

Tourmaline activated persulfate for degradation of Sirius Türkis GL 01

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Abstract The high Fe^{2+} content of tourmaline (TM) has potential of activating a persulfate reaction. However, information pertaining to using TM as an activator in persulfate oxidation process is currently unavailable. In this study, powdered TM was used to activate persulfate (PS) oxidation for decolorization synthetic direct azo dye, Sirius Türkis GL 01 (STGL). Findings revealed that decolorization was significantly enhanced by TM/PS combined with ultrasound. A suitable oxidation condition for removal true color was TM 1.5 g/L, PS 5×10^{-4} M, US 106 W/cm² (20 min sonication at 20 kHz), and initial pH 6.0, which could completely remove the color and COD of 40 mg/L STGL after 20 min treatment. Oxidation condition under higher TM dosage with higher sonication power is beneficial for generation of sulfate radicals, consequently, promoting the oxidation performance of TM/PS process. Results clearly indicated that Fe-tourmaline, can be potentially used to activate PS oxidation for effective decolorization of wastewater containing direct azo dyes.

Keywords Tourmaline · Persulfate oxidation · Direct azo dye · Ultrasound · Decolorization

1 Introduction

Although persulfate ($\text{S}_2\text{O}_8^{2-}$) itself is considered as a strong oxidant ($E^0 = 2.01$ V), it can only oxidize specific organic contaminants. PS when it is activated to sulfate radicals ($\text{SO}_4^{\cdot-}$), which have relatively high oxidation power ($E^0 = 2.60$ V). As such, they are capable of non-selectively oxidize recalcitrant organic compounds. $\text{SO}_4^{\cdot-}$ radicals can be generated via activation of PS using transition metals (Me^{n+}), base, ultraviolet light, heat, and ultrasound (US) (Darsinou et al. 2015; Gao et al. 2017; Liu et al. 2016a, b). Fe is commonly used to activate PS due mainly to its environmental safe and low cost. Although ferrous iron (Fe^{2+}) salts provides Fe^{2+} ions directly for PS activation, Fe^{2+} can scavenge $\text{SO}_4^{\cdot-}$ at a rate higher than its generation (Li et al. 2014). Thus, a well-controlled supply of Fe^{2+} is necessary in a Fe^{2+} -activated PS. Recently, there has been increasing attention to study Fe^0 -activated PS for contaminant removal (Li et al. 2014; Liu et al. 2016a, b; Weng and Tsai 2016). Compared with Fe^{2+} salts, Fe^0 can trigger a series of reactions (Li et al. 2014) enabling a continuous generation of $\text{SO}_4^{\cdot-}$ radicals. However, the high cost and difficulties in handling have prevented nanosized Fe^0 from practical application in PS process (Liu et al. 2016a, b). Other Fe^0 -based activator, such as Fe^0 aggregates have been successfully applied in the activation of PS for dye degradation (Liu et al. 2016a; Weng and Tsai 2016). Tourmaline (TM) are widely available distributed in metamorphic formations and commonly occurs as Fe tourmaline (schorl), Mg tourmaline (dravite), and alkali tourmaline depending on the relative abundance of elements in TM (Harraz and EL-Sharkawy 2001). Because of the possession of unique properties, such as the emission of far infrared rays and the occurrence of an electric field, tourmalines has been applied to enhance the performance

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of a photocatalytic decontamination process (Yu et al. 2016). The high electric fields on the surface of tourmaline particles promotes enhance electrostatic interactions during adsorption (Liu et al. 2016b). The presence of Fe^{2+} in Fe-bearing tourmaline has great potentials for application in PS activation. The electric field on the surface of tourmaline may induce Fe^{3+} ions to Fe^{2+} ions, and therefore promote the production of $\text{SO}_4^{\cdot -}$ radicals. However, information pertaining to using TM as an activator in persulfate oxidation process is currently unavailable. In this study, a direct azo dye, Sirius® Turkis GL01 (STGL), a widely used dye in textile processing industries for coloring cellulose-based fibers, was selected as target compound to evaluate the decolorization efficiency using tourmaline activation PS. Findings from this study provide valuable information on the applicability of this natural Fe-mineral for the treatment of dye-laden wastewaters.

