

Coating techniques for glass beads as filter media for removal of manganese from water

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ABSTRACT

Dry as well as wet coating techniques were developed to coat glass beads as filter media to remove manganese from water. For dry coating, powdered manganese oxide ore was fixed on the media surface. Wet coating was achieved by depositing synthetic manganese oxides onto the bead surface. The media were characterized by electron microscopy as well as by testing the removal of Mn^{2+} in a continuous stirred tank reactor. Image analysis of microscopic pictures illustrated that the surface area could partly be coated by powdered material using dry coating methods, whereas complete coverage was achieved using wet coating approaches. With regard to dry coating techniques, Mn sorption uptake was higher for the adhesively dry coated glass beads than for beads where a binding agent was used. The wet coating column approach proved to be more successful than the coating of beads in a stirred tank reactor. Mn removal capability of the beads increased with higher reactant concentrations during coating. Oxide-coated glass beads applied in filter systems have the potential to improve conventional demanganization processes.

Key words | coating techniques, demanganization, filter media, glass beads, manganese removal

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INTRODUCTION

Manganese (Mn) is naturally occurring in drinking water resources worldwide (Frisbie *et al.* 2012). It is frequently present in many surface water and groundwater sources, particularly in anaerobic or low oxidation conditions (WHO 2003). For a long time, Mn in drinking water had only been considered as an aesthetic water quality problem that was responsible for a metallic taste, discoloration and the cause of black stains on plumbing fixtures (Kohl & Medlar 2006). Recent studies have documented the neurotoxic effects of Mn in children and adults (Frisbie *et al.* 2012). Thus, several authors have recommended the reexamination of the 400 $\mu\text{g}/\text{l}$ health-based guideline recommended by the WHO for drinking water (Ljung & Vahter 2007).

The removal of soluble manganese is commonly achieved through oxidation by potassium permanganate, chlorine dioxide, ozone, or other strong oxidants. The

objective of this process is to oxidize Mn^{2+} to manganese oxide [$MnO_{x(s)}$], a solid precipitate that can be removed by solid-liquid separation processes such as sedimentation or deep-bed-filtration through granular media such as quartz sand or anthracite (Chiswell & Huang 2006; Kohl & Medlar 2006). Removal is also possible using granular filter media for microbial oxidation under aerobic conditions (Mouchet 1992; Chiswell & Huang 2006). In the presence of soluble Mn^{2+} , granular filter media used in deep-bed filtration naturally develops an exterior coating of $MnO_{x(s)}$. Mainly depending on the pH and O_2 concentration, this oxide-coated material removes Mn^{2+} from water by an abiotic adsorption and oxidation process known as the 'natural greensand effect' (NGE), which has been extensively studied (Knocke *et al.* 1991, 2010; Hargette & Knocke 2001). NGE is a natural process in which deposits

of $\text{MnO}_{x(s)}$ develop *in situ* within weeks to months on new uncoated filter media during normal filter operations (Knocke et al. 1988). Various products that are rich in $\text{MnO}_{x(s)}$, such as Manganese Greensand[®] or granular filter media composed of natural occurring manganese ores such as GENO[®]-Fermanit, are commercially available and commonly applied in filters to shorten or even avoid the start-up period of the filter for manganese and iron removal.

Since 2007, glass beads have been used for filtration purposes (Klaus 2015). They are commercially applied as filter pack media and have been proved to be successful as filter media in deep-bed filtration (Klaus et al. 2014; Klaus 2015). In contrast to conventional granular filter media, glass beads possess considerable advantages regarding their physico-chemical stability as well as their hydraulic performance (Treskatis 2011; Klaus et al. 2014). Although the large-scale production of glass beads for filtration purposes is limited to the areas of application stated above, various coating techniques have been applied to glass beads so that new materials for the selective removal of metals from water were successfully prepared (Liu et al. 2002; Ozmen et al. 2009; Torkshavand et al. 2014).

The removal of manganese by NGE has been described as reactions between a sorptive mineral surface of $\text{MnO}_{x(s)}$ (where x varies from 1 to 2), dissolved Mn^{2+} and an oxidant such as HOCl. The following equations describe NGE (Nakanishi 1967; Coffey et al. 1993):



NGE can be divided into two essential steps: the adsorption of Mn^{2+} onto the media surface (Equation (1)) and the catalytic transformation of the reaction product (MnO_2MnO_s) to $\text{MnO}_{2(s)}$ in the presence of HOCl (Equation (2)). Metal oxides in aqueous solution are charged depending on the pH of the solution. The Mn atoms of $\text{MnO}_{x(s)}$ have a lower coordination number than the O atoms. On the solid-liquid interface, the Mn atoms coordinate the H_2O molecules, where they dissociate and OH^- is adsorbed by the media surface (Stumm 1997). Mn^{2+} in water is surrounded by H_2O ligands. With increasing pH values, an

exchange or a deprotonation of ligands is taking place, i.e. instead of H_2O OH^- is bound to the central Mn^{2+} ion forming Mn^{2+} complexes with a water-hydroxide-sheath. Instead of an adsorption of isolated OH^- from water, OH^- from the Mn^{2+} complex is bound by the solid media surface, forming MnO_2MnO_s followed by catalytic conversion and oxidation to $\text{MnO}_{2(s)}$ (Morgan 2005).

$\text{MnO}(\text{OH})_{2(s)}$ molecules on the media surface are capable of repeatedly adsorbing Mn^{2+} . The result is a self-regenerating process, which enables the continuous adsorption of Mn^{2+} onto the media surface. Cerrato et al. (2011) showed that in the presence of sufficient chlorine, Mn^{2+} adsorbed to $\text{MnO}_{x(s)}$ -coated media is quickly oxidized to Mn(IV), which does not dissolve back into the water. Over time, this self-regenerating process produces an adequate surface coverage of manganese oxides.

