



Investigation of manganese greensand activation by various oxidants

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ARTICLE INFO

Keywords:

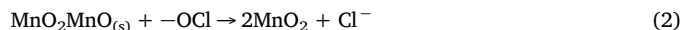
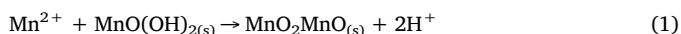
Fe(II)
Greensand
Mn(II)
MnO₂
Oxidation
Surface

ABSTRACT

Manganese greensands are used routinely in industry for Mn(II) and Fe(II) removal from drinking water and groundwater, however little is understood about the effect of changing the activation conditions on removal performance. This study directly compared the change in removal performance for Mn(II) and Fe(II) across five commercially available greensands when using bleach or potassium permanganate as the oxidant for greensand activation. The performance of these medias when no activation process was employed was also compared. The results indicated that enhanced performance was achieved when higher concentrations of oxidant were used. Activating the medias with potassium permanganate was found to achieve slightly higher removal performance for both Mn(II) and Fe(II), although bleach was found to limit the effect of reductive dissolution when treating Fe(II) solutions. A notable observation was that activation of the medias induced a discrete removal mechanism that involved a negatively charge surface species. This species was thought to exist as a higher oxidation state than Mn(IV), analogous to a Mn(VII) species. XPS spectra indicated that activation influenced the greensands' surface structure, and supported the change in surface Mn oxidation state, however the surface speciation was inconclusive as to an exact structure. This study used fixed bed columns to examine the various activation conditions, as well as XPS to observe any changes in Mn oxidation state.

1. Introduction

Manganese (II), Mn(II), is a naturally occurring contaminant that's typically found in environmental bodies of water [1,2]. Untreated water that contains Mn(II) can promote scaling and fouling in industrial applications and cause aesthetic aberrations in domestic use; thus it is essential Mn(II) is removed from solution prior to water release or reuse [1–3]. A common treatment option for Mn(II) remediation is the use of manganese greensands due to their relatively low cost and treatment efficacy [1]. Manganese greensands (or simply greensands) are manganese dioxide (MnO₂) coated substrates; historically glauconite but in recent times the substrate is either silica or zeolite [4–6]. Greensands are typically used in a fixed bed column and operated in continuous regeneration mode, where a suitable oxidant such as bleach (NaOCl) or potassium permanganate (KMnO₄) is dosed into the influent stream prior to contact with the greensand bed [1,2]. The prevalent removal mechanism is proposed to involve adsorption of Mn(II) onto the MnO₂ surface where it is subsequently oxidised to MnO₂ by the residual oxidant in the liquid phase. In turn, the surface becomes available for further Mn(II) adsorption (Eqs. (1) and (2)) [7,8].



The adsorption-oxidation mechanism satisfactorily explains the removal behaviour for continuously regenerated greensands; however, the outlined equations may not describe how Mn(II) is removed when greensands are operated using intermittent regeneration. Intermittent regeneration is where the greensand bed is activated using a suitable oxidant, rinsed, and used to treat contaminated water without in-line dosing [2]. Since there is no oxidant present in the influent stream, it would be unreasonable to assume Eq. (2) is true in this instance.

Consequently, there is a need to understand critical aspects pertinent to the intermittent regeneration approach for greensand use which includes: (1) recommended activation process; (2) redox properties of the manganese oxide surface; and (3) identification of active sites. In relation to the activation process for greensands with bleach or KMnO₄ for Mn(II) and Fe(II) removal, there was found to be limited information [7]. Posselt et al. [9] studied the sorption of various cations on hydrous manganese dioxide and reported that the sorptive capability of MnO₂ for Mn(II) was significantly greater than other cations studied. This latter outcome was postulated to be due to an equilibrium between the Mn(II) and the MnO₂ surface with no need to activate the manganese material mentioned [9]. Solution pH had a major influence on the

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surface charge of the hydrated MnO_2 , where alkaline pH generated a negative surface charge on the MnO_2 surface, increasing the adsorptive capacity of MnO_2 [9]

With respect to the redox properties of a manganese oxide surface, Bernard et al. [10] studied electrochromic cycling of MnO_2 using Raman spectroscopy. The authors showed the appearance/disappearance of a peak at 650 cm^{-1} which was attributed to the oxidation of Mn_3O_4 to MnO_4 [10]. Consequently, it was inferred that for MnO_2 to be electrochromic, there must be defects or vacancies (for example, Mn(III)) present in the oxide framework [10]. Similarly, De Guzman et al. [11] investigated the electrochemical properties of manganese oxide molecular sieves, namely todorokite and hollandite, and pyrolusite. Electrochemical cycling of these materials showed that todorokite was electrochemically active, whereas the latter two phases showed relatively low electroactivity [11]. This latter observation was ascribed to the presence of Mn^{2+} in the todorokite framework which was suggested to be coupled to electrochemical reactions involving manganese oxides due to Mn^{2+} immobility, thus enabling it to be regenerated through cycling [11]. Qiu et al. [12] investigated the effects of surface area, exchangeable oxygen and Lewis acid sites in relation to catalytic oxidation using manganese oxides. This study agreed with the results of De Guzman et al. [11] wherein large MnO_x tunnel structures (with high surface areas) showed significant electrochemical properties, including oxygen reduction and supercapacitance [12]. The authors also suggested that the increased presence of Lewis acid sites enhanced the oxidation properties of MnO_x in non-aqueous environments [12]. Although these cited studies provided insight into electrochemical analysis of MnO_2 , they did not elucidate the redox behaviour of MnO_2 in contact with an oxidising solution.