2 Materials and methods

Powdered TM with a particle size smaller than 0.074 mm was purchased from the Inner Mongolia Embellish Lung Chemical Co., China. The TM as purchased was used without pretreatment. Crystal phase confirmation of the tourmaline powder was previously determined to have a chemical formula of $\text{Na}(\text{Fe}^{2+}, \text{Fe}^{3+})_3\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_4$ and is classified as schorl (Liu et al. 2016a, b). Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, PS) was purchased from Nippon Shiyaku (Japan). All other reagents were analytical grade. Synthetic STGL (direct blue 86, C.I. 74180, $\text{C}_{32}\text{H}_{14}\text{CuN}_8\text{Na}_2\text{O}_6\text{S}_2$) was obtained from DyStar (Germany). A UV-visible spectrophotometer (Thermo Scientific Evolution 201, USA) was used to quantify the concentration of STGL at a wavelength of 618 nm. A calibration curve was established to correlate measured absorbance with the concentration of STGL. The concentration of ferrous iron (Fe^{2+}) in the solution was analyzed by measuring absorption at 510 nm using Hach FerroVer® iron reagent (Hach Co., Loveland, USA). Chemical oxygen demand (COD) was determined by Hach Method 8000 reactor digestion method with a Hach DR/3900 spectrophotometer, which was approved for wastewater analyses (Standard Method 5220D) (American Public Health Association 2012). All reagents were prepared at an ambient temperature of $25 \pm 2^\circ\text{C}$ using distilled water. Unless otherwise stated, the experimental procedures were as follows: The pH of the dye solution (1 L) was adjusted to a predetermined value using 0.01 M HCl/NaOH. Before conducting experiment, specific dosages of TM and PS were added to the solution while agitating the solution with a mechanical stirrer (Shin-Kwang, Taiwan) at 800 rpm for 30 min. At selected time intervals, 10-mL of the solution was taken

from the reactor and filtered immediately through a 0.45 μm membrane filter (Advantec, Japan) to collect the supernatant. Based on the results of the control experiments, the filter did not adsorb the dye. The residual dye in the supernatant was determined as described aforementioned. In the experiments of PS coupled with US, the dye solution was sonicated by an ultrasonic generator (S-450A, Branson, USA) equipped with a titanium horn transducer. The sonication was administered in pulses with a 60% duty cycle at 20 kHz and an US intensity of 106 W/cm² for 20 min. Detail experimental setup and procedure were the same as described in Weng and Tsai (2016). Each decolorization experiment was conducted triplicate, and an average value was used in analysis. The rate of STGL decolorization was analyzed with pseudo-second-order (PSO) kinetic equation:

$$C_t = 1/(k_{\text{obs}}^2 t + 1/C_0) \quad (1)$$

where k_{obs}^2 is the observed second-order rate constant (L/mg-min).

3 Results and discussion

3.1 Comparison between different decolorization processes

A comparison of different reaction systems was made to identify the effectiveness of TM activated PS reaction for STGL decolorization (Fig. 1a). Despite PS has high oxidation potential, the degradation of STGL was merely negligible in the PS-only system. Application of ultrasound in the PS system (PS/US) did progressively degrade STGL because ultrasound can activate PS to generate $\text{SO}_4^{\cdot -}$ radicals (Eq. 2).



In the TM-only system, only fairly amount of color was removed, indicating that adsorption reaction was insignificant in the decolorization. Compared with the aforesaid processes, TM activated PS (TM/PS) could reach a 56% decolorization efficiency within 30 min with only 0.4 g/L TM. In TM/PS system, the introducing of $\text{S}_2\text{O}_8^{2-}$ decreased the solution pH significantly from 6.52 to around 3.0 (Fig. 1b) due to the hydrolysis of persulfate (Eq. 3).



At such low pH, Fe^{2+} released (Fig. 1c) from TM facilitated PS decomposition to generate $\text{SO}_4^{\cdot -}$ radicals (Eq. 4) for STGL degradation.