This NGE can be used for synthetic coating. Merkle et al. (1997) successfully coated anthracite with a layer of synthetic manganese oxides by a wet chemical process in a batch reactor. Coating with the required stoichiometric concentrations of reactants proved unsuccessful. Precipitation of colloidal $\text{MnO}_{x(s)}$ in solution was immediate, and the media remained uncoated. Merkle et al. (1997) eventually developed methods based on the gradual addition of oxidants in less than stoichiometric increments.

The success of a particle filtration process and its economic performance depend on the type of filter material and its physical properties. Every new filter material must fulfil various requirements before it should be used. These include form, grain size, number of grains, grain surface, density, pore volume, solubility, durability, settling rate and purity (Mörgili & Ives 1979). The general suitability of coated glass beads for filtration purposes was not an objective in this particular study and needs to be further investigated.

The objective of this study was the laboratory-scale production of robust manganese oxide-coated glass beads as filter media and the assessment of their efficiency to remove Mn^{2+} from water.

Two principally different coating techniques were examined and compared.

1. Dry coating methods

A catalytically active manganese ore was pulverized and fixed on the glass bead surface.

2. Wet chemical coating methods

NGE was utilized to produce a layer of synthetic oxides on the surface of modified glass beads. Batch experiments were modelled after the approach described by Merkle *et al.* (1997). To minimize $\text{MnO}_{x(s)}$ precipitation from solution, further experiments were conducted by applying an alternative experimental setup that uses a packed-bed column.

METHODS

Media preparation

For microbial oxidation and the removal of Mn^{2+} under aerobic conditions, quartz sand with grain-sized fractions of 0.71–1.25 mm to 1.0–2.0 mm are used (DVGW Regelwerk 2005). Commercially available products such as Manganese Greensand[®] have a grain-sized fraction of 0.25–1.25 mm (DIN EN 12911 2012). Thus, as raw materials, glass beads with a grain-sized fraction of 0.75–1.0 mm (product of Sigmund Lindner GmbH) were used to further prepare the media.

1. Dry coating techniques

(a) Coating with a binding agent: in total, 2 kg of glass beads were tumbled in a rotating barrel (model: Baier's Enkel #71050) with 20 g of a sol-gel material (silane) as a coating agent at 30 rpm for 1 h. At the beginning of the silane hardening process, 10 g of coating material was added and tumbled again under the same conditions for 1 h. As coating material, a granular manganese ore (GENO[®]-Fermanit) was finely ground ($d_{50} \sim 15 \mu\text{m}$) with a vibratory discmill (model: Siebtech, type T250). With a proportion of 78% manganese oxides, subsequently termed as MnO_x -78, GENO[®]-Fermanit is commonly used in water treatment to remove iron and manganese from water. To

remove excess coating material, the beads were sieved (mesh size 400 μm) and packed for further testing.

(b) Adhesion coating: to achieve surface roughening, 40 kg of glass beads were tumbled in a rotating barrel (model: Walther Trowal A220) with 1 kg silicon carbide [SiC (110 μm)] at 40 rpm for 12 h. Following this, the material was thoroughly rinsed to remove fine particles with demineralized water and air-dried. The matted glass beads were mixed with 10 g MnO_x -78 and 2 ml of water to prevent dust formation and tumbled again by a rotating barrel (model: Baier's Enkel #71050) for 1 h. Subsequently the beads were sieved (mesh size 400 μm) and packed for further testing.

Conditions of media preparation using dry coating techniques are summarized in Table 1.

2. Wet chemical coating techniques

(a) Synthetic $\text{MnO}_{x(s)}$ -coating in a batch reactor: the experiments were modelled according to Merkle *et al.* (1997). Conditions of the media synthesis process are summarized in Table 2 (samples 3–5). The general procedure regarding samples 3 and 4 can be described as follows: a buffered (HCO_3^-) solution of Mn^{2+} (added as $\text{MnSO}_4 \cdot \text{H}_2\text{O}$) was prepared, and a defined quantity of matted glass beads was added. In total, 500 ml of an oxidant solution (HOCl) was prepared and gradually added to the gently stirred manganese solution at 50 ml/min. After this addition, stirring continued for a certain amount of time. To reduce the formation of $\text{MnO}_{x(s)}$ precipitates from the solution, the pH of each stirred solution was periodically checked and adjusted to be maintained between 7.2 and 8.0 by dropwise addition of 0.5 mol/l NaOH or 0.5 mol/l HCl as required. For the production of sample 3, a stepwise approach was pursued. To apply this sequential batch method, two solutions were prepared: solution 1 was 250 ml of a Mn^{2+} solution (1,000 mg/l), and solution 2 was an oxidant solution (HOCl 138 mg/l). In the first step, 25 g of matted glass beads were added to solution 1.

