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Bimetallic oxide-coated sand filter for simultaneous removal of bacteria, Fe(II), and Mn(II) in small- and pilot-scale column experiments

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ABSTRACT

The aim of this study was to examine the simultaneous removal of bacteria, Fe(II), and Mn(II) by iron-manganese bimetallic oxide-coated sand (IMCS) using small-scale (length = 20 cm, inner diameter = 2.5 cm) and pilot-scale (length = 140 cm, height of filter media = 100 cm, inner diameter = 20 cm) column experiments. Small-scale column experiments showed that the Mn(II) removal capacity of IMCS ($q_{eq} = 0.027\ \mathrm{mg\ g^{-1}}$) was greater than that of iron oxide-coated sand (ICS) ($q_{eq} = 0.020\ \mathrm{g\ g^{-1}}$), manganese oxide-coated sand (MCS, $q_{eq} = 0.012\ \mathrm{mg\ g^{-1}}$), and dual media containing ICS and MCS ($q_{eq} = 0.015\ \mathrm{mg\ g^{-1}}$). The Fe(II) removal capacity of IMCS ($q_{eq} = 0.034\ \mathrm{mg\ g^{-1}}$) was similar to that of ICS ($q_{eq} = 0.035\ \mathrm{mg\ g^{-1}}$), MCS ($q_{eq} = 0.035\ \mathrm{mg\ g^{-1}}$), and ICS/MCS ($q_{eq} = 0.034\ \mathrm{mg\ g^{-1}}$). Simultaneous removal experiments in small columns indicated that the bacterial removal capacity of IMCS ($q_{eq} = 7.158\ \mathrm{mg\ g^{-1}}$) in solution containing Fe(II) and bacteria was greater than that in solution with Mn(II) and bacteria ($q_{eq} = 4.031\ \mathrm{mg\ g^{-1}}$). For solutions with Fe(II), Mn(II), and bacteria, the bacterial removal capacity of IMCS was $6.636\ \mathrm{mg\ g^{-1}}$, which was greater than that in samples with Mn(II) and bacteria. These results indicated that bacterial removal capacity was improved in the presence of Fe(II). Pilot-scale column experiments (46-day operation) showed that the removal capacities of IMCS for Fe(II), Mn(II), and bacteria were 0.059, 0.068, and $1.187\ \mathrm{mg\ g^{-1}}$, respectively. The long-term experiments demonstrated that IMCS was effective as an adsorptive filter medium for the simultaneous removal of Fe(II) and bacteria. However, chemical additions might be necessary for Mn(II) removal to meet the water quality limit.

Keywords: Bacteria; Bimetallic oxide-coated sand; Column experiment; Iron; Manganese

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1. Introduction

Soluble forms of Fe(II) and Mn(II) are released from sediments to aquatic environments in anoxic conditions [1]. These soluble forms can cause several aesthetic and health problems, such as water discoloration, a metallic taste, odor, turbidity, biofouling, corrosion of plumbing fixtures, and staining of laundry [2]. Manganese concentrations of 0.05 mg L^{-1} and iron concentrations of 0.3 mg L^{-1} have been regulated by the United States Environmental Protection Agency [3], while the World Health Organization [4] has not established the maximum concentrations for both iron and manganese in drinking water. The toxicity associated with most heavy metals is the result of chronic exposure, and in general, very low concentrations do not result in acute toxicity. A single bacterium, however, can cause disease, leading to a tremendous public health problems in cases where epidemics arise. Diarrhea, cholera, typhoid, and schistosomiasis are the leading water-borne diseases caused by pathogenic bacteria in contaminated water [5]. The annual number of deaths caused by diarrheal diseases due to lack of access to safe drinking water and inadequate sanitation is 1.8 million. Diarrheal disease is the second most common cause of infant deaths worldwide [6].

Filtration has been a widely used water treatment method for centuries because of its low cost, low energy requirement, and ease of operation. In 4,000 B.C., ancient Sanskrit and Greek writings suggested different ways to treat water—one of which was purifying water by filtration through sand and coarse gravel [7]. Since particles are removed from water during filtration, both the esthetic and microbial quality of water are improved, in contrast to other inexpensive processes such as solar disinfection, chlorination, and boiling, which only destroy micro-organisms. Although granular media filtration is inexpensive and effective for removal of particulate matter, filtration by sand cannot effectively eliminate contaminants such as bacteria and some heavy metals because of their small size and negative charge. To overcome this limitation, several researchers have investigated the use of metal oxide-coated sand as a filter medium [2,8–15]. Because the synthesis of metal oxide-coated sand does not require complex manufacturing processes or expensive equipment, this filtration method could be easily used for household water treatment.