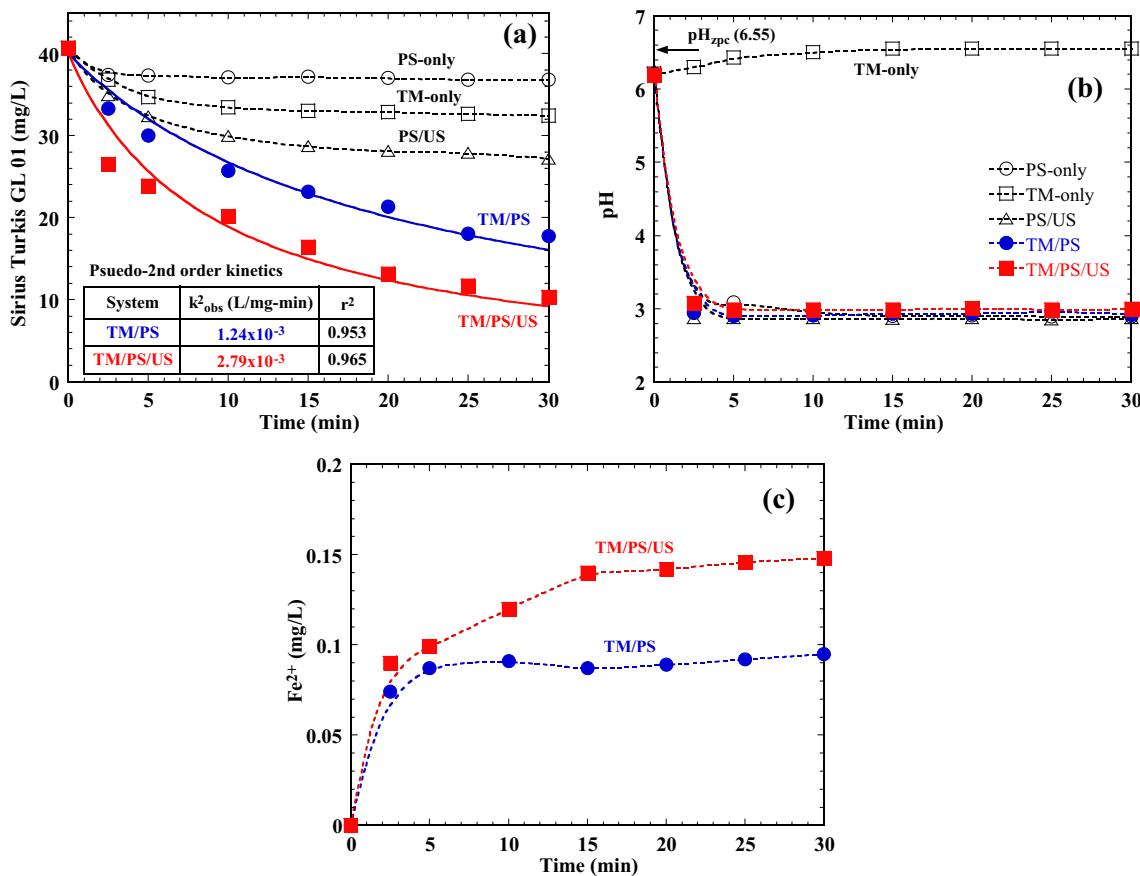


Fig. 1 Comparison different persulfate processes for decolorization of STGL. Condition: initial pH 6.2, TM 0.4 g/L, PS 5×10^{-4} mol/L, 25 °C, US intensity 106 W/cm² for 20 min

3.2 Effects of TM dosage

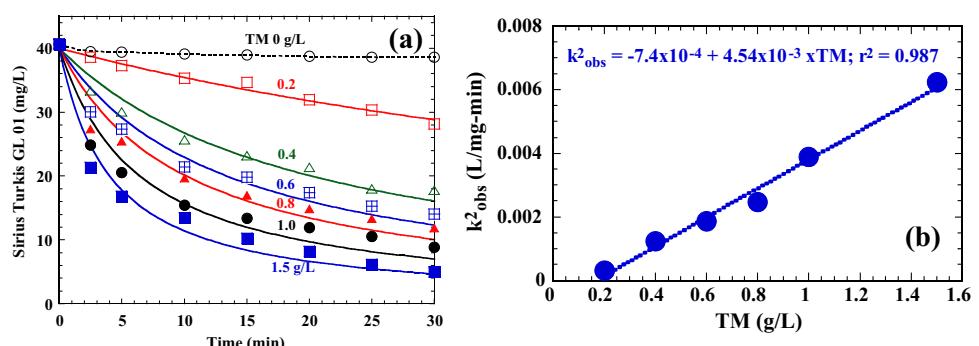
Figure 2a shows that a short supply of TM led to unsatisfactory decolorization. However, the system achieved a satisfactory decolorization efficiency (90%) within 30 min using a TM dosage of 1.5 g/L. In general, the decolorization efficiency in TM/PS system is directly proportional to the TM dosage. The data of decolorization under different TM dosages well-fitted by a PSO kinetics model with a linear relationship being retained (Fig. 2b). The system with higher TM dosages resulted in producing a

greater amount of Fe^{2+} ions, which in turn generate more $\text{SO}_4^{\cdot -}$ radicals for oxidizing STGL.