Table 1 | Summary of dry coating techniques

Sample number	Coating method	Surface conditioning	Media input [g]	Coating material	Binding agent [g]	Tumbling time [min]
1	Gluing	None	2,000	10 g MnO_x -78	20 g silane	60
2	Adhesion coating	Matting	2,000	10 g MnO_x -78	none	60

Table 2 | Summary of wet chemical coating techniques

Sample number	Reactor type	Media input [g]	Initial sample volume [l]	Initial Mn ²⁺ [mg/l]	Oxidant addition [mg]	Initial HCO ₃ ⁻ [M]	Dosage time [min]	Total reaction time [min]
3	beaker	50	10	100	1,100 (HOCl)	10 ⁻⁴	10	40
4	beaker	50	2.5	1,000	1,100 (HOCl)	10 ⁻⁴	50	90
5	beaker	25	1	1,000	138 (HOCl)	–	stepwise	15
6	column	500	2.5	1,000	1,100 (HOCl)	10 ⁻⁴	50	90
7 ^a	column	500	2.5	1,000	1,100 (HOCl)	10 ⁻⁴	50	90
8	column	500	2.5	11,140	8,970 (HMnO ₄)	10 ⁻⁴	50	90

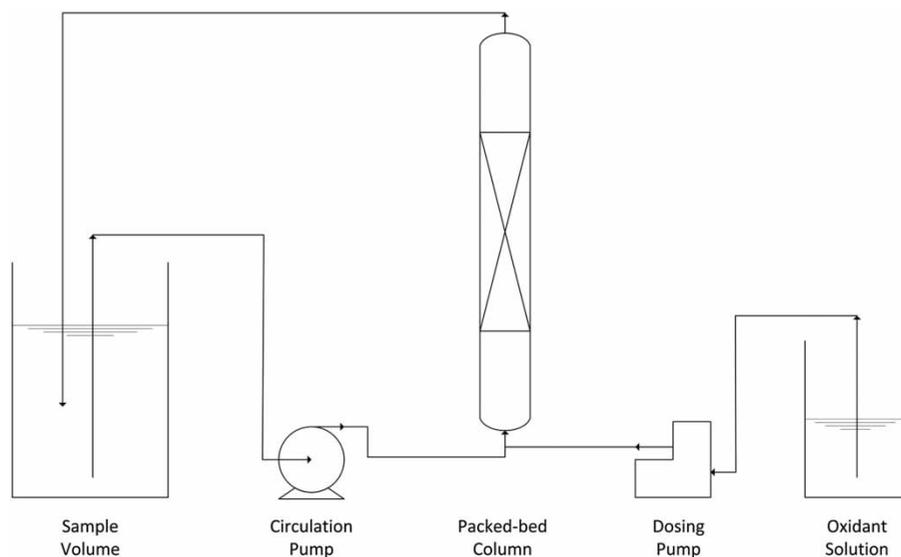
^aAs raw material sample 2, i.e. glass beads prepared by adhesion coating, were used.

The solution was gently stirred for 2 min, drained off and saved. In the second step, solution 2 was added, stirred, drained off and saved. The procedure was repeated for 15 min.

At the end of all the experiments, the solution was decanted, the media removed, carefully rinsed with demineralized water and air-dried. To minimize precipitation of MnO_{x(s)} from solution, the concentration of manganese and the oxidizing agent were chosen in different, less than stoichiometric concentrations.

(b) Synthetic MnO_{x(s)} coating in a packed-bed column: the most suitable batch experiment in terms of manganese removal was adapted to be conducted in a packed-bed

column (Figure 1). A 29-mm-diameter glass column was packed with 500 g of matted glass beads. A buffered (10⁻⁴ M HCO₃⁻) manganese solution (Mn²⁺ added as MnSO₄·H₂O) was prepared and pumped by a drill-powered circulation pump (model: Wolfcraft 1300 L/H 2202000) in an upward direction through the packed-bed column in a closed circuit. The bed fluidisation was adjusted to 40% hold-up and realized by a volume flow rate of 0.8–1.0 l/min. In total, 500 ml of an oxidant solution (NaClO, KMnO₄) was incrementally added by a dosing pump (model: Grundfos Smart Digital DDA 7.5-16) at the bottom of the column before entering the bed at 500 ml/h for a period of 50 min. Analogous to the batch experiments, the pH of the sample volume was regularly checked and adjusted to be maintained

**Figure 1** | Experimental setup for MnO_{x(s)} coating in a packed-bed column.

between 7.2 and 8.0 by adding 0.5 mol/l NaOH or 0.5 mol/l HCl, respectively. The circulation was continued for 40 min before the solution was discarded. Following this, demineralized water was pumped upflow until there was no visible particulate matter left in the effluent. Finally, the glass beads were removed and air-dried for further testing. For the preparation of sample 6 (column experiment), identical conditions in comparison with sample 5 (batch experiment) were chosen. For the preparation of sample 7, instead of matted glass beads, adhesive dry coated glass beads [sample 2] were used. Sample 8 was prepared by the column approach. Chemical concentrations of a manganese sand preparation technique described by *Teng et al. (2001)* were transferred to the packed-bed column setup. The initial Mn^{2+} concentration in the sample solution was set to 11,140 mg/l. As an oxidizing agent, KMnO_4 (HMnO_4 8,970 mg) was used, whereas the dosage time and the total reaction time remained constant at 50 min and 90 min, respectively.

Conditions for media synthesis by wet chemical coating are summarized in [Table 2](#).

Determination of Mn^{2+} , pH, O_2 and T

Before Mn^{2+} determination, the sample volume was filtered by a syringe filter (0.2 μm) to remove particulate matter. Partitioning of the sample was performed for threefold determination. The Mn^{2+} concentration of each 5-ml volume was determined by a rapid test (Merck 1.114770.0001), followed by an absorption measurement at 450-nm wavelength using a photometer (Analytik Jena, model: Specord 200).

Analogous to each sampling pH, temperature and O_2 concentration were monitored.

Temperature and pH were measured with a pH meter (Mettler Toledo, model: FG2/EL2). The O_2 concentration was determined using an oxygen sensor (PreSens, model: Fibox 3 trace v3).