The application of metal oxide-coated sand for water/wastewater treatment has been studied by two different approaches. The first method has focused on the removal of micro-organisms such as bacteria and viruses by using various metal oxide-coated sands, including aluminum oxide-coated sand (ACS) [8], iron hydr(oxide)-coated sand (ICS) [10,12,13,16], and aluminum/iron oxide-coated sand [14,16,17]. The second approach involves the use of metal oxide for the removal of inorganic pollutants such as arsenic, cadmium, chromium, copper, and lead from water [11,18–27]. Benjamin et al. [28] reported that iron oxide-coated sand (ICS) was effective for the removal of both heavy metals (Cu, Cd, Pb, Ni, and Zn) and oxyanions (SeO_3, AsO_3) from wastewater. Among inorganic pollutants, arsenic removal by metal oxide-coated sand has attracted much attention and has been widely investigated by many researchers. Batch studies and column studies for the removal of As(III) and As (V) by iron-coated sand and binary iron and manganese-coated sand, respectively, have been reported [29].

Only a few research groups have investigated the simultaneous elimination of bacteria and heavy metals using metal oxide-coated sand. Ahammed and Meera [13] conducted laboratory-scale column experiments packed with manganese oxide-coated sand (MCS) and ICS for the removal of both bacteria and heavy metals from natural waters. However, further experiments with different filter media would be required to improve the applicability of metal oxide-coated sand for water/wastewater treatment. Fe(II)and Mn(II) are positively charged, while bacteria have negatively charged surfaces. Therefore, the simultaneous removal of Fe(II), Mn(II), and bacteria is challenging.

This study is a follow-up of a previous study where several factors (filter media, bacterial injection concentration, flow rate, and oxyanions) influencing removal of bacteria from aqueous solutions by iron-manganese bimetallic oxide-coated sand (IMCS) were investigated [15]. In this study, we extended our previous research by assessing the feasibility of using IMCS as a filter medium for the simultaneous removal of bacteria, Fe(II), and Mn(II) through small- and pilot-scale column experiments.

2. Materials and methods

2.1. Filter media

IMCS was prepared from quartz sand (Jumunjin Silica, Kangreung, Korea), which was sieved to a grain size of 0.5–1.0 mm. Samples of 0.1 M $Fe(NO_3)_3 \cdot 9H_2O$ and 0.1 M $Mn(NO_3)_2 \cdot 6H_2O$ were dissolved in deionized water (100 mL), and the pH of the solution was adjusted to pH 7 with 6 N NaOH. Quartz sand (200 g) was added to the solution and then mixed in a heated rotary evaporator (90°C, 80 rpm, and 20 min) (Hahnvapor, Hahnshin Scientific Co., Korea) to remove the water in the suspension. The coated sand was dried at 150°C for 6 h, and the coating procedure was repeated.

Finally, the coated sand was washed with deionized water and dried again under the same conditions [15].

MCS and ICS were prepared with 0.2 M Mn $(NO_3)_2{\cdot}6H_2O$ and 0.2 M $Fe(NO_3)_3{\cdot}9H_2O$, respectively, following the same procedures. The point of zero charge (PZC) of the IMCS was determined by measuring the zeta potential at various pH conditions (pH 6–10), which were prepared using dilute HNO_3/NaOH. The specific area of the IMCS was determined using a Brunauer–Emmett–Teller (BET) analyzer (ASAP 2010, Micromeritics Instrument Corporation, GA, USA). The amounts of Fe and Mn in the ICS, MCS, and IMCS were quantified according to EPA Method 3050B. Powder X-ray diffraction (XRD) analysis was conducted with CuKα radiation ($\lambda = 1.5406$ Å) and step size of 0.02° (2θ), at 40 kV and 40 mA over a scan range of 20–80 θ [15].

