



Efficient degradation of selected polluting dyes using the tetrahydroxoargentate ion, $\text{Ag}(\text{OH})_4^-$, in alkaline media



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HIGHLIGHTS

- We applied the reported tetrahydroxoargentate ion $\text{Ag}(\text{OH})_4^-$ for oxidation of surrogate organic recalcitrant dyes, by indirect redox oxidation.
- Through UV-Vis and chromatography techniques, we showed the possibility to degrade recalcitrant compounds such as fluorescein and rhodamine.
- Possible mechanisms of this indirect oxidation dye process using $\text{Ag}(\text{OH})_4^-$ are suggested.

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ABSTRACT

The use of soluble and highly oxidizing $\text{Ag}(\text{III})$ in the form of the tetrahydroxoargentate ion $\text{Ag}(\text{OH})_4^-$ is reported for the oxidation of surrogate organic recalcitrant dyes (i.e., rhodamine 6G (Rh6G) and fluorescein (Fl)). The possible use of $\text{Ag}(\text{OH})_4^-$ for the treatment of these and other refractory compounds is assessed. Such dyes were selected due to their common occurrence, stability, refractory nature, the relatively high toxicity of Rh6G, and their structural similarity to Fl. Several reaction intermediates/products were identified. The results showed that the highly oxidizing tetrahydroxoargentate anion was capable of degrading these recalcitrant dyes. Furthermore, the final degradation products do not represent a higher environmental risk than the original surrogates themselves. In addition, the partial mineralization of the dyes was proven.

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1. Introduction

Textile industries often release large volumes of problematic wastewaters associated with intense coloration and adverse effects on human health (Farida et al., 2009). More than 10^5 dyes are available today; the industrial use of these dyes generates over 7×10^5 tons of dyes in wastewaters worldwide (Wu and Jane, 2003), particularly from the textile, paper, food, cosmetic, and pharmaceutical industries (Natarajan et al., 2011). Their elimination

has prompted the use of new technologies. The most common physicochemical remediation methods include membrane filtration, coagulation, flocculation, oxidation and photoprocesses (such as UV, Fenton, H_2O_2 and O_3 oxidation), and adsorption (Farida et al., 2009; Natarajan et al., 2011; Yu et al., 2009; Peralta et al., 2008; He et al., 2009a,b; Li et al., 2007). Ozonation is particularly suited for this undertaking, but it is expensive. Membrane filtration, coagulation, flocculation and adsorption can remove color, but they are typically associated with bulky sludge production and intense requirements for added chemicals.

The photocatalytic approach using UV-irradiated semiconductor suspensions offers high chemical stability, high catalytic activity, and relatively low toxicity and cost (Natarajan et al., 2011; Yu et al.,

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2009; He et al., 2009a,b; Li et al., 2007). Unfortunately, most photocatalysts are active only in the UV region (Li et al., 2007). NaBiO_3 , Bi_2WO_6 , and Bi_2O_6 extend the usable sunlight wavelength range, but their photoactivity is relatively low, with concomitant slow degradation rates (Yu et al., 2009; He et al., 2009a,b; Li et al., 2007).

Electrochemical methods offer promising alternatives. In this context, Ag(III) can be explored as a possible redox mediator in its soluble form, which is the tetrahydroxoargentate anion $\text{Ag}(\text{OH})_4^-$ in alkaline media (Cohen and Atkinson, 1968). Its notably high standard potential (1.8 V vs. NHE) makes it attractive for the treatment of many organic compounds. We have previously reported its preparation by electrolysis from metallic silver in alkaline solutions and its characterization (Zamora-Garcia et al., 2013). The usage of the tetrahydroxoargentate ion has not been reported for the transformation of recalcitrant organic species in water.

In the present work, we report the indirect electrodegradation with $\text{Ag}(\text{OH})_4^-$ of two types of dyes as pollutant models: rhodamine (Rh6G) and fluorescein (Fl). Rh6G has a rigid structure, extraordinary photostability, and a bio-refractory nature (Yu et al., 2009; Li et al., 2009; Zheng et al., 2012; He et al., 2009a,b; Fu et al., 2005), but low solubility in alkaline media. Conversely, Fl exhibits a similar structure and properties but with high solubility in such media.

Rhodamines and their derivatives contain fluorophores and chromophores that have attracted considerable attention due to specific photophysical properties, such as high molar extinction coefficients (e.g., that for Rhodamine 6G is $116,000 \text{ M}^{-1} \text{ cm}^{-1}$) (Farida et al., 2009), which allow their use in dye-lasers, molecular imaging, and selective ion chemosensing (He et al., 2009a,b; Fang-Jun et al., 2010). A highly sensitive, rhodamine-based colorimetric off-on fluorescent chemosensor has been developed for Hg^{2+} in aqueous solution and for live cell imaging (Wang et al., 2011; Hochberger et al., 1998). Rh6G is a very soluble cationic dye (Zheng et al., 2012) that is typically used as a dye for paper and for natural (e.g., silk, cotton, wool, leather, bast fibers) and synthetic fibers, as well as a water pollution tracer, an absorption indicator, and in personal care and cosmetic products. Criminologists use it for latent printing and identification purposes (Masters, 1990).