Electron microscopy and image analysis

For scanning electron microscopy (SEM) analysis of the bead surface, samples were air-dried, glue-mounted and

coated with a gold-layer to a thickness of 8 nm by a Sputter Coater (Bal-TEC SCD005 70S). Electron micrographs were recorded by detecting secondary electrons at nominal magnifications of 80 \times , 300 \times and 2,500 \times using a JEOL JSM-5900LV electron microscope operated at 15 kV. For better contrast of the coated areas in comparison with the uncoated areas, additional images were taken at 300 \times magnification by detection of backscattered electrons (BSEs). Energy-dispersive X-ray spectroscopy (EDX) was performed at 300 \times magnification used for the chemical characterization of the top 1–2 μm of the bead surface.

Representative images of the media surface (300-fold magnification) from the BSE microscopy analysis were examined by the Java-based image processing program, ImageJ. The total coated area was determined using false-colour imaging.

Continuous stirred tank reactor

To determine the efficiency of the coated glass beads in terms of their efficiency to remove manganese from water, a reactor modelled after a system that was first described by *Carberry (1964)* was used. The reactor vessel (2 l) was placed in a heatable water bath. The vessel was filled with a buffered 20 mmol/l TRIS solution and adjusted to pH 8.5 by addition of H_2SO_4 . Then a concentration of 8 mg/l Mn^{2+} was adjusted by addition of MnSO_4 . The solution was heated to 35 $^\circ\text{C}$ and continuously aerated by a glass frit with pressurized air. The three wire cages of the rotating shaft were filled with 6 g of coated glass beads each, to form a thin layer of active material in each cage. The stirrer shaft was rotated at 200 rpm. In total, 15 ml of sample volume was withdrawn at the beginning and every 20 min until the end of the experiment at 80 min.

RESULTS AND DISCUSSION

Electron microscopy and image analysis

As part of SEM analysis, samples were viewed in secondary and BSE modes. The glass beads consist of soda-lime glass with its main constituents SiO_2 (72.5%) and other diverse types of metal oxides. The powdered coating material

MnO_x-78 consists of 78% MnO_x as well as Fe₂O₃, SiO₂ and Al₂O₃ as the main minor components. In the wet coating process, pure MnO_{x(s)} is deposited onto the media surface, as confirmed by EDX analysis. When examining the BSE image, brighter areas correspond with a higher relative nuclear density and atomic weight, i.e. in this case, the coating appears brighter than the bead. Thus, visual evaluation using ImageJ as an image processing software gives a measure for the success of the coating process. For elemental identification of the surface or surface features, EDX analysis was conducted.

SEM analysis of sample 1 shows a sparse distribution of the powdered coating material on the media surface (Figure 2(a) and 2(b)). The visual evaluation of Figure 2(b) by ImageJ shows that around one-third (35%) of the bead surface was successfully coated with the application of a silane binding agent. EDX analysis confirmed the presence of Mn on bright areas.

Figure 3(a) and 3(b) show raw matted glass beads and illustrates that the matting could be successfully accomplished by tumbling the beads with the addition of SiC. Figure 3(a) shows an even distribution of layered spalling on the bead surface, which results in an increase in the possible coating area.

Figure 4 shows an even distribution of the coating material on the bead surface of sample 2. Image analysis of Figure 4(b), as a result of a BSE microscopy analysis, shows that around 50% of the surface was successfully coated. EDX analysis of the bead surface of Figure 4(b) shows the same image in the BSE mode in Figure 5.

EDX analysis was performed on a representative dark and bright spot of the image (Figure 5). The X-rays emitted from the sample surface, plotted as a spectrum, illustrate that there are different elements present on the bead's surface. Si, Na, O, Ca and Au are detected on dark as well as bright areas. Other than Au, which is present because of sample preparation (gold coating), these are the primary elements of the glass bead. Except for O, which is present not only in the bead but also in the coating material MnO_x-78, these elements are more prevalent on dark spots. Mn is absent on dark spots, in contrast to bright areas where Mn is detected. Thus, it can be concluded that the flaky and finely ground material seen on those bright spots is MnO_x-78, proving the occurrence of the coating material on the bead surface even after rinsing the beads. Thus, provided laminar conditions, it can be assumed that those beads are suited for deep bed filtration.

Figure 6(a) and 6(b) show a smooth distribution of synthetic MnO_{x(s)} on the media surface of sample 6. On top of a solid cementation, fine particles of manganese oxides can be observed on the bead surface, which are similar in appearance to the media surface of synthetically coated anthracite in a study performed by Merkle *et al.* (1997). The ubiquitous presence of Mn on the media surface detected by EDX analysis implies that there is a uniform and complete coating of the surface. BSE microscopy analysis shows brighter and darker spots, indicating a coating layer with a different layer thickness of MnO_{x(s)}. On darker spots, the electron beam could penetrate the MnO_{x(s)} layer, and detected, besides Mn and O, the elements

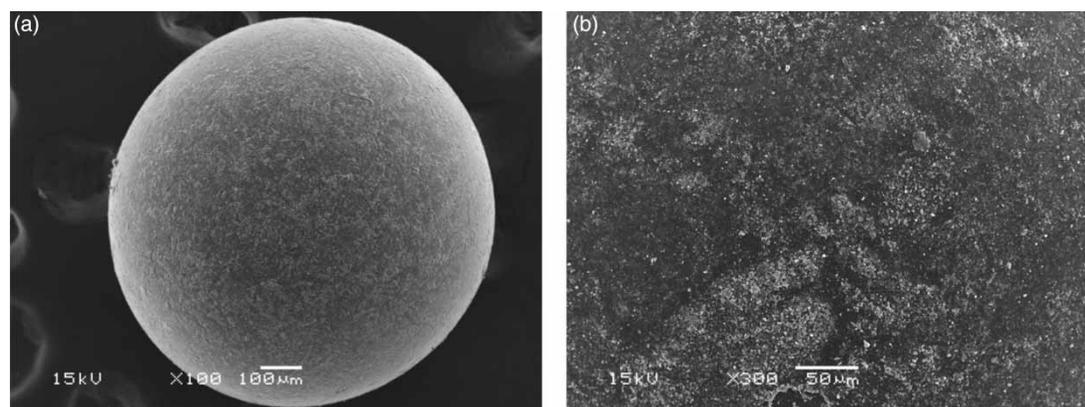


Figure 2 | Sample 1, dry coating with powdered MnO_x-78 by silane as a binding agent: (a) BSE image 100× magnification; (b) BSE image 300× magnification.