2.2. Small-scale column experiments

Small-scale column experiments (Table 1) were conducted using a Plexiglas column (length = 20 cm, inner diameter = 2.5 cm) packed with filter media (mass of medium 165.1 ± 0.8 g) using the tap-fill method to attain a bulk density of $1.682 \pm 0.008\ \text{g cm}^{-3}$ and a porosity of 0.365 ± 0.003. The column was connected to an HPLC pump (Series II, Scientific Systems, Inc., USA) operating at a constant flow rate of $2.0\ \text{mL min}^{-1}$.

To compare the removal of Fe(II) and Mn(II) by different filter media (ICS, MCS, ICS/MCS, and IMCS), column experiments (Exps. 1–4) were performed (Table 1). Mn(II) solution ($1\ \text{mg L}^{-1}$) and Fe(II) solution (3 mg/L) were prepared by dissolving Mn $(NO_3)_2{\cdot}6H_2O$ (Kanto Chemical, Japan) or $FeSO_4{\cdot}7H_2O$ (Kanto Chemical, Japan) in deionized water, to which N_2 was purged before use in order to prevent oxidation of Mn(II) and Fe(II). $NaNO_3$ (10 mM) (Daejung Chemical, Korea) was added to Fe(II) and Mn(II) solutions as background electrolyte. Before injection of Fe(II) and Mn(II) solutions, the packed column was flushed with 7 pore volumes of 10 mM $NaNO_3$ solution to remove impurities and to achieve a steady state flow. Effluent samples were collected at regular intervals using an auto collector (Retriever 500, Teledyne, USA) to analyze pH, electric conductivity (EC), and bacterial concentration. pH and EC were measured with a pH probe (9107BN, Orion, USA) and an EC probe (815PDL, Istek, Korea), respectively.

To test the applicability of IMCS for the removal of Fe(II) or Mn(II) in the presence of bacteria, two sets of column experiments (Exps. 5–6) were conducted (Table 1). Fe(II) ($1\ \text{mg L}^{-1}$) or Mn(II) ($3\ \text{mg L}^{-1}$) in a solution of *Escherichia coli* ATCC 11105 at an $OD_{600} = 0.15$ was added to the column at a flow rate of $2.0\ \text{mL min}^{-1}$. With the exception of the composition of the injected solution, all experimental conditions were the same as described above. *E coli* ATCC 11105 used in this experiment was obtained from the Korea Culture Center. Bacteria were prepared as described previously [15]. Briefly, bacteria were cultured in LB medium (10 g

Table 1
Experimental conditions and results for small-scale column experiments

Exp.	Filter media	Contaminant	Injection conc. (mg L^{-1})	m_{total} (mg)	q_{total} (mg)	Re (%)	q_{eq} (mg g^{-1})
1	ICS	Fe(II)	1.0	5.76	5.73	99.5	0.035
		Mn(II)	3.0	17.28	3.35	19.4	0.020
2	MCS	Fe(II)	1.0	5.76	5.74	99.6	0.035
		Mn(II)	3.0	17.28	1.98	11.4	0.012
3	ICS/MCS	Fe(II)	1.0	5.76	5.60	97.2	0.034
		Mn(II)	3.0	17.28	2.54	14.7	0.015
4	IMCS	Fe(II)	1.0	5.76	5.64	97.9	0.034
		Mn(II)	3.0	17.28	4.39	25.4	0.027
5	IMCS	Fe(II)	1.0	5.76	5.71	99.2	0.035
		Bacteria	300	1728.0	1181.8	68.4	7.158
6	IMCS	Mn(II)	3.0	17.28	5.70	33.0	0.035
		Bacteria	300	1728.0	665.5	38.5	4.031
7	IMCS	Fe(II)	1.0	5.76	5.54	96.2	0.035
		Mn(II)	3.0	17.28	5.46	31.6	0.033
		Bacteria	300	1728.0	1095.7	63.4	6.636
7B[a]	IMCS	Fe(II)	1.0	5.76	5.54	96.2	0.035
		Mn(II)	3.0	17.28	2.16	12.5	0.013
		Bacteria	300	1728.0	1191.7	69.0	10.466

[a] Denotes that this experiment followed the backwashing process of Exp. 7.