Surface characterization of greensand and MnO_2 coated media by X-ray Photoelectron Spectroscopy (XPS) has been used to evaluate surface changes after media service [13,14]. Cerrato et al. [14] compared XPS spectra of post-service MnO_2 coated media when the inlet stream was dosed with and without dissolved oxygen (DO) and free chlorine. The XPS results showed that without any dosing, the MnO_2 coated media relied mostly on adsorption (XPS data suggested that the media surface was comprised of Mn(IV) and Mn(II) and not Mn(III)) [14]. Additional research by Cerrato et al. [13] showed that a greater Mn(III) content was measured for used pyrolusite when compared to unused pyrolusite (exclusively Mn(IV)) [13]. Post service MnO_x anthracite media from four different treatment plants were also tested and the XPS interpretation again showed a Mn valence mixture of Mn(III) and Mn(IV) for these media. The media were, however, in contact with free chlorine during service, thus the results did not translate to intermittent regeneration methods. Further, it was noted that previous studies focussed on *ex situ* analysis methods which intrinsically do not capture MnO_2 activation and removal mechanisms.

In summary, the impact of activation methodologies on greensand performance is not yet completely understood with gaps in knowledge relating to not only the influence of activation procedure upon active site formation but also the mechanism of the oxidation process. Therefore, the aim of this study was to investigate the change in the Mn (II) and Fe(II) removal behaviour of greensands when activated with different concentrations of bleach or KMnO_4 . Additionally, the secondary aim of this work was to help elucidate the activation mechanism for different commercial greensands.

It was hypothesised that MnO_2 exhibits a higher surface Mn oxidation state when in contact with bleach or KMnO_4 , and that formation of this surface state was dependent upon contact time and oxidant concentration. Specific research objectives included: (1) determination of the stability of greensands when in contact with different oxidant solutions; (2) investigation on the impact of oxidant type and concentration during activation, and how it influenced the Mn(II) and Fe (II) removal performance of manganese greensands; (3) identification of optimal activation conditions for Mn(II) and Fe(II) removal; (4) evaluation of the effect of MnO_2 contact with bleach upon the surface

Mn oxidation state; and (5) an improvement in the understanding of the surface-liquid redox mechanism responsible for Mn(II) removal using manganese greensand. The methodology employed was to monitor the water quality of both greensand activation and treatment effluents, and by determining any MnO_2 phase change and redox properties when in contact with a suitable oxidant using *in-situ* Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) on preserved activated greensands.

2. Materials and methods

2.1. Materials

Manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), iron(II) chloride dihydrate ($\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$), and KMnO_4 were purchased from ChemSupply as analytical reagent (AR) grade and were not altered prior to use. Technical grade NaOCl solution (12.5 wt%) was purchased from Ajax Chemicals and colourmetrically standardised (as ppm free chlorine) prior to use using *N,N*-diethyl-1,4-phenylenediamine sulfate (DPD) reagent at 530 nm.

Commercial manganese greensands were purchased from domestic and international suppliers (Australia and USA) and were used as received, unless otherwise stated. Due to commercial sensitivity, the names of the products were not disclosed and instead were labelled GS1 to GS5. Previous work by Outram et al. [6] has characterised GS1 and GS2 as MnO_2 coated silica (quartz) with poor surface area ($< 0.5\text{ m}^2\text{ g}^{-1}$), and GS3, GS4 and GS5 as solid MnO_2 ores of various grades with increased surface areas (11.40, 9.02 and $19.66\text{ m}^2\text{ g}^{-1}$). Hence, the general terms ‘coated media’ and ‘solid media’ corresponded to GS1 and GS2, and GS3 to GS5, respectively.

2.2. Experimental procedure

2.2.1. Stability of greensands in oxidant solution

Greensand stability experiments were conducted wherein 1 g (accurately weighed) of each manganese greensand was added to separate 50 mL Falcon tubes. Next, 50.0 mL of either pH adjusted DI water using 0.1 M hydrochloric acid (HCl) or 0.1 M sodium hydroxide (NaOH), bleach or KMnO_4 solutions were added to each tube and capped. The pH of the 130 and 260 ppm bleach solutions were 10.29 and 10.93, respectively; the corresponding KMnO_4 solutions were 6.36 and 6.34, respectively. The mixtures were then gently stirred in a rotary stirrer for 24 h at ambient temperature. After the allocated time, the supernatants were $0.45\text{ }\mu\text{m}$ syringe filtered and prepared for analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES).

2.2.2. Column experiments

Commercial greensands were placed in a 15.4 mm internal diameter (ID) column with a bed height of 400 mm. The material was initially backwashed to remove fine particulates until the effluent was clear. The material was then activated overnight with appropriate oxidant solution (bleach or KMnO_4). After activation of the media, the column was flushed with a minimum of 1 L (12 bed volumes, BV) of deionised water or until the residual oxidant was determined to be absent. The column was then used to treat a 2 ppm Mn(II) (as MnCl_2) or 10 ppm Fe(II) (as FeCl_2) solution for a minimum six hours or until breakthrough was achieved at a linear velocity of 8 m/h (or 20 bed volumes (BV) per hour). These concentrations were selected as upper limits found in groundwater contamination based on previous literature [8,15]. The effluent stream pH was monitored through-out and effluent sampled for ICP-OES analysis every 30 min. The column process parameters were kept constant across the five greensand samples.

2.2.3. Greensands activation

Manganese greensands (GS1 and GS2) were activated as a 400 mm fixed bed in a 15.4 mm internal diameter column. The greensand bed

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