



Comparitive analysis of the physical, chemical and structural characteristics and performance of manganese greensands

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ABSTRACT

Greensands have found widespread use in the water treatment industry for the removal of pollutants such as dissolved iron and manganese. Nevertheless, a detailed understanding of the materials used in industry is currently lacking. There is a need to develop improved knowledge of their composition and physical properties in order to discover means of enhancing performance. This study focussed on the evaluation of five commercially available materials and used modern characterization methods such as X-ray diffraction, infrared spectroscopy, Raman microscopy, scanning electron microscopy, energy dispersive spectroscopy, X-ray fluorescence, particle size distribution and surface area measurements, to elucidate differences. None of the samples contained glauconite as a primary phase, in contrast to previous literature. Two samples were found to essentially be quartz supported manganese oxides and the remaining three were predominantly manganese oxide with low levels of hematite, phyllosilicate (montmorillonite) and quartz supports. The manganese species present were mainly pyrolusite (β - MnO_2), ramsdellite (R- MnO_2), hollandite (α - MnO_2) [as cryptomelane ($\text{KMn}^{\text{II}}\text{Mn}^{\text{IV}}_8\text{O}_{16}\cdot\text{H}_2\text{O}$)] and romanechite ($(\text{Ba},\text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$). Preliminary experiments for the removal of Mn(II) using the commercial greensands showed that the greensands behaviours and removal efficiencies differed greatly between the samples.

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1. Introduction

Dissolved iron (Fe(II)) and manganese (Mn(II)) species are common heavy metal contaminants found in groundwaters [1,2]. In order to not only make the water drinkable but also to prevent scaling and fouling in industrial processes, these elements are often removed using various technologies such as ion exchange and oxidation-filtration operations [2]. Manganese oxides are frequently reported in literature to be an ideal heavy metal adsorber due to their poor crystallinity, large surface area, microporous structure and high affinity for metal ions (arising from the negative surface charge) [3,4]. In particular, manganese greensands have been used for many years to remove Mn(II) and Fe(II) ions from solution in numerous water treatment facilities [1]. Traditionally, manganese greensand has been reported to comprise of a manganese oxide (MnO_x) coating on natural phyllosilicate (glauconite), which is activated and regenerated with a potassium permanganate solution (KMnO_4) [1,5–8]. The manganese oxide coating is represented as MnO_x due to the variety of valence states the Mn

ions in the coating may adopt [9]. Manganese greensand has been proposed to operate through catalytic oxidation (Mn(II)) and redox (Fe(II)) mechanisms [1,6].

The term 'greensand' is historically used to describe the mineral glauconite, a phyllosilicate containing iron and potassium [10]. Glauconite was used by Inversand Company in the New Jersey to produce a product called 'manganese greensand', which was, as described earlier, glauconite coated with MnO_x [10]. In recent times, the production of glauconite has declined in the wake of using cheaper materials for the manganese greensand support, however the name 'manganese greensand' is still frequently used as a product name [10]. In the remainder of the work, the terms 'greensand' and 'manganese greensand' are used colloquially to refer to the commercially advertised manganese greensand products.

There are a number of articles concerning the compositional characterization of glauconite samples used for the analysis of ancient wall paintings and sedimentary clays, however, no publications are specific to manganese greensands [11–15]. Moretto et al. [12] spectroscopically studied the celadonite and glauconite pigments in Roman wall paintings as these two minerals were reported to be used as green pigments. Energy dispersive X-ray spectroscopy (EDS) results showed that the major elements in glauconite were silicon, aluminium, magnesium, potassium, and iron [12,13]. These

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results were supported by previously published work by Ospitali et al. [13] relating to the vibrational and elemental properties of glauconite, celadonite and other historical pigments.

Surprisingly, despite the long term use of greensands for water treatment applications, minimal information has been published about the detailed characterization of commercial manganese greensand samples. Instead, researchers have characterised their own materials such as manganese oxide coated silica and zeolites [1,5–8]. In a study of manganese oxide coated sand by Han et al. [9] it was demonstrated that the manganese oxide layer was a mixture of Mn^{3+} and Mn^{4+} valencies, with the Mn^{4+} valency being predominant. Research by Chang et al. [16] supported this latter conclusion when they found that pyrolusite (MnO_2) was the predominate mineral in manganese oxide coated sand. Examination of MnO_x surfaces in filter media from water treatment plants was conducted by Islam et al. [17]. These researchers analysed the cross-section of the filter media by scanning electron microscopy (SEM)-EDS and found that manganese uptake capability increased when the amount of manganese oxide coating was enhanced. Moreover, it was determined that the manganese uptake capability was related to the extent the solution was exposed to the MnO_x surface [17]. Vibrational spectroscopy methods such as infrared (IR) and Raman spectroscopy have been employed to probe the composition of various manganese oxide phases [18]. Manganese dioxide coatings and their respective reactivity have also been studied in relation to the removal of trace heavy metals [19,20].