tryptone, 5 g yeast extract, and 5 g NaCl per liter of deionized water at pH 7.0) over a period of 84 h. The suspension was harvested by centrifugation at 10,000 rpm for 15 min at 4˚C. The supernatant was removed and replaced with deionized water to prevent bacterial growth. Diluted bacteria were centrifuged again under the same conditions, washed three times with deionized water, and resuspended in distilled water or a sodium-based solution to adjust the bacterial concentration. Bacterial concentration was determined by measuring the optical density of the effluent using a UV–vis spectrophotometer (Helios, Thermo, USA) at 600 nm (OD_{600}). The mass of bacteria in solution had a strong linear correlation ($R^2 = 0.99$) with OD_{600} (OD_{600} of 1.0 corresponded to a bacterial mass concentration of 2.0 g L^{-1} and 6.0×10^9 CFU mL^{-1}) [15].

Two small-scale column experiments for the simultaneous removal of bacteria, Fe(II), and Mn(II) were carried out consecutively to investigate the effect of backwashing on the removal capacity of IMCS. Both Exp. 7 (before backwashing) and Exp. 7B (after backwashing) were performed under identical conditions. The column packed with IMCS was charged with tap water, and a solution of bacteria (300 mg L^{-1}), Fe(II) (1 mg L^{-1}), and Mn(II) (3 mg L^{-1}) was added at a flow rate of 2 mL min^{-1} for 48 h. After Exp. 7, the IMCS was backwashed with 0.1 mM HCl at a flow rate of 4 mL min^{-1} for 40 min.

2.3. Long-term pilot-scale column experiment

The pilot-scale column experiment (Table 2) was performed for 46 days using a Plexiglas column (length = 140 cm, inner diameter = 20 cm) with four sampling ports at 30, 50, 70, and 90 cm distance from outlet, i.e. four sampling port located at 20, 40, 60, and 80 cm far from the surface of filter media as shown in Fig. 1. The columns were filled with the same type of IMCS used in the small-scale column experiments. Layers of gravel (5 and 10 cm) were placed at the top and bottom of the column, respectively, to prevent erosion of the top layer of filter media and loss of filter media while the solution flowed through the column. In the experiment, bacteria (4.2×10^7 CFU mL^{-1}, $OD_{600} = 0.015$) were seeded in tap water (pH = 7.67 ± 0.21; EC = 145.9 ± 10.3 μS cm^{-1}) that had been subjected to room air for two days. Seeded tap water was prepared daily. Bacterial solution was added to the column using a peristaltic pump (Masterflex L/S, Cole-Parmer, PA) at a flow rate of 45.8 mL min^{-1}, which was equivalent to 5.8×10^{-3} cm sec^{-1} (5 m day^{-1}) of linear velocity and 4.8 h of empty bed contact time. The sample from each port and outlet were collected once a day, and bacteria, Fe(II), and Mn(II) concentrations were analyzed.

Table 2
Experimental conditions for long-term pilot-scale column experiments

Parameters	Values
Column material	Acryl
Filter media	IMCS
Height of column	140 cm
Height of filter media	100 cm
Inner diameter	20 cm
Flow rate	45.8 mL min^{-1}
Linear velocity	5.8×10^{-3} cm sec^{-1} (5 m day^{-1})
Hydraulic retention time	4.8 h

Bacterial concentration in the effluent was determined using the spread plate method on LB agar (LB medium with 1.5 g agar per 100 mL). The collected samples were serially diluted and 0.1 mL of each sample was spread over the prepared agar plates with pre-sterilized metal loops and incubated at 37˚C for 24 h. The bacterial concentration was expressed as CFU mL^{-1} [15]. Samples were filtered with 0.45-μm syringe filters, and iron and manganese were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 2000 DV, Perkin–Elmer).

2.4. Data analysis

The total mass of Fe(II), Mn(II), and bacteria injected into the column (m_{total}, g) during the experiment was calculated as follows:

$$m_{\text{total}} = \frac{C_0 Q t_{\text{total}}}{1000} \tag{1}$$

where C_0 is the influent concentration of Fe(II), Mn(II), and bacteria; Q is the volumetric flow rate; and t_{total} is the total flow time. The removal capacity of the column for Fe(II), Mn(II), and bacteria (q_{total}) at a given flow rate and influent concentration was quantified as follows:

$$q_{\text{total}} = \frac{Q}{1000} \int_{t=0}^{t=t_{\text{total}}} (C_0 - C)\,\mathrm{d}t \tag{2}$$

where C is the effluent concentration of Fe(II), Mn(II), and bacteria. The total removal percentage of Fe(II), Mn(II), and bacteria during the experiment (Re, %) was determined as follows:

