet available. Thus, this research hoped to gives insight result and discussion on how different pairing of catalyst and radical agent could affect the degradation performance of textile dyes wastewater.

２．Material and Method

Synthetic textile dye (Direct Red 28/DR28) wastewater was prepared by adding 350 mg of dyes to 3.5 L of ultrapure water, which resulted in 100 mg/L dye concentrations, continuously agitated in a stainless-steel reservoir equipped with a 254 nm UV lamp. The pH of the solution was adjusted by using 1 M NaOH solution

or concentrated H_2SO_4. Combination of 10 mM of radical source and 0.5 mM of metal catalyst was added to the
system as per the variation shown in Figure 1. Samples were taken from the initial dye solution prior to chemical addition (0 minutes), and after 15, 30, 60 and 90 minutes. Portion of the samples were also filtered by 0.45 μm filter as comparison, and underwent similar analysis. Color degradation is quantified by measuring the reduction of absorbance after Fenton-based treatment with a spectrophotometer (Jasco V-670). Spectrum analysis between wavelength of 200 – 800 nm with 1 nm increment was done in order the measure the absorbance in each wavelength. Absorbance reduction for each dyes' respective maximum wavelength was identified to determine color reduction. Visual appearance (color, formed sediment) was noted for comparation between the samples. TOC concentration was analyzed by using TOC machine (Shimadzu TOC-VCSH).

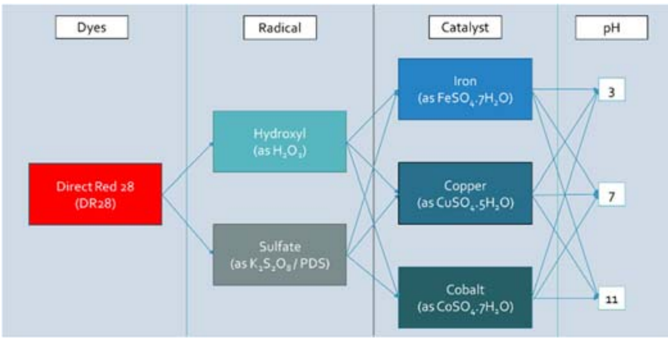


Figure 1. Experiment variation

3. Results and Discussion

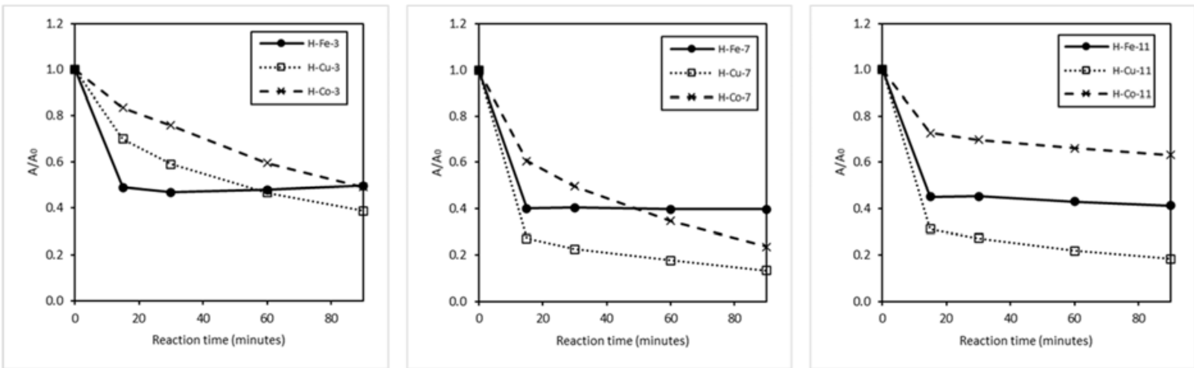
Dyes degradation mechanism in general can be described in 2 main steps: the breakdown of the chromophore, or the main skeleton of the dyes structure, followed by mineralization of degraded chromophore [5]. In most cases, fading color due to treatment was caused by the degradation of said chromophore into smaller compound, which is detected in the reduction of the absorbance at the dyes respective optimum wavelength. Afterwards, smaller compound produced by chromophore breakdown can be further deteriorated into compound with lowest energy level (carbon dioxide and water), known as mineralization process, which can be detected in the reduction in the concentration of total organic carbon (TOC) [6].

Color reduction and TOC reduction performance on DR28 can be observed in Figure 2 and 3, respectively. In general, sulfate radical shown better performance under any pH condition and catalyst pairing. In almost all cases, sulfate system could achieve >90% decolorization. On the other hand, hydroxyl-radical system exhibits lower decolorization performance than sulfate-radical system. Higher redox capabilities of sulfate radical compared to hydroxyl radical has already been established on many researches, mainly due to higher redox potential (2.5-3.1 V) than hydroxyl radical (1.8-2.7 V) [4]. Sulfate radical also has longer half-life than hydroxyl radical, improving the contact time between radical and pollutant [7].

TOC reduction result showing similar trend with decolorization result, albeit with lower value. Copper catalyst in sulfate system still exhibit the best performance in all pH situation, with >75% TOC removed, while maximum performance achieved in pH 11 with 85% TOC reduced. Iron and cobalt also shown better performance in sulfate system than hydroxyl. Performance on hydroxyl radical was mostly minimal. Noticeable removal only occurred on copper system at pH 7, with 53% TOC removed. Slight reduction also detected on cobalt at pH 7, as well as iron copper and cobalt at pH 3, with around 20% TOC content reduced. Only negligible reduction seen in the other cases.