Since most synthetic dyes pose environmental risks to some degree, we selected Rh6G as a model pollutant considering that its rigid closed ring structure contributes to its stability and bio-refractivity (Zheng et al., 2012; He et al., 2009a,b; Farida et al., 2009; Yu et al., 2009; Fu et al., 2005), and its relative toxicity. For example, Rh6G is a potent inhibitor of oxidative phosphorylation (Gear, 1974); rat mortality after Rh6G injection is well documented (French, 1989) as well as its toxic effect on rat retinal ganglion cells (Thaler et al., 2008).

Even though its toxicity is generally regarded as low (TOXNET, 2017), the yellow dye fluorescein was also selected for the present study due to its structural similarity with Rh6G and to its much higher solubility in alkaline media. Fluorescein is used in many applications: as a presumptive reagent for dilute blood detection; in cosmetics, cleansers, and other household products; as a tracer for water leaks and water pollution sources; as an adsorption indicator; as a chemical intermediate for other dyes; and as a fluorescent pH indicator (Lide, 2007). Its sodium salt has several uses in ophthalmology (Dolak et al., 2008).

In the present work, UV–Vis spectrophotometry, total organic carbon (TOC), and high-pressure liquid chromatography (HPLC) were used to identify the species involved at different reaction stages and to evaluate the degree of mineralization. Gas chromatography with flame ionization detection (GC-FID) was used as a qualitative way to monitor the rupture and degradation of the dyes. Lastly, gas chromatography with mass spectrometry (GC-MS) detection was used to identify the final reaction products.

2. Materials and methods

2.1. Preparation of $\text{Ag}(\text{OH})_4^-$

A conventional three-electrode cell was used with a silver mesh ($0.15 \times 10 \times 10 \text{ mm}$, 99.99%, NILACO) as the working electrode, a 5-cm-long, $\Phi = 0.7 \text{ mm}$ Pt wire as the counter electrode (Sigma-Aldrich, USA), and a Ag/AgCl reference electrode (Bioanalytical systems, USA). The Ag mesh was prewashed with 10% HNO_3 (prepared from 70% HNO_3 , Karal) to eliminate its natural passivation layer. The supporting electrolyte was 4.0 M NaOH (Karal, 97%). Milli-Q water was used at room temperature throughout the entire experimental procedure. Potentials were applied with a PAR 273A potentiostat (Princeton Applied Research, USA). $\text{Ag}(\text{OH})_4^-$ was electrogenerated by applying a constant potential of 1.2 V to this cell for 10 min, which produced a 0.113 mmol/L solution (Zamora-Garcia et al., 2013).

2.2. UV–Vis spectrophotometry

In a 2-mL Eppendorf tube, 1 mL of the $\text{Ag}(\text{OH})_4^-$ solution described above was mixed with either an aliquot from an 880-ppm Rh6G stock solution (prepared with 100 mL of Milli-Q water and 0.088 g of Rh6G, Sigma, 98%) or with an aliquot from an 800-ppm Fl stock solution (prepared with 100 mL of 4.0 M NaOH and 0.080 g of Fl, Wako, 98%), to generate a 40-ppm solution of dye in each case. Wavelength scans from 250 to 800 nm were performed with an AVA Spec 048 spectrophotometer (Avantes, The Netherlands). Reaction times varied up to 120 min; the dye-to-oxidant ratios were 1:18 Rh6G: $\text{Ag}(\text{OH})_4^-$ and 1:9 Fl: $\text{Ag}(\text{OH})_4^-$, and the pH was ca. 16 in all cases.

2.3. TOC measurements

A 1110-ppm Fl stock solution (dissolved in 4.0 M NaOH) and a 500-ppm Rh6G solution (dissolved in water) were used. Aliquots of these dye stock solutions were used to generate 10–50 ppm solutions for the ensuing experiments. The TOC content of the stock solutions was measured at different dilutions with a Shimadzu TOC-V_{CPH} instrument (Japan), which required 15 mL of sample for every determination. Prior to injection into the TOC apparatus, samples were acidified to $\text{pH} \leq 3$ with HCl (J.T. Baker, 75%), purged with bubbling air to eliminate the CO_2 produced in this acidification step, and centrifuged to separate any remaining solid particles.

2.4. Sample preparation for the chromatographic characterization

These samples also required acidification to $1 < \text{pH} < 3$ with HCl (J.T. Baker, 75%) prior to injection into the different chromatographic analytical systems. The procedure also involved the following: a) salting out with NaCl (Karal, 99%) to saturate the aqueous phase and make the extraction more efficient, b) three successive extractions with CH_2Cl_2 (J.T. Baker, 99.5%) to recover the highest possible amount of analytes, c) solvent evaporation with air, and d) redissolution in CH_3OH (Karal, 99.5%), $\text{C}_6\text{H}_5\text{CH}_3$ (Karal, 99.5%), or CH_3CN (Karal, 99.5%), as needed.

2.5. HPLC

Reversed-phase chromatography was performed with a PM-80 BAS chromatograph using a C_{18} , $15 \text{ cm} \times 4.6 \text{ mm}$ column (Supelco, $5 \mu\text{m}$). For the detection of possible N-de-ethylated intermediates generated during the degradation of dyes (He et al., 2009a, 2009b), a 45% ammonium acetate (13 mM) and 55% methanol solution was used as the mobile phase. Samples were analyzed

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