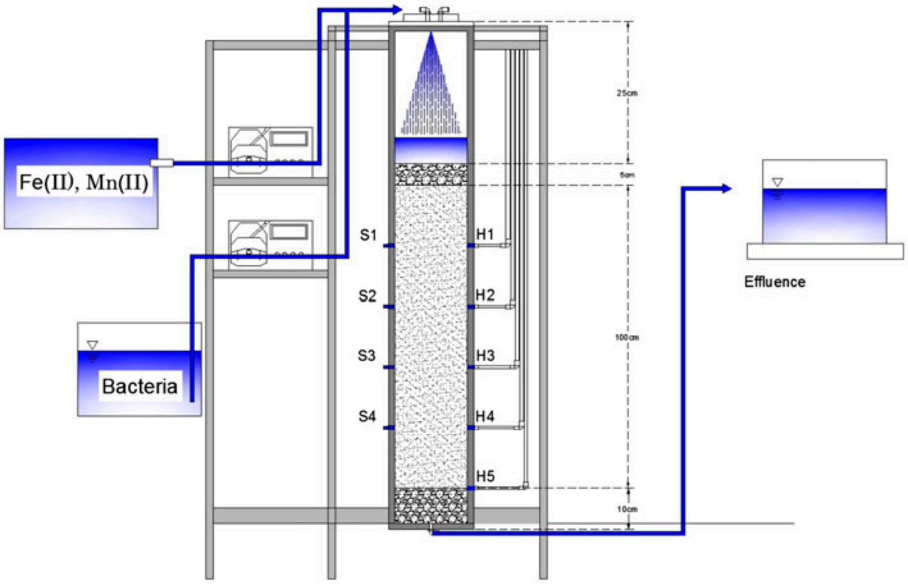

Fig. 1. Schematic diagram of long-term pilot-scale column experiment. Sampling ports (S1–4) and hydraulic head measurement ports (H1–5) are shown.

$$\mathrm{Re} = \left(\frac{q_{\mathrm{total}}}{m_{\mathrm{total}}}\right) \times 100 \tag{3}$$

The mass of removed Fe(II), Mn(II), and bacteria per unit mass of filter medium (q_{eq}) was calculated as follows:

$$q_{\mathrm{eq}} = \frac{q_{\mathrm{total}}}{M_f} \tag{4}$$

where M_f is the mass of filter medium in the column.

3. Results and discussion

3.1. Removal of Fe(II) and Mn(II) in small-scale columns

The evaluation of Fe(II) and Mn(II) removal with ICS, MCS, ICS/MCS, and IMCS was conducted through analysis of breakthrough curves (BTCs) obtained from column experiments (Fig. 2). The BTCs for Fe(II) and Mn(II) were analyzed for removal, as solutions containing these compounds moved through the fixed bed columns packed with different filter media. BTCs were constructed as plots of the operation time vs. the relative concentration of the injected metal in the effluent. The BTCs for Fe(II) were at the bottom of the plots, indicating that Fe(II) was almost completely removed while it passed through the columns packed with ICS, MCS, ICS/MCS, and IMCS. By contrast, the BTCs for Mn(II) showed high concentrations of this compound in the effluent with the early breakthrough starting points, and the peak height and breakthrough starting points of the BTCs were substantially different depending on the filter medium.

The comparison of Mn(II) BTCs in different filter media is shown in Fig. 3. The BTCs for IMCS had the lowest plateaus and the most delayed saturation, indicating that IMCS was the most effective media for removing Mn(II). Based on the BTC shape and breakpoint, the Mn(II) removal efficiency of the fixed-bed columns was ranked in decreasing order as IMCS > ICS > ICS/MCS > MCS. Table 1 shows that the Mn(II) removal efficiency (Re) was listed in decreasing order as IMCS, ICS, ICS/MCS, and MCS. The Mn(II) removal efficiency in IMCS (Re = 25.4%) was higher than that in other filter media. The Mn(II) capacity of IMCS ($q_{\mathrm{total}} = 4.39\,\mathrm{mg\,g^{-1}}$) was also the highest among the filter media used in this study. In addition, the value of q_{eq} for IMCS ($q_{\mathrm{eq}} = 0.027\,\mathrm{mg\,g^{-1}}$) was more than two times higher than that for MCS ($q_{\mathrm{eq}} = 0.012\,\mathrm{mg\,g^{-1}}$). The results indicated that IMCS was much more effective for Mn(II) removal than other filter media.

