Oxidative breakdown of acid orange 7 by a manganese oxide containing mine waste: Insight into sorption, kinetics and reaction dynamics

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ABSTRACT

The reaction rates and orders of azo dye, acid orange 7 (AO 7), oxidation by a Mn oxide containing mine tailings were determined. The reaction is pseudo-first order with respect to the tailings surface area concentration [SA] and pseudo-fractional (0.6) order with respect to AO 7 concentration. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to probe surface sorption and oxidation of AO 7 on a synthetic manganite surface. Sorption is rapid, pH dependent and predominantly outer-sphere. At pH 2.7 a distinct lag phase of 8 min has been observed between dye sorption and the initiation of oxidation. This lag phase suggests that either transfer of the first electron is rate limiting or there is a time consuming re-orientation and inner-sphere sorption step prior to electron transfer.

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1. Introduction

Manganese oxides have the potential to oxidise and breakdown a number of organic contaminants. Recently it has been demonstrated that a Mn oxide containing mine tailings from South Africa can oxidatively decolorise a number of acid azo dyes including acid orange 7 (AO 7) [1]. The reaction mechanism for AO 7 oxidation was shown to involve successive electron transfers from the dye to the Mn oxide surface, resulting in the asymmetrical cleavage of the azo bond. The terminal reaction products of this reaction were shown to be 1,2 naphthoquinone (NQ) and 4-hydroxybenzenesulfonate (4HBS). In order to assess the viability of treating wastewaters with the mining by-product an understanding of the reaction kinetics is necessary, however kinetic information is often challenging to obtain when the reagents (in this case the Mn tailings) are complex and heterogeneous.

Reactions occurring at the water–mineral interface involve a sorption step. This results in reaction kinetics that are often more complex than solution based reactions. The Langmuir–Hinshelwood kinetic model has been used with mixed success to describe the kinetics of a number of photo-catalytic dye-oxidation studies involving Ti oxides [2–5]. When investigating photo-catalysed reactions it is possible to gather sorption parameters, such as equilibrium concentration and partitioning coefficient, before the light-dependent reaction is initiated [4–6]. In the case of Mn oxide mediated oxidations, sorption studies are difficult to characterize due to the rapid sorption and subsequent reaction of the reductant on the oxide surface [7,8]. For this reason many kinetic studies involving Mn oxides have based kinetic calculations on the generation of Mn^{2+} and not solely on the disappearance of the reductant [7–14]. This approach has the limitation that Mn^{2+} may not immediately be released from the Mn oxide lattice and once released, Mn^{2+} can be re-adsorbed and incorporated into the mineral lattice [15]. Despite this limitation Mn^{2+} release can give an approximation of reaction kinetics especially if additional methods are used to verify results.

Infrared spectroscopy has frequently been used to probe sorption and oxidation reactions of dyes on Ti, Al and Fe oxide surfaces [2,6,16–20]. The majority of these studies used diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The DRIFT techniques allow a 'snap shot' view before and after the reaction has taken place, but cannot provide kinetic or dynamic information about the reaction. Another limitation of the DRIFT technique arises from the need for samples to be dried after the reaction has taken place. Drying has been shown to change the coordination of sorbed compounds [21,22], as well as surface acidity [23,24], which can create difficulties in data interpretation [21].

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy has the benefit of allowing real time surface analysis in a fully hydrated system and thus is a powerful in situ technique for probing oxidation [25] and sorption [21,22] reac-

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tions at the mineral–water interface. It is particularly well suited to differentiating between inner- and outer-sphere sorption of compounds onto mineral surfaces [21,22,26], through the splitting, shifting and formation of new IR peaks.

In the study of Clarke et al. [1], it was shown that the kinetics of AO 7 oxidation are pH dependent, with the dye decolorisation rate increasing with decreasing pH. The objective of this study is to establish insights into the kinetics and dynamics of the reaction between the model azo dye AO 7 and the Mn oxide phase of mine tailings. Reaction rates and orders of the dye oxidation by the Mn tailings are determined using a batch technique and real time in situ information on the sorption and oxidation behaviour of AO 7 on a synthetic manganite surface is presented.

2. Materials and methods

Details on the physical, chemical and mineralogical properties of the Mn tailings are given in Clarke et al. [1]. Acid orange 7 was obtained from Sigma–Aldrich and used without purification.

2.1. Initial reaction rates and orders

Reaction rates and orders were determined by continuous stirring reactions using the initial rate method described by Lasaga [27]. All experiments were conducted at 25 °C. The general experimental design was as follows: AO 7 stock solutions were prepared in 0.2 M acetate buffers adjusted to pH 4. A volume of 250 mL dye stock or blank (acetate buffer alone) solution was added to a 500 mL flask and stirred at 50 rpm using a magnetic stirrer. The reaction was initiated by adding the tailings to the stirred solution. Aliquots of 5 mL were extracted at increasing time intervals and filtered through syringe membrane filters (0.2 μm). The shortest practical sampling time interval was 30 s, which included the residence time in the syringe. The filtrates were analysed by atomic absorption spectroscopy (Varian SpectraAA FS200), UV–vis spectroscopy (Varian Cary 50 spectrometer) and HPLC (Perkin Elmer Series 200 fitted with a Genesis, C-18 column (4.6 mm × 250 mm) containing 4 μm packed particles (Alltech, Deerfield, Germany)) to determine concentrations of soluble Mn, dye and breakdown products. Details of the HPLC pump program are given in Clarke et al. [1].

