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Short Communication

Quantitative methylene blue decolourisation assays as rapid screening tools for assessing the efficiency of catalytic reactions

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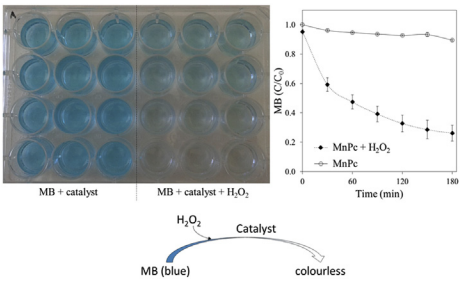
HIGHLIGHTS

- MB decolourisation assay can screen possible catalysts for oxidative processes.
- MB reacts broadly to oxidative processes, beyond hydroxyl radical production.
- Catalysts performed similarly for both MB decolourisation and bisphenol A removal.

GRAPHICAL ABSTRACT



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ABSTRACT

Identifying the most efficient oxidation process to achieve maximum removal of a target pollutant compound forms the subject of much research. There exists a need to develop rapid screening tools to support research in this area. In this work we report on the development of a quantitative assay as a means for identifying catalysts capable of decolourising methylene blue through the generation of oxidising species from hydrogen peroxide. Here, a previously described methylene blue test strip method was repurposed as a quantitative, aqueous-based spectrophotometric assay. From amongst a selection of metal salts and metallophthalocyanine complexes, monitoring of the decolourisation of the cationic dye methylene blue (via Fenton-like and non-Fenton oxidation reactions) by the assay identified the following to be suitable oxidation catalysts: $CuSO_4$ (a Fenton-like catalyst), iron(II)phthalocyanine (a non-Fenton oxidation catalyst), as well as manganese(II) phthalocyanine. The applicability of the method was examined for the removal of bisphenol A (BPA), as measured by HPLC, during parallel oxidation experiments. The order of catalytic activity was identified as FePc > MnPc > $CuSO_4$ for both BPA and MB. The quantitative MB decolourisation assay may offer a rapid method for screening a wide range of potential catalysts for oxidation processes.

1. Introduction

Many anthropogenic, organic compounds are non-biodegradable and recalcitrant in the aqueous environment (Basile et al., 2011). Degradation, and even mineralisation, of these molecules is often possible through the use of oxidation processes. An example of these processes is Fenton's reaction, which produces highly reactive hydroxyl radical (•OH) species by the catalytic decomposition of hydrogen peroxide (H_2O_2) by ferrous iron (Fe^{2+}) (Bokare and Choi, 2014). By a combination of electrophilic addition and hydrogen abstraction by •OH, organic molecules

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are fragmented and complete mineralisation can be achieved (Poerschmann et al., 2010). Iron salts in other oxidation states e.g. Fe^{3+} (Watts and Dilly, 1996), iron-containing minerals e.g. magnetite (Kong et al., 1998), as well as other metals (Bokare and Choi, 2014) also catalyse the formation of •OH from peroxides, and are collectively classified as Fenton-like catalysts. Similarly, the generation of other reactive oxygen species such as singlet oxygen ($^1O_2$) and superoxide ($O_2^{\bullet -}$) have also been investigated for their application in the oxidative treatment of pollutants (Wang et al., 2015; Zhou et al., 2013).

To investigate the efficiency of oxidation processes aimed at the remediation of textile waste water, the cationic dye methylene blue (MB) has been used as a model pollutant (Melgoza et al., 2009; Salem and El-Maazawi, 2000; Zhou et al., 2015). In the presence of oxidising compounds, MB undergoes a colour change from blue to colourless: this arises from either a change in the redox state of the MB cationic dye (Kishore et al., 1989) or degradation of the dye molecule (Zhou et al., 2015). MB was used by Satoh et al. (2007) to develop a MB-impregnated test strip: decolourisation of this strip was reported to indicate •OH production by Fenton's reaction reagents. Similarly, the decolourisation of dissolved MB has been reported to compare the photo-Fenton catalytic activity of two heterogeneous iron-based catalysts (De León et al., 2008).

The work presented here demonstrates, instead, the use of the previously reported rapid MB test strip assay (Satoh et al., 2007) in conjunction with a newly developed quantitative MB decolourisation assay, to screen potential oxidation reaction catalysts in the presence of H_2O_2. The test is then based on the extent of MB decolourisation as a result of oxidising species produced, but is neither limited to Fenton-type reactions, nor the production of •OH, in order to function. MB decolourisation is thus attributable to a wide range of oxidative activity resulting from the introduction of catalyst to H_2O_2-containing reactions. The inclusion of quantitative screening of the decolourisation would allow for comparison of different catalysts as well as the ability to assess changes in reaction conditions (e.g. catalyst and H_2O_2 concentration). The oxidising ability of the resulting species was validated by the removal extent of a model pollutant, bisphenol A (BPA), in parallel oxidation studies. The applicability of this developed assay towards unconventional oxidation catalysts, such as metallophthalocyanines (MPc) (Hadasch et al., 1998; Sorokin et al., 1996), was also investigated.