The removal of Fe(II) and Mn(II) by different metal oxide-coated sands varied, in that the removal efficiency of Mn(II) by the four different filter media was low, ranging from 11.4% to 25.4%, but was greater than 97.2% for Fe(II). The higher removal efficiency of Fe(II) compared to Mn(II) can be explained by the fact that the precipitation of Fe(II) was more favorable than Mn(II). From the simulation of the aqueous

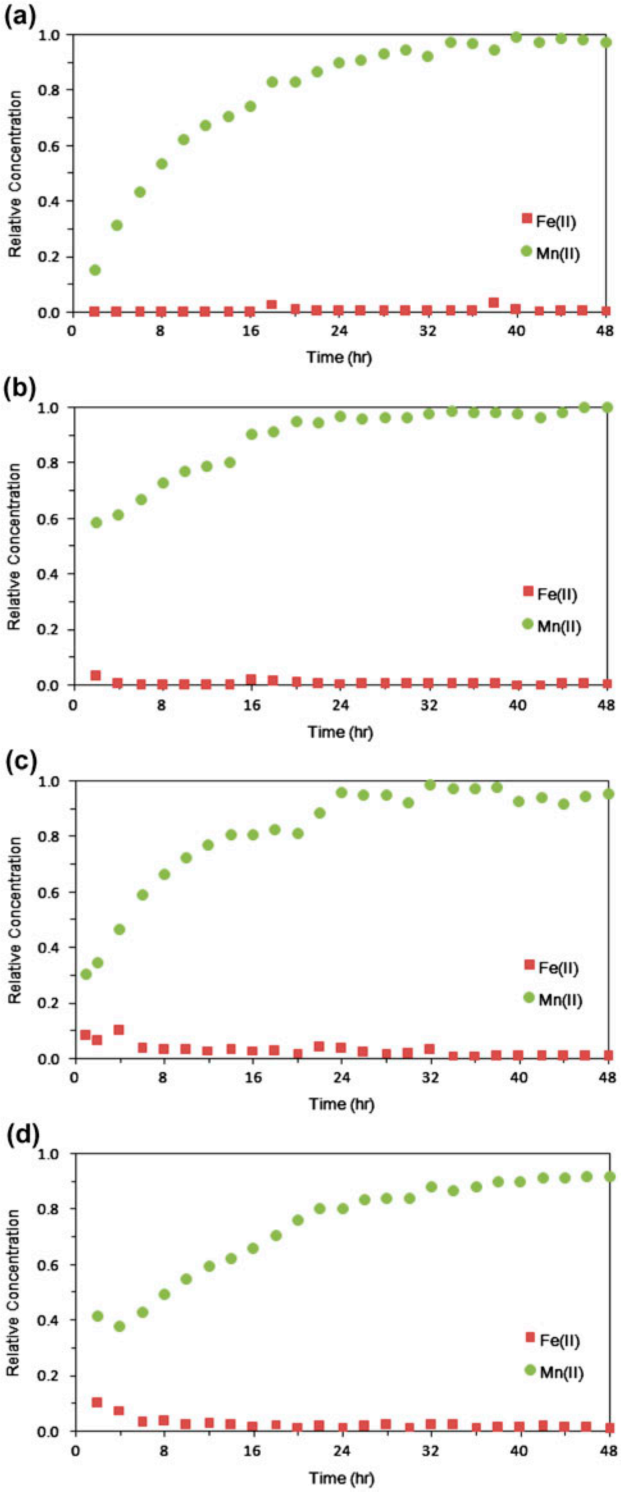

Fig. 2. Breakthrough curves of Fe(II) and Mn(II) obtained from small-scale column experiments packed with different filter media: (a) ICS (Exp. 1), (b) MCS (Exp. 2), (c) ICS/MCS (Exp. 3), and (d) IMCS (Exp. 4).

