



Characterization of refractory matters in dyeing wastewater during a full-scale Fenton process following pure-oxygen activated sludge treatment



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HIGHLIGHTS

- In-depth analysis/characterization of refractory compounds present in dyeing wastewater.
- Dyeing WWTP (world's biggest in terms of daily treatment capacity) currently employs biological process followed by Fenton oxidation.
- Pure-oxygen A/S treatment removed 53% of SCOD and 13% of color.
- Fenton process removed 66% of SCOD and 73% of color.
- Overall performance of the current hybrid technology was moderate and warrants further improvement.

ARTICLE INFO

Article history:

Received 18 September 2014

Received in revised form 20 January 2015

Accepted 21 January 2015

Available online 24 January 2015

Keywords:

Color removal

Dyeing wastewater

Electrospray ionization-mass spectrometry

Fenton process

Molecular weight cut-off (MWCO)

ABSTRACT

Refractory pollutants in raw and treated dyeing wastewaters were characterized using fractional molecular weight cut-off, Ultraviolet–vis spectrophotometry, and high-performance liquid chromatography–electrospray ionization–mass spectrometry (HPLC–ESI/MS). Significant organics and color compounds remained after biological (pure-oxygen activated sludge) and chemical (Fenton) treatments at a dyeing wastewater treatment plant (flow rate ~100,000 m³/d). HPLC–ESI/MS analysis revealed that some organic compounds disappeared after the biological treatment but reappeared after the chemical oxidation process, and some of that were originally absent in the raw dyeing wastewater was formed after the biological or chemical treatment. It appeared that the Fenton process merely impaired the color-imparting bonds in the dye materials instead of completely degrading them. Nevertheless, this process did significantly reduce the soluble chemical oxygen demand (SCOD, 66%) and color (73%) remaining after initial biological treatment which reduced SCOD by 53% and color by 13% in raw wastewater. Biological treatment decreased the degradable compounds substantially, in such a way that the following Fenton process could effectively remove recalcitrant compounds, making the overall hybrid system more economical. In addition, ferric ion inherent to the Fenton reaction effectively coagulated particulate matters not removed via biological and chemical oxidation.

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1. Introduction

Textile wastewater contains many refractory organics such as surfactants, dyes, resins, synthetic sizing compounds (e.g.,

polyvinyl alcohol), chlorinated organics, and carrier organic solvents [1]. Synthetic dyes have replaced natural ones in the textile industry, in part because of their superior qualities such as high stability against chemical/biological degradation, which also makes dyeing wastewater difficult to treat. Such dyes include acidic, basic, disperse, azo, diazo, anthraquinone-based, and metal complexed agents.

The release of dyes into water bodies is known to reduce the photosynthesis rate of aquatic plants [2], and some dyes and their degradation products are mutagenic and carcinogenic, posing a

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threat to human and animal health [3]. As a result, the development of technologies to remove dyes has gained considerable attention and has been the subject of substantial recent academic researches.

Dyeing wastewater is commonly treated by physicochemical treatment processes including adsorption [4], flocculation combined with flotation [5], electroflotation/electrocoagulation [6], chemical coagulation and flocculation [7], membrane filtration [8], ozonation [9], photochemical oxidation [10,11], and Fenton oxidation [12]. The physicochemical methods are considered more expensive than biological treatment technologies, but the latter are usually less efficient in removing color materials and other refractory compounds [13,14]. Considering both cost-effectiveness and treatment efficiency, a combination of both types of technologies, for example, biological treatment followed by an advanced oxidation process, or vice versa, could be a feasible option to treat dyeing wastewater [15–17], since the two technologies can work synergistically. The characterization of dyeing wastewater before and after each treatment is an important tool for evaluating the performance of hybrid technologies.

Many studies on the decolorization/degradation of dyes have been performed previously [1,3,11,12,14], most of which were carried out in batch modes using synthetic dye solutions. Some studies developed hybrid technologies to degrade dyes in synthetic wastewater at bench- [18,19] and pilot- [20] scale. There have been studies that employed real dye wastewater [21,22], but mostly at smaller scales. To the best of our knowledge, there has been no previous research dealing with the characterization of real dyeing wastewater and the application of full-scale hybrid technology to remove organic compounds and color.

Therefore, the current study aimed to investigate the characteristics of refractory compounds present in real textile wastewater (flow rate, $\sim 100,000 \text{ m}^3/\text{d}$) generated from 61 dyeing factories and how these compounds, including organics and colorants, were transformed and removed by a hybrid technology combining biological and chemical treatment. The chemical treatment adopted was Fenton oxidation via reaction with H_2O_2 and Fe^{2+} , with ferric ion (Fe^{3+}) produced from the Fenton reaction promoting coagulation. The whole treatment process, therefore, was a combination of biological treatment (advanced oxidation) and chemical coagulation in series. The fractional molecular weight distribution of organics and colorants was investigated via ultrafiltration. UV/vis spectrophotometry, high performance liquid chromatography with electrospray ionization (HPLC–ESI/MS), and gas chromatography–mass spectrometry (GC–MS) were used to characterize the refractory pollutants present in raw dyeing wastewater and the effluents from biological/chemical treatment.