3.3 Effect of US power intensity

US irradiation is capable of enhancing oxidative degradation of organic contaminants in Fenton's and persulfate systems (Darsinou et al. 2015; Weng and Tsai 2016; Weng and Huang 2015). In theory the generating of turbulences around the solid-liquid interface in an US irradiation system promotes mass transfer and reaction rate. In addition,

Fig. 2 Effect of TM dosage on depletion of STGL by TM/PS process. Condition: initial pH 6.2, PS 5×10^{-4} mol/L, 25 °C. Solid lines are the best fits of pseudo-second-order kinetics



the cavitation bubbles induced by the irradiation also provides a continuous cleaning mechanism on the solid surface (Cai et al. 2015). Moreover, the sonolysis of PS in solution also generates $\text{SO}_4^{\cdot-}$ radicals (Eq. 2). Therefore, US can be used as an enhancement tool for oxidative degradation of STGL. Nevertheless, it is necessary to optimize the irradiation power for energy efficiency because of the consumption of energy during a irradiation

period (Liu et al. 2016a, b). Figure 3 shows the system efficiency of TM/PS increases with increasing the US power intensity. PSO rate constant increased from 6.24×10^{-3} to $3.82 \times 10^{-2} \text{ L/mg-min}$ as US power intensity raised from 0 to 124 W/cm^2 (inset table in Fig. 3). Since increasing the power intensity up to 124 W/cm^2 did not improve the decolorization efficiency further, an optimal dose of US power intensity for achieving satisfactory decolorization was 106 W/cm^2 .

3.4 UV-visible spectra and formation of intermediates during reaction

To relate the changes in chemical structure of STGL and color depletion during the treatment of TM/PS and TM/PS/US processes, the changes of UV-visible spectra, color, and COD were measured (Fig. 4). Before oxidation, one main absorption peaks at 618 nm in the visible region was observed, corresponding to the chromophores of STGL dye. A narrow absorbance peak at 330 nm in the ultraviolet region was associated with naphthalene ring and benzene ring in dye molecules. After the oxidation, the characteristic peaks in both visible and ultraviolet regions gradually reduced to minimum within 30 min (Fig. 4a), indicating that the $-\text{N}=\text{N}-$ links were broken down by TM/PS oxidation. In particular, when TM/PS assisted with ultrasound, the chromophores of STGL disappeared within 15 min (Fig. 4b) and the color became transparent (inset

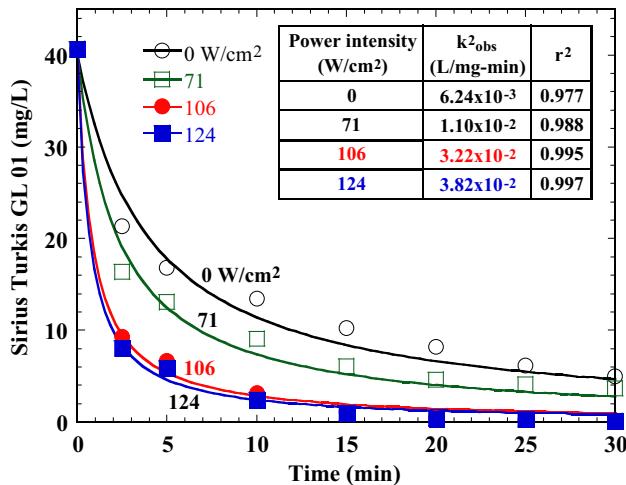


Fig. 3 Effect of US power intensity on depletion of STGL by TM/PS process. Condition: Initial pH 6.2, TM 1.5 g/L, PS 5×10^{-4} mol/L, 25°C , US intensity 106 W/cm^2 for 20 min. Solid lines are the best fits of pseudo-second-order kinetics