As outlined above, there is a gap in the knowledge relating to the characterization of commercial manganese greensand samples. There are a number of commercial greensand producers and suppliers around the world that purport to supply different types of manganese greensand. Nevertheless, there is minimal information regarding the composition of these materials, physical properties, performance or indeed which sample is superior and why. Consequently, this study has the major aim of comparing and contrasting the compositional, physical, and chemical characteristics of a range of commercial manganese greensands.

2. Experimental

2.1. Materials

Five commercial manganese greensands were sourced from domestic (Australia) and international (USA, China) suppliers. Representative samples of each manganese greensand were taken and labelled GS1 through to GS5 for characterization. The GS3–GS5 manganese greensands purchased were marketed as a manganese greensand. GS1–GS2 were disclosed to be a MnO_2 coated silica, however GS1 was still marketed as a manganese greensand. Due to commercial sensitivity issues, the supplier for each sample will not be disclosed.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were collected using a Panalytical X'Pert wide angle X-ray diffractometer with $Co\ K\alpha$ radiation (1.7903 Å), operating in step scan mode. Patterns were collected every 0.02° over the range of $5\text{--}90^\circ 2\theta$ at a rate of 30 s per step. Samples were micronized and prepared as a pressed powder. The XRD patterns were matched with ICSD reference patterns using the software package HighScore Plus. XRD patterns were profile matched which used a model that employed twelve intrinsic parameters to describe the profile, with instrumental aberration and wavelength dependent considerations.

Infrared spectra were obtained using a Nicolet Nexus 870 Fourier Transform infrared spectrometer (FTIR) with a smart endurance single bounce diamond attenuated total reflectance

(ATR) cell. Spectra were obtained over the range of $4000\text{--}200\text{ cm}^{-1}$ using the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 m/s . Spectral manipulation such as baseline correction and smoothing was performed using the GRAMS software package. Jandel PeakFit software package was used for band component analysis, where band fitting was undertaken using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Raman spectra were obtained using a Renishaw inVia Raman Microscope using a 785 nm Renishaw PLC HPNIR laser. Spectra over the range of $800\text{--}100\text{ cm}^{-1}$ were obtained using 0.5% laser power with $16 \times 40\text{ s}$ single scan acquisitions. Spectral manipulation such as baseline correction, smoothing and normalisation was performed using the GRAMS software package.

Scanning electron microscopy (SEM) was conducted using a JEOL JSA 6360A SEM equipped with a JEOL EX-54175 JMH X-ray microanalyser. Samples were prepared by mounting whole greensand particles in non-conductive resins, where they were cut, polished and carbon coated to observe the cross-section of the particles. Whole greensand samples were mounted on carbon tape and carbon coated for surface analysis.

Particle size distribution was analysed using a Retsch AS 200 pan sieve stack with 4000, 2000, 1000, 500, 250, 125, $63\ \mu\text{m}$ mesh gradings. Approximately 250 g of greensand material was added evenly to the top pan sieve and shaken for 20 min at 1.00 mm/g . The corresponding graduated masses were determined by mass difference.

Brunauer-Emmett-Teller (BET) surface area measurements were obtained using a Micrometrics TriStar II 3020 surface area and porosity analyser. The N_2 gas adsorption isotherm used a 99 data point BET curve. Samples were degassed in $\frac{3}{8}$ in. samples tubes at 110°C for 24 h under vacuum. Adsorption data was analysed using the software package MicroActive.

X-ray fluorescence spectrometry was conducted on a Spectro XEPOS 03 Energy Dispersive X-ray Fluorescence (ED-XRF) spectrometer. Micronized GS1 and GS2 greensand samples were placed in the oven at 950°C for 2 h to remove moisture and carbonate species and determine the loss on ignition (LOI). Fused glass discs were prepared from the samples with a 50:50 flux ratio using the OX Claisse Fluxer.

Multi-element quantitation was performed using a Perkin Elmer 8300DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) fitted with an ESI SC-4DX autosampler and PrepFAST 2 sample handling unit for online internal standardisation and auto-dilution of samples and calibration standards. Purified nitric acid was used for the preparation of all standards and blank solutions used throughout the analysis. Instrument calibration was performed using multi-element standards prepared in-house from Inductively Coupled Plasma Mass Spectrometer (ICP-MS) grade single element stock solutions (High Purity Standards, Charleston, USA). Method robustness, accuracy and precision was verified by continuing analysis of a number of Certified Reference Materials (CRM's) covering a range of common matrices and analyte concentrations (National Institute of Standards and Technology, Gaithersburg, MD, USA, United States Geological Survey, Reston, VA, USA). GS3–GS5 samples were prepared by digesting 0.8 g of dried, micronized solid in hydrochloric acid (purified by sub-boiling distillation) for 4 h then diluted to 50 mL with Milli-Q water. Residual silica solids were quantitatively collected using pre ignited quartz fibre filter papers. Captured solids were then ignited at 850°C for 24 h prior to determining the mass difference.

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