It was noticeable that cobalt performed quite poorly in majority of the cases. Cobalt was actually considered to be prevail on sulfate radical generation from peroxymonosulfate (PMS), more than iron [8], [9], but it seems that such performance is not applicable on PDS. The case of performance of iron vs copper is interesting to note. Plateauing performance of iron has always been imminent in many cases, often attributed to the non-thermodynamically favorable of catalyst regeneration ($Fe^{3+} \rightarrow Fe^{2+}$, E = -0.724 V) that leads to lower catalyst available to activate the radical source [10]. However, this situation should be fixed by adding UV lamp that provides the energy required to regenerate spent catalyst. Things that is rarely mentioned is, however, the tendency of iron to form complex with dyes compound and the side product of dyes degradation process in a reaction known as mordanting [11]. This reaction cause sediment to form in the solution and makes mineralization failed to occur.

All in all, sulfate radical exhibit satisfying performance and could be potential to replace hydroxyl radical as currently readily applicable Fenton-based system. Copper as iron alternative is also exhibit good possibilities due to the natural limitation exist in the iron.



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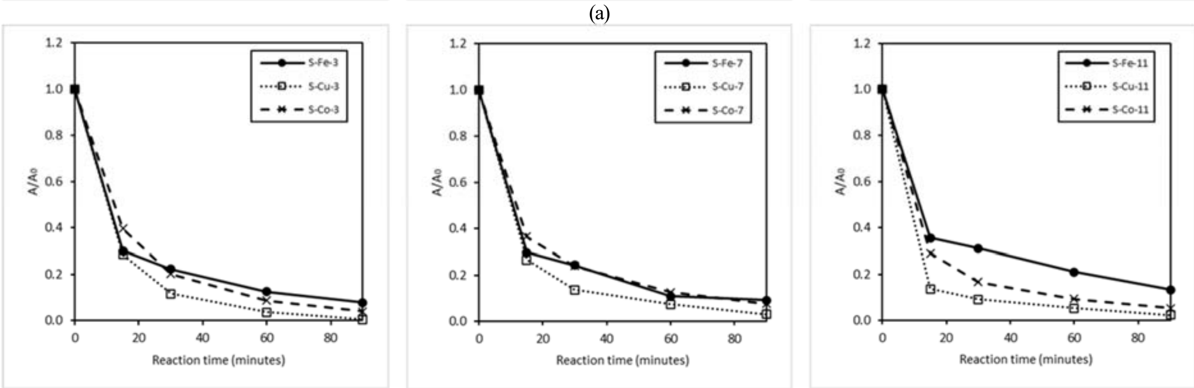
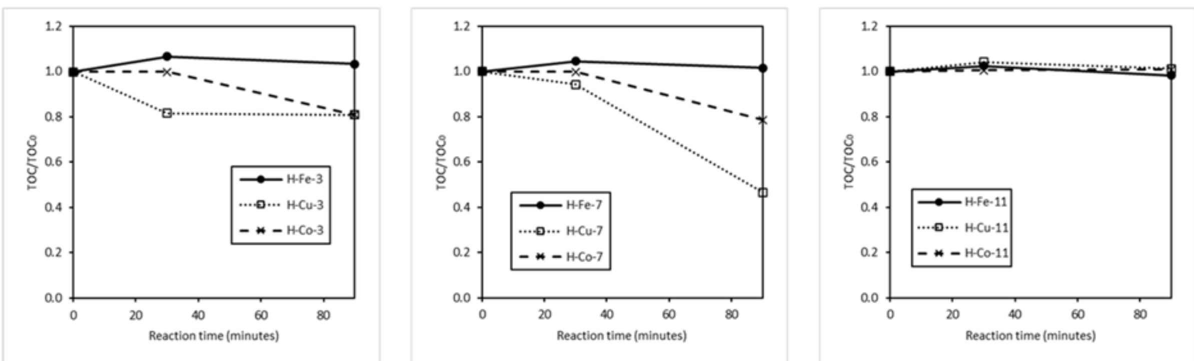


(b)

Figure 3. DR28 decolorization with (a) hydroxyl radical and (b) sulfate radical under different catalyst and initial pH



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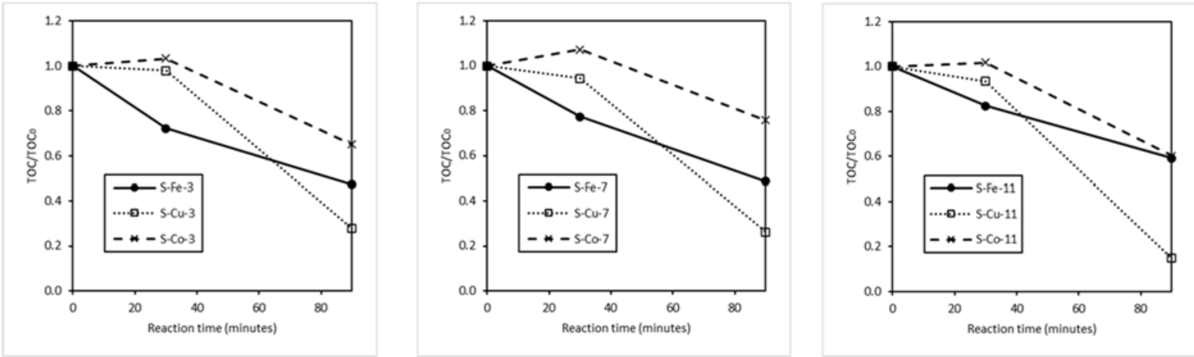

(b)

Figure 4. TOC reduction on DR28 in (a) hydroxyl and (b) sulfate radical system with different initial pH and catalyst

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