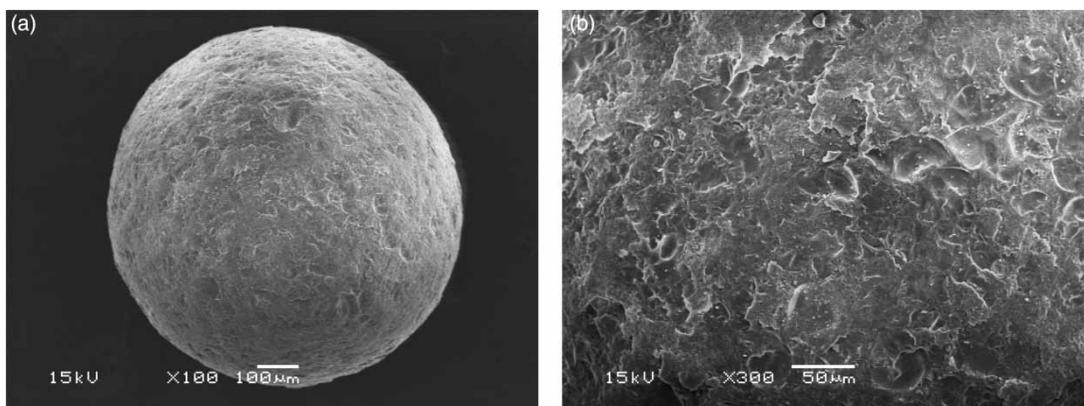


Figure 3 | Matted (roughened) glass bead as carrier material: (a) BSE image 100× magnification; (b) BSE image 300× magnification.

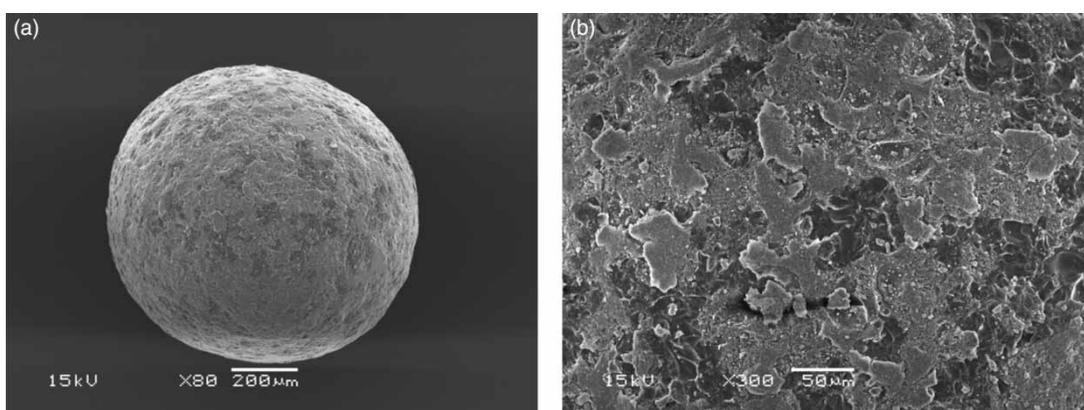


Figure 4 | Sample 2, adhesive dry coating with powdered MnO_x-78: (a) BSE image 80× magnification; (b) BSE image 300× magnification.

of the carrier bead. Considering the coarse surface of the matted carrier bead in [Figure 3\(a\)](#) in comparison with the smooth appearing surface of sample 6 in [Figure 6\(a\)](#), it can be concluded that MnO_{x(s)} deposited more quickly in recessed sites and evened out the bead surface.

The synthetic coating of sample 8 observed at the micron scale ([Figure 7\(a\)](#) and [7\(b\)](#)) is composed of small particles on the top of globular patches of manganese oxides. Merely O, Mn and Au (from media preparation for SEM) were detected by EDX analysis, which proves a complete and thick covering of the bead surface by synthetic MnO_{x(s)}.

[Figure 8](#) shows a BSE image at 2,500× magnification of a representative glass bead coated using the batch approach (sample 3). Compared with a bead coated using the column approach ([Figure 6\(b\)](#)), fine particles of MnO_{x(s)} are less prevalent on the bead surface. In addition, the MnO_{x(s)} foundation appears to be less solid. The bead surface shows

cracks and spalling, as can be seen in the upper left portion of [Figure 8](#). Within the region seen on the right hand side of the image, no foundation is visible at all.

An X-ray spectrum of a representative bright spot of the differently coated samples at 300-fold magnification ([Figure 9](#)) proves that more Mn was deposited on the bead surface using the column approach. Si, Na, Mg and Ca as primary elements of the glass beads were found in considerably higher concentrations on sample 3 (batch approach) than on sample 6 (column approach), whereas Mn was found in larger quantities on sample 6, confirming that coating using the column approach proved to be more successful.

