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Methylene blue discoloration by heated persulfate in aqueous solution

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HIGHLIGHTS

- ▶ Methylene blue (MB) can be easily degraded in thermally activated persulfate systems.
- ▶ Activation temperature and reagent loads greatly affect the discoloration kinetics.
- ▶ MB degradation follows pseudo-first order kinetics under specific conditions.
- ▶ Sulfate and hydroxyl radicals are responsible of MB oxidation.
- ▶ Solid phase MB can be degraded without prior dissolution.

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ABSTRACT

Advanced oxidation process based on thermally activated sodium persulfate (SPS) is used in this work to degrade methylene blue (MB). The impact of temperature (30–70 °C), MB concentration (15.6–311.8 μM), SPS load (1–100 mM) as well as phosphate buffer (PB) capacity were characterized in short term (1–2 h) and long term (1–2 weeks) experiments. Results showed complete MB discoloration under tested conditions. The observed degradation rates (k_{obs}) from the pseudo-first order kinetics model changed upon concentration of MB and were found closely dependent on the $[SPS]_0/[MB]_0$ ratio. An acceptable Arrhenius behaviour was noticed for solutions of $[SPS]_0/[MB]_0 \geqslant 32$ in which SPS is in excess. Upon addition of SPS to MB at room temperature, the solution turned purple due to the formation of a non-stable flocky precipitate. However, spectral analysis showed complete disappearance of MB and its derivative precipitate after heat as well. The HPLC/MS analysis indicated the formation of non-stable transformation products identified as sulfonic acid and hydroxylated MB derivatives via $SO_4^{-\cdot}$ and $HO^{\cdot}$ oxidation. Those disappeared totally by the end of the treatment making from thermally activated SPS an excellent choice for the treatment of industrial effluents of the dyes industry even at room temperature.

1. Introduction

Some low biodegradable compounds are very difficult to remove from aqueous solutions [1–5]. These compounds typically result from industrial processes and are quantitatively present in resulting wastewaters. Their quantitative removal from these effluents is a challenge to the scientific community. A common approach to mitigate the environmental and health impact of recalcitrant organic compounds is to destroy them by an oxidation or a reduction reaction (redox process) in order to ease their biodegradability [6–12]. In recent years; oxidation by heated persulfate has been discussed within the literature as an efficient and affordable process [13–20]. Because of its very moderate cost (930 $/ton) and its high redox potential ($E^0 = 2.7$ V/SHE), sodium persulfate (SPS) has recently attracted the attention of the scientific community and started to be one of the best oxidant used to degrade organic contaminants. However, SPS cannot be reactive without being activated. Its activation into powerful sulfate radicals $SO_4^{-\cdot}$ can occur via chemical (Eq. (1)) or thermal (Eq. (2)) processes. Only thermal activation will be considered for this study.

1. Chemical activation (Eq. (1))

$$S_2O_8^{2-} + Fe^{2+} \xrightarrow{\text{Chemical-activation}} SO_4^{2-} + SO_4^{-\cdot} + Fe^{3+} \qquad (1)$$

2. Thermal activation (Eq. (2))

$$S_2O_8^{2-} \xrightarrow{\text{Thermal-activation}} 2SO_4^{-\cdot} \quad (30\,^{\circ}C < T < 99\,^{\circ}C) \qquad (2)$$

An intrinsic short coming of oxidation by heated persulfate is the necessity of an energy consuming thermal bed (30–99 °C). Accordingly, it is of practical importance to find out the optional operational parameters for the oxidation of each compound or class of compounds. A survey of published data regarding oxidation by heated persulfate suggests that the transferability of

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