2. Materials and methods

2.1. Dyeing wastewater and treatment processes

The wastewater discharged from the Banwol dyeing industrial complex (composed of 61 dyeing factories) was treated at a dyeing wastewater pre-treatment plant (design treatment capacity, $100,000 \text{ m}^3/\text{day}$) in Ansan, Korea. The wastewater had very complex characteristics because it was generated from various types of dyeing processes, but had the following qualitative characteristics: influent pH, 10–12; influent water temperature, approximately 40°C ; influent total chemical oxygen demand (TCOD), approximately 1150 mg/L ; influent soluble COD (SCOD), approximately 1100 mg/L ; and influent color, approximately 1180ADMI units, on average [23].

The dyeing wastewater first entered the treatment plant through the collection pipelines. After removal of suspended matter by screening and primary settling, the wastewater was

neutralized and then transferred to an equalization tank. The equalized raw wastewater was first treated in the pure-oxygen activated sludge (A/S) tank [hydraulic retention time (HRT), 6 h] to reduce degradable compounds and consequently enhance chemical treatment efficiency, and then in the Fenton oxidation unit (HRT, 30 min), which was operated at pH 3.5. For Fenton reaction, H_2O_2 (4.0 mM) was injected twice (30% at 12 min and 70% at 16 min), while $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (4.2 mM) was added once to the influent and mixed rapidly for 30 min. Hydrogen peroxide disappeared within a few minutes, while ferrous ion was oxidized gradually over 20 min, indicating that there was an additional source of electron acceptor (e.g., ambient oxygen) for ferrous ion oxidation [24]. The Fenton-oxidation effluent was mixed slowly and coagulated for 15 min at pH 5.8–6.0 with the ferric ion produced from the Fenton reaction, followed by final clarification and discharge to a public sewer flowing into a regional municipal wastewater treatment plant. In this study, we defined the ‘Fenton process’ as a combination of Fenton oxidation and subsequent coagulation by oxidized ferric ion.

According to Arslan-Alaton et al. [25], the advanced oxidation of organic compounds is rapid when the Fe^{2+} concentration varies between 2 and 5 mM. In the current study, the Fe^{2+} concentration was pre-investigated in the range of 1–5 mM at 30°C , similar to the temperature of the Fenton reactor at the plant, from which the highest color removal was obtained at 4.2 mM. Then, the optimal dose of hydrogen peroxide was investigated between 1 and 10 mM, while Fe^{2+} dose (4.2 mM) and temperature (30°C) were kept constant. Greatest color removal was obtained at $4.0 \text{ mM H}_2\text{O}_2$ and further increase caused no significant change in color degradation. Therefore, the adopted average doses of H_2O_2 and Fe^{2+} were 4.0 and 4.2 mM, respectively, for Fenton oxidation.

2.2. Determination of characteristics of refractory compounds

2.2.1. Ultrafiltration

All aqueous samples (raw wastewater, biological treatment effluent, and Fenton oxidation effluent) were first fractionated by serial vacuum filtration of 200 mL of sample through 1.2- and $0.45\text{-}\mu\text{m}$ nominal pore sized, mixed cellulose ester membrane filters (Millipore, MA, USA), followed by serial ultrafiltration through 100,000-, 30,000-, 10,000-, 3000-, 1000-, and 500-Da nominal molecular weight cut-off (MWCO) filters (YM and YC series; Millipore). Ultrafiltration was conducted in 200-mL stirred cells (Amicon; Model 8200) using He at 345 kPa, and the ultrafiltration membranes were pre-conditioned according to the manufacturer’s instructions, stored face-down in distilled water containing 10% ethanol, and discarded after 10 cycles. Two hundred milliliters of distilled water were passed through the membrane before the experiment. For each sample collected during the serial filtrations, 20-mL aliquots were analyzed for COD and color.

2.2.2. High performance liquid chromatography with electrospray ionization (HPLC–ESI/MS) analysis

HPLC–ESI/MS was used to analyze molecules of various polarities according to their mass per charge (m/z) characteristics. To avoid suppression of ionization as a result of matrix interference, a fast high performance liquid chromatography (HPLC) was applied prior to MS analysis to separate non-volatile compounds from the sample [26].

Since the chemical composition of dyeing wastewater was unknown and complex (generated from 61 dyeing factories), it was difficult to apply the extraction methods reported in the literature to improve the accuracy of analysis. In this study, apolar solvent (*n*-hexane) was used to separate apolar and polar compounds from dyeing wastewater. Both organic and aqueous layers were analyzed by HPLC/MSD, and analytical conditions such as mobile phase, flow rate, and detection wavelength were optimized by trials and errors.

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