BSE images of samples 5 and 7 are not shown in these findings. Because of the omnipresence of Mn on all areas of the representative BSE image, as detected by EDX analysis, a complete covering of the bead surface by synthetic

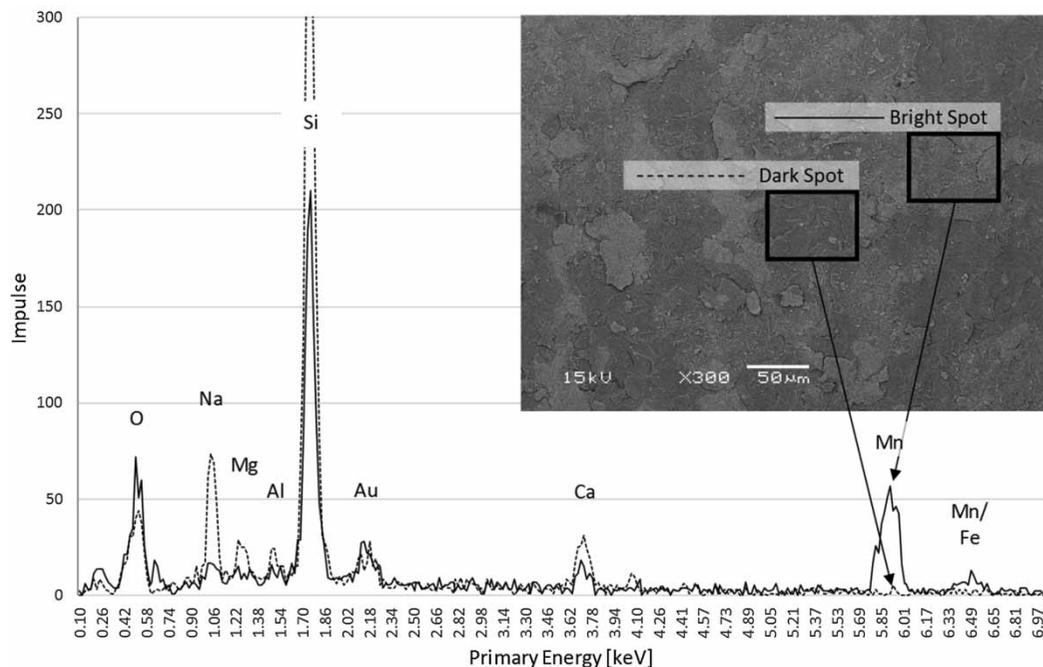


Figure 5 | EDX spectrum of sample 2 on dark and bright spots.

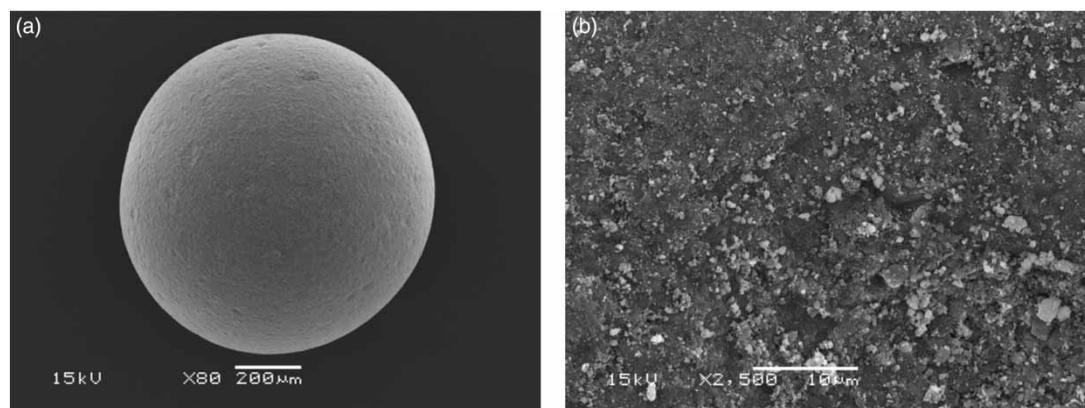


Figure 6 | Sample 6, synthetic $\text{MnO}_{x(s)}$ coating with NaClO as an oxidant: (a) BSE image $80\times$ magnification; (b) BSE image $2,500\times$ magnification.

$\text{MnO}_{x(s)}$ can be concluded. EDX results of samples 3–6 (batch approach) showed a higher presence of Si, Na, Mg and Ca than those of samples 6–8 (column approach), indicating a generally thinner layer of $\text{MnO}_{x(s)}$ on the bead surface.

Continuous stirred tank reactor

Experimental conditions in the continuous stirred tank reactor are summarized in Table 3. Figure 10 shows the

course of the Mn^{2+} concentration in the stirred tank reactor investigating dry coated glass beads. The graph of sample 1 illustrates that there is a marginal slope, indicating an inadequate performance of those beads with regard to demanganization purposes. Under the given conditions (Table 3), the beads coated by applying silane as a binding agent (sample 1) were exhausted after 20 min and showed a total sorption uptake of $0.04 \text{ mg Mn}^{2+}/\text{g}$ filter media. The low performance of this sample may be explained by a comparably low coverage of surface area