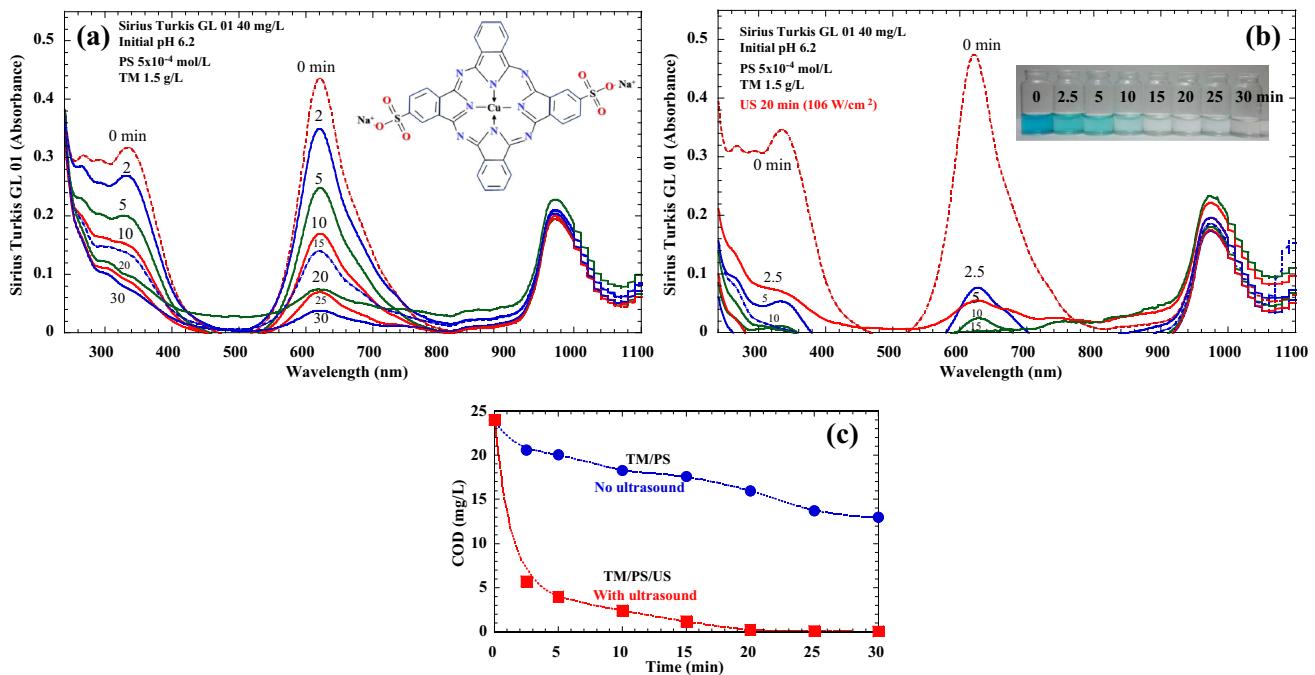


Fig. 4 UV-vis spectra of STGL depletion during the treatment of **a** TM/PS and **b** TM/PS/US. Conditions: initial pH 6.2, TM 1.5 g/L, PS 5×10^{-4} mol/L, 25°C , US intensity 106 W/cm^2 for 20 min in TM/PS/US

graph in Fig. 4b). Figure 4c shows the degradation of COD in the TM/PS and TM/PS/US. In TM/PM system, only 40% of COD was removed within 30 min even though the color was nearly disappeared. The residual COD was mainly associated to the formation of intermediates of STGL, such as benzene, phenol, and carboxylic acids. In the TM/PS/US, completely COD removal was observed, indicating all STGL in this process was completely oxidized into low molecular weight organic compounds including organic acids and carbon dioxide. This implies that the TM/PS process in conjunction with ultrasound enabled macro-molecular organic compounds of STGL oxidizing to smaller organic compounds and ultimately mineralization.

4 Conclusions

The high Fe^{2+} content of Fe-tourmaline can be used to activate persulfate for the degradation of STGL direct azo dye. Decolorization efficiency of the TM/PS/ Fe^0 system is highly dependent on the dosage of TM and US power intensity, and all data follow a pseudo-second-order kinetics. The US irradiation provides an enhancement tool in TM/PS system for degradation of STGL, particularly the destruction of chromophore structures of STGL molecules, the removal of COD, and mineralization. Tourmaline is an effective PS activator and is abundantly available. Therefore, it can potentially apply in treating dye laden wastewaters.

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Compliance with ethical standards

Conflict of interest The author declare that he has no conflict of interest.

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