2. Experimental

2.1. Materials

Methylene blue (MB), $CuSO_4$, H_2O_2 (9.79 M), NaOH, NaH_2PO_4, Na_2HPO_4, dimethyl formamide (DMF) and acetonitrile (MeCN; LiChrosolv) were purchased from Merck (Germany). Bisphenol A (BPA, $\geq$ 99%), iron(II) phthalocyanine (FePc), manganese(II) phthalocyanine (MnPc), copper(II) phthalocyanine (CuPc) and cobalt (II) phthalocyanine (CoPc) were sourced from Sigma Aldrich (Germany). Copper(II) tetrasulphonated phthalocyanine (CuTSPc) was received as a gift from Prof T. Nyokong (Rhodes University, South Africa). All phthalocyanines, other than CuTSPc, were unsubstituted.

Aqueous studies were conducted in 50 mM NaH_2PO_4/Na_2HPO_4 buffer (pH 7.0) in the dark at 35 °C.

2.2. MB decolourisation test strip

The preparation of MB test strips was adapted from Satoh et al., 2007. Briefly, strips of filter paper (Whatman™ cotton filter paper, ashless, Grade 42, UK) were dipped in MB solution (1 mM, in 10% $^v/_v$ aqueous MeOH) and left to dry overnight. To the test strip was added 10 μL of H_2O_2 (0.979 M in 0.1 M H_2SO_4, adjusted with NaOH to pH 3.0) and 10 μL of either a metallophthalocyanine suspension (5 mM in H_2O for CuTSPc and in DMF for all other unsubstituted MPc) or $CuSO_4$ solution (36 mM in 0.1 M H_2SO_4, pH 3.0). Bleaching of the MB test strips was captured by digital photography after 15 min reaction time.

2.3. Spectrophotometric quantitative MB decolourisation assay

Aqueous MB decolourisation studies were performed in 24-well microtitre plates. Reactions (1 mL) contained 20 μM MB (1 mM in 10% $^v/_v$ MeOH), 40 mM H_2O_2 and 100 μL MeCN. As catalysts, either 32 μM MPc (from 5 mM suspensions in H_2O for CuTSPc or DMF for all other MPc) or 320 μM $CuSO_4$ (36 mM in 50 mM NaH_2PO_4/Na_2HPO_4 buffer, pH 7.0) was added. Plates were shake incubated (160 rpm). MB decolourisation was measured spectrophotometrically, and quantified at 664 nm using a SynergyMX spectrophotometer (Biotek, USA).

2.4. BPA removal studies

BPA removal studies were performed in microfuge tubes. Solutions (1 mL) contained 75 μM BPA and 40 mM H_2O_2. As catalyst, either 160 μM of MPc suspension or 1.6 mM $CuSO_4$ was added. Tubes were incubated under constant agitation. A 150 μL aliquot extracted from BPA oxidation reactions was quenched with 3 μL of NaOH (4 M) to decompose remaining H_2O_2 (Nicoll and Smith, 1955), diluted with 600 μL MeCN, vortexed, and centrifuged at 8000 *g* for 5 min, removing 500 μL of the supernatant for analysis. BPA removal was measured by HPLC (Cui et al., 2009), using a Supelcosil LC-18 column (100 mm × 4.6 mm, 5 μm, Supelco, USA) coupled to a Prominence HPLC system (Shimadzu, Japan) consisting of a SPD-M20A diode array detector and SIL-20A autosampler. A 10 μL injection volume was eluted at 0.5 mL min^{-1} under 550 psi, using a water: acetonitrile (50: 50 $^v/_v$) mobile phase. BPA eluted after ~5.1 min and was detected at a wavelength of 278 nm.

For improved comparison of the two catalyst selection studies, H_2O_2 and catalyst (MPc and $CuSO_4$) concentrations were decreased 5.3 fold for additional MB decolourisation and BPA removal studies.

2.5. Statistical treatment and kinetic modelling

Paired, two-tailed, Student's t-test was used to assign statistical significance between compared samples. The pairing of samples and rationale for analysis are outlined in text.

For the decolourisation of MB and removal of BPA, the apparent order of reaction kinetics was determined through non-linear modelling of the dependence of decolourisation/removal with time, using zero-, first- and second-order kinetic models, using Microsoft Excel's Solver function. Least-squares minimisation, weighted by the reciprocal of experimental data, was employed to determine the best-fitting reaction order and rate constants.

3. Result and discussion

3.1. MB decolourisation test strip assay

Decolourisation of MB, observable as bleaching of the MB test strip in Fig. 1, served as a general indicator of catalytic activity (Satoh et al., 2007). This test identified FePc, MnPc, CuPc, CoPc and $CuSO_4$ as potential catalysts for H_2O_2-mediated oxidation reactions. In particular, FePc and MnPc resulted in extensive bleaching of MB in the presence of H_2O_2, indicating strong catalytic activity of these organometallic compounds. As a Fenton-like catalyst (Bokare and