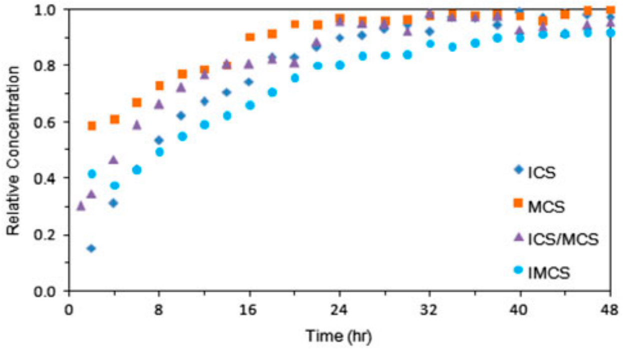

Fig. 3. Comparison of Mn(II) breakthrough curves for ICS, MCS, ICS/MCS, and IMCS.

speciation of Mn(II) and Fe(II) with the MINTEQ+ geochemical program, the distribution and saturation index (SI) of the sorptive ions at various pH regions were obtained to elucidate the mechanism involved at the solid–solution interface. More than 90% of Mn and Fe exist in their ionic forms, i.e. Mn^{2+} and Fe^{2+}, up to pH values of ~9.0 and ~8.5, respectively. The saturation index, which describes if an aqueous solution is supersaturated ($SI > 0$) or undersaturated ($SI < 0$), changes from positive to negative at pH 8.9 for Fe(II) and at pH 11.1 for Mn(II). It is also well documented that the rates of manganese oxidation are much slower than those of iron oxidation [30], which is in agreement with Mn(II) and Fe(II) removal in IMCS. Katsoyiannis and Zouboulis [31] reported that Fe(II) removal could be accomplished at 2 mg L^{-1} dissolved oxygen, a redox value of 200 mV, and pH 7.2, but higher dissolved oxygen and redox values at the same pH were required for the removal of Mn(II). This result supports that the removal of Mn(II) is more difficult than that of Fe(II).

MCS removed 11.4% of Mn(II), but the use of IMCS as a filter medium improved removal efficiency values for Mn(II) up to 25.4%. Moreover, a comparison of the Mn(II) BTCs for ICS and MCS clearly indicated that ICS was more effective than MCS for removal of Mn(II). As well as higher specific surface area of ICS (2.268 $m^2 g^{-1}$) than that of MCS (1.063 $m^2 g^{-1}$), higher adsorption strength of ICS to Mn(II) can be an additional reason for higher Mn(II) removal of ICS. As mentioned above, it is well known that ICS can adsorb significant amounts of heavy metals. Further, although MCS can adsorb heavy metal ions, the adsorption capacity of this medium is lower than that of ICS. Low Mn(II) removal by MCS can be attributed to slow chemical oxidation of Mn(II) at low

Table 3
Experimental results for long-term pilot-scale column experiments

Position	Contaminant	m_{total} (mg)	q_{total} (mg)	Re (%)	q_{eq} (mg g^{-1})	Average C/C_0	Maximum C/C_0
20 cm	Fe(II)	2,968	2936.5	98.9	0.294	1.06×10^{-2}	6.30×10^{-2}
	Mn(II)	8,904	1616.0	18.2	0.162	8.19×10^{-1}	1.04
	Bacteria	59,357	59353.3	99.994	5.935	6.19×10^{-5}	3.49×10^{-4}
40 cm	Fe(II)		2945.0	99.2	0.147	7.73×10^{-3}	3.00×10^{-2}
	Mn(II)		1893.3	21.3	0.095	7.87×10^{-1}	1.01
	Bacteria		59355.7	99.998	2.968	2.12×10^{-5}	1.07×10^{-4}
60 cm	Fe(II)		2948.8	99.4	0.098	6.47×10^{-3}	2.70×10^{-2}
	Mn(II)		2234.3	25.1	0.074	7.49×10^{-1}	1.02
	Bacteria		59355.7	99.998	1.979	2.15×10^{-5}	2.06×10^{-4}
80 cm	Fe(II)		2946.2	99.3	0.074	7.33×10^{-3}	3.00×10^{-2}
	Mn(II)		2694.9	30.3	0.067	6.97×10^{-1}	1.04
	Bacteria		59355.2	99.997	1.484	3.08×10^{-5}	2.96×10^{-4}
Outlet	Fe(II)		2934.7	98.9	0.059	1.12×10^{-2}	1.29×10^{-1}
	Mn(II)		3379.2	38.0	0.068	6.20×10^{-1}	1.06
	Bacteria		59356.7	99.999	1.187	5.82×10^{-6}	7.14×10^{-5}

pH as well as Mn(II) release by Fe(II) adsorption. Adsorption of both Fe(II) and Mn(II) is strongly pH dependent, and the saturation indices of both metal ions are different. MCS can oxidize heavy metals such as As(III), Fe(II), and Mn(II) rather than being used as adsorbents [29]. It is well known that MnO_2 has a catalytic effect on Mn(II) oxidized with dissolved oxygen to form insoluble products, accelerating the process of manganese removal [32]. However, it has been reported that the chemical oxidation of Mn(II) is very slow at pH <8.5 [30,33]. In addition to low pH, the retention time of Mn(II) in the column was too short to be oxidized by MCS, leading to inefficient removal of Mn(II) in this medium. Adsorption of Fe(II) on MnO_2 leads to the release of Mn(II) from MnO_2 through an exchange process, accompanied by the formation of FeOOH [9].

3.2. *Simultaneous removal of Fe(II), Mn(II), and bacteria in small-scale columns*

The applicability of IMCS for the simultaneous removal of Fe(II), Mn(II), and bacteria was assessed by column studies. The operating parameters for column experiments were the same as those described above for the removal of metals. Fig. 4 and Table 1 show the results of Fe(II) or Mn(II) removal in the presence of bacteria by using IMCS. When both Fe(II) and bacteria were injected, the BTC for Fe(II) was not as distinct compared with those obtained from other column experiments, i.e. the effluent C/C_0 of Fe(II) was lower than 0.05 throughout the column experiment. The effluent concentration of bacteria increased sharply up to 0.394 C/C_0 and gradually increased up to 0.529 C/C_0, ranging from 0.090 to 0.529 C/C_0 with an average of 0.341 C/C_0.

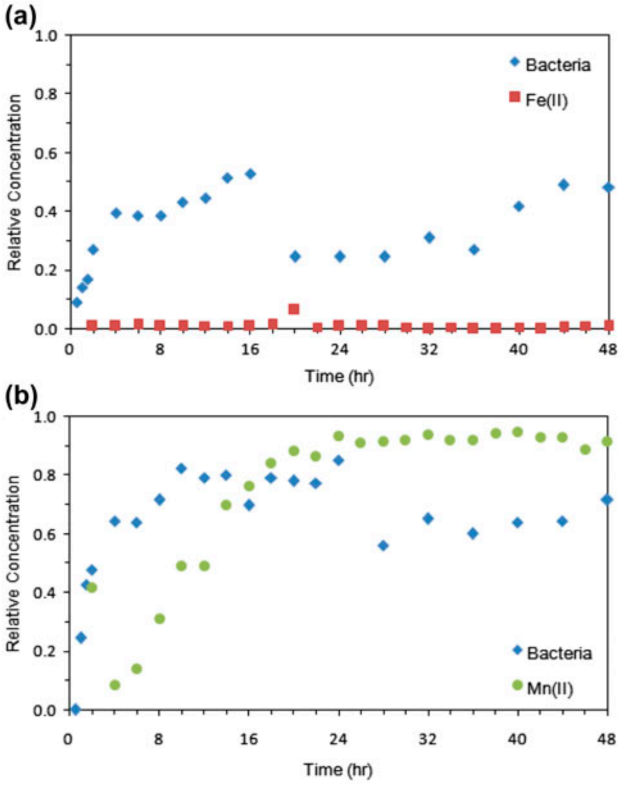

Fig. 4. Breakthrough curves for (a) Fe(II)/bacteria (Exp. 5) and (b) Mn(II)/bacteria (Exp. 6) obtained from small-scale column experiments with IMCS.

When Mn(II) and bacteria were injected, the slope of the BTC for Mn(II) was more gradual compared with BTCs in other experiments in the absence of bacteria. The bacterial concentration in the effluent increased steeply up to 0.826 C/C_0, and high concentrations were maintained until 24 h, scattering at approximately 0.8 C/C_0. As shown in Table 2, Fe(II) removal by IMCS in the