The soluble Mn concentrations in the blanks and treatments were used to calculate $[Mn]_{diss}$ which is the amount of Mn not retained on the filter, and is taken as representing the Mn concentration beyond that measured in the blank solutions [10,13].

The order of the initial reaction rate was determined with respect to the surface area concentration [SA] of the tailings and dye concentration. The order with respect to available Mn tailings' surface area was determined by varying the [SA] between 4.8 and 48 m^2 L^{-1} while the pH and dye concentration were held constant at pH 4 and 0.14 mM, respectively. Similarly, the order with respect to dye concentration was determined by varying the dye concentration between 0.07 and 0.71 mM (pH 4; [SA] = 48 m^2 L^{-1}). The initial rate was calculated between 0 and 15 min when reaction concentrations would be closest to initial conditions.

2.2. ATR-FTIR experiments

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Thermo Electron Nexus FTIR fitted with a liquid-N$_2$ cooled MCT detector and a Horizontal ATR flow-through assembly (PIKE Technology) containing a germanium (Ge) Internal Reflectance Element (IRE). Omnic 32 software was used for all spectral processing.

The ATR experiments were conducted following the procedure outlined by Hug [22] whereby the IRE is coated with a clay film. Synthetic manganite was prepared following the method of Macrdell

[28]. X-ray diffraction analysis confirmed the synthesis of manganite (MnOOH).

A 1 g/L suspension of manganite was prepared in a 30:70 ethanol:water solution. This suspension was used to deposit a thin clay film on the Ge IRE by pipetting a 2 mL aliquot onto the crystal and allowing it to dry. The dry clay film was re-hydrated in the flow cell with 0.5 mL DI water (>18 MΩ cm) adjusted to pH 4 and a background scan was collected of the fully hydrated clay. All subsequent scans were ratioed against this hydrated-clay background, allowing peak intensity due the sorbed compound to be observed. Acid orange 7 solutions were prepared in DI water and the pH adjusted to 2.3, 2.7, 3.0, 3.7, 4.5 and 6.0 by the addition of 0.01 M HCl. At the start of the reaction 0.5 mL of the dye solution was injected into the flow cell. The final concentration of dye in contact with the clay was 0.14 mM. This concentration was confirmed to be below the infrared detection limit for aqueous species on the IRE of the system used. This permitted any dye solution detected to be considered surface-bound. A set of control spectra (as above but without the clay film) and blanks (pH adjusted DI water injected onto the clay film with no dye) were collected. Scans were displayed within 5 s of the dye being injected into the cell. During the reaction period spectra were collected every 80 s using 64 co-added scans at 4 cm^{-1} resolution. Standard spectra of pH adjusted (2.3–6.0) 25 mM solutions of AO 7 were collected on a clean Ge crystal.

3. Results and discussion

The mineralogical, chemical and physical properties of the tailings have been presented elsewhere [1]. Briefly, the tailings (<2 mm) are a by-product of Mn ore extraction in the Kalahari Mn fields. They contain high proportions of Mn oxides with accessory carbonate and silicate minerals. The net oxidation state of Mn in the tailings is 3+, and manganite is one of the dominant Mn oxide phases. The point of zero charge is less than pH 4 and the pH of the tailings, measured in water, is 8.8.

3.1. Reaction rates and orders

To determine the rate of dye oxidation by the tailings both dye removal and reductive dissolution of the Mn tailings were measured. Fig. 1 shows the change in AO 7 concentration and $[Mn]_{diss}$ over time for two dye concentrations (0.07 and 0.32 mM) reacted at pH 4. There is an initial sharp decrease (~30%) in AO 7 concentration in the first 30 s of the reaction, after which dye removal rate slows down. This initial dye decrease is not reciprocated by a similar sharp increase in $[Mn]_{diss}$ (Fig. 1b), which displays a more gradual evolution with time, suggesting that sorption may be responsible for the initial removal of dye from solution. The possibility that the Mn^{2+} initially released is rapidly re-adsorbed to the solid phase would seem unlikely based on the more linear increase in Mn^{2+} after 30 s.

Due to the difficulties of obtaining reductant sorption data, as mentioned in Section 1, kinetic studies have been confined to the rate of $[Mn]_{diss}$ release. In an earlier investigation a tentative AO 7:Mn(III) reaction stoichiometry was determined as 1:3 [1], thus the rate of Mn^{2+} release is expected to be approximately three times greater than AO 7 removal rates.

The ln(initial rate) vs ln[SA] plot, given in Fig. 2a, is linear ($R^2 > 0.95$) with a slope of 1.19 ± 0.08 (not significantly different to 1 at a 5% confidence level ($t = 3.4$; $f = 2$)), indicating a pseudo-first-order dependence on [SA]. This result is expected for surface-dependent reactions. Due to the heterogeneous nature of the Mn tailings the initial Mn oxide concentration is unknown thus the rate constants (k) could not be calculated.

The effect of increasing dye concentration, at a constant [SA], had less of an effect than varying [SA] on reaction rate, with a 10-fold increase in dye concentration only resulting in a 4-fold increase