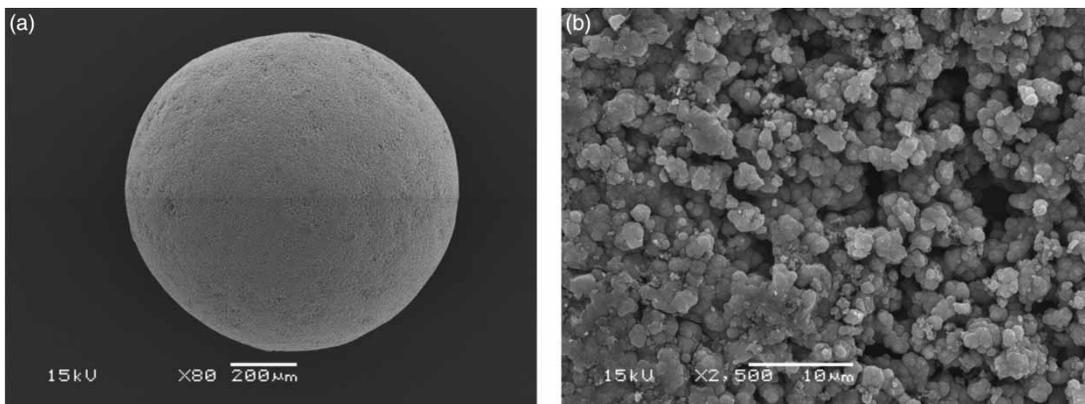


Figure 7 | Sample 8, synthetic $\text{MnO}_{x(s)}$ coating with KMnO_4 as an oxidant: (a) BSE image $80\times$ magnification; (b) BSE image $2,500\times$ magnification.

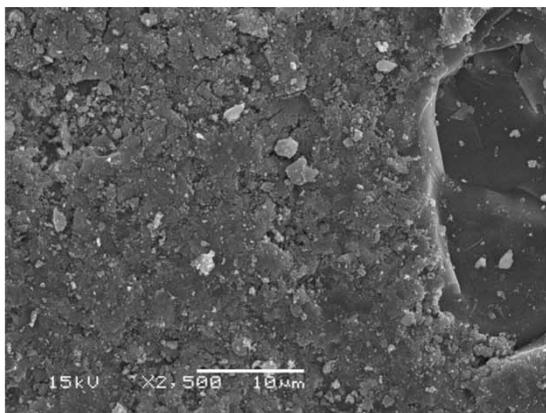


Figure 8 | BSE image $2,500\times$ magnification, synthetic $\text{MnO}_{x(s)}$ coating with NaClO as an oxidant: bead coated using the batch approach (sample 3).

(35%, Figure 2). However, the coverage of active adsorption sites on the MnO_x -78 coating material by silane is more likely; thus, the performance was significantly inhibited. Glass beads coated by adhesive dry coating are able to uptake 0.20 mg/g after 80 min of test time. When investigating the most effective beads, instead of reaching a steady state, a progressive constant decline of Mn^{2+} in solution was observed. This can be explained by the fact that at a pH of 8.5 and in the presence of oxygen and Mn^{2+} , $\text{MnO}_{x(s)}$ on the bead surface coordinates H_2O molecules, i.e. $\text{MnO}(\text{OH})_{2(s)}$ is formed, which is repeatedly capable of adsorbing Mn^{2+} (Stumm 1997) so that the collector beads are never fully exhausted.

Figure 11 presents the course of the Mn^{2+} concentration in the continuous stirred tank reactor investigating

wet coated glass beads. The graphs of the samples 3 to 5 present the results of the samples prepared in a beaker, i.e. using the batch approach. Samples 6 to 8 were prepared in a packed-bed column using a continuous closed circuit to pump the Mn^{2+} solution through the column in an upflow direction (column approach). The results illustrate an early exhaustion of the beads coated using the batch approach (samples 3 to 5), which means that no further decrease in the Mn^{2+} concentration in the reactor can be observed after 80 min. The reduction of Mn^{2+} by samples 7 and 8 proved to be more successful. Sample 8 reduced the Mn^{2+} concentration in the reactor by 97% within 80 min and showed a sorption uptake of 0.42 mg/g. Sample 6 adsorbed 0.09 mg/g and sample 7 adsorbed 0.26 g/mg Mn^{2+} within the 80 min test time, indicating that a combination of the two approaches (dry and wet method) results in higher sorptive capacity of the filter medium. Samples 4 and 6 were prepared under the same conditions but using a different experimental setup (batch vs. column approach). As illustrated before, compared with sample 4, a thicker and more homogenous layer of $\text{MnO}_{x(s)}$ was deposited on the surface of sample 6, which indicates that the column setup is a more efficient approach to coat glass beads. Because of the use of a higher concentration of reactants to prepare sample 8, strong colloidal precipitation as well as flock formation of $\text{MnO}_{x(s)}$ occurred. Nonetheless, a uniform and thick layer of $\text{MnO}_{x(s)}$ was deposited on the surface (Figure 7), resulting in a very potent filter medium with a distinct ability to adsorb Mn^{2+} from water.

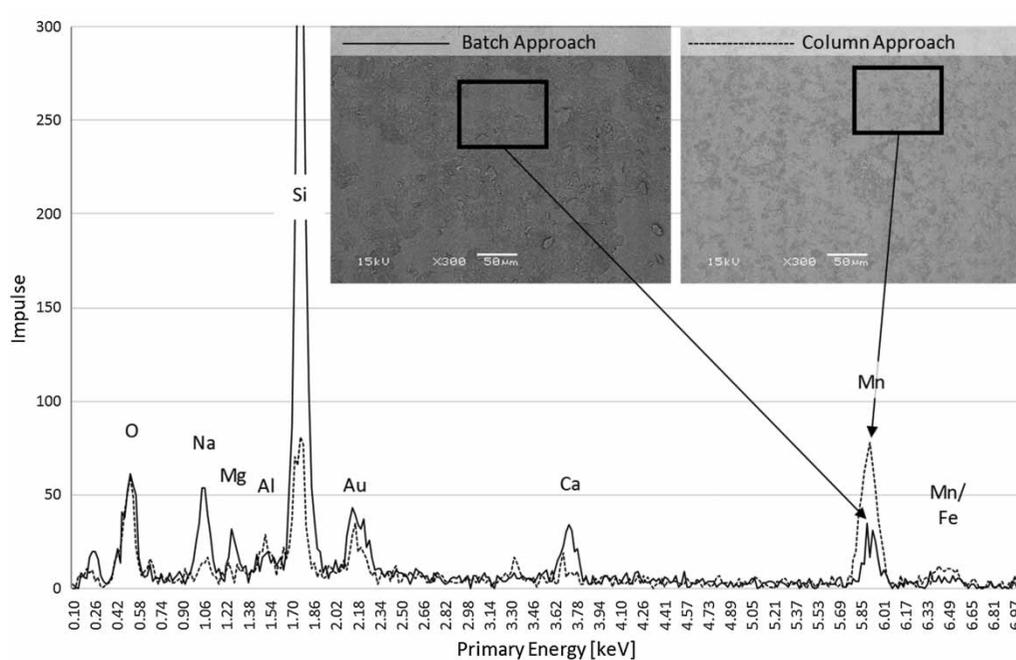


Figure 9 | EDX spectrum of a bead coated using the column approach (sample 6) in comparison with a bead coated using the batch approach (sample 3).

Table 3 | Experimental conditions in the continuous stirred tank reactor

Sample number	Test time [min]	Temperature T [°C]	c(O ₂) [mg/l]	pH ₀	pH _{end}	Sorption uptake q _{80min} [mg/g]
1	80	35	5.8	8.55	8.48	0.04
2	240	35	5.8	8.46	8.37	0.20
3	60	35	5.8	8.45	8.41	0
4	80	35	5.8	8.44	8.39	0.09
5	80	35	5.8	8.45	8.40	0.06
6	240	35	5.8	8.46	8.39	0.09
7	180	35	5.8	8.54	8.45	0.26
8	80	35	5.8	8.34	8.17	0.42

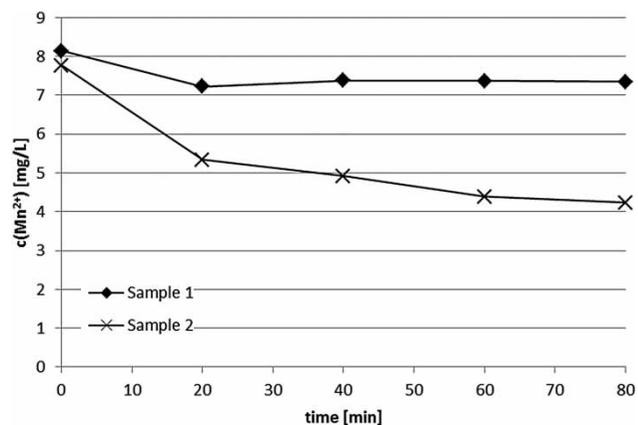


Figure 10 | Course of Mn²⁺ concentration in the continuous stirred tank reactor while testing dry coated glass beads.

With regard to the column approach, the controlled dosage of an oxidizing agent directly before entering the filter bed causes the sample solution to immediately contact the glass beads. The fluidization of the filter bed to a defined bed height ensures optimal mixing and contact of the sample solution with the filter media, which results in uniform coating. The simple operation as well as an uncomplicated rinsing by backwashing at the end of the coating procedure indicates that the

column approach may be economically advantageous for scale-up.

CONCLUSIONS

Different techniques for coating glass beads with a powdered sorptive material as well as methods to synthetically coat glass beads with MnO_{x(s)} were newly developed or

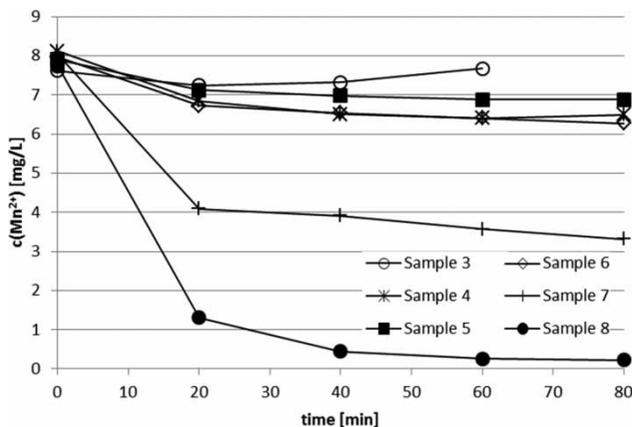


Figure 11 | Course of Mn^{2+} concentration in the continuous stirred tank reactor while testing wet coated glass beads.

refined. Glass beads prepared by dry adhesive coating successfully remove Mn^{2+} from water at a given pH of 8.5 and an O_2 concentration of 5.8 mg/l. By refining the experimental setup from a batch approach described by Merkle et al. (1997) to a setup where the filter media are coated in a packed bed column, potent filter media with an even and homogenous coating can be produced. In contrast to the use of conventional filter media such as quartz sand, where foreign inclusions such as feldspar will reduce the adsorption capacity of the filter media after a number of backwashings (Mörgili & Ives 1979), glass beads are uniformly composed. In conjunction with their high physico-chemical stability as well as their optimal hydraulic performance (Treskatis 2011; Klaus et al. 2014), $\text{MnO}_{x(s)}$ -coated glass beads promise to be a viable alternative to conventional filter media, such as quartz sand and granular manganese ores. The ability of Mn oxides to adsorb heavy metals such as Pb^{2+} , Cu^{2+} , Co^{2+} , Cd^{2+} , Zn^{2+} and Tl^+ (Gadde & Laitinen 1974; Xiong Han Fenga et al. 2007) suggests additional applications of glass beads for the adsorption of contaminants in water, which are commonly associated with mine drainages or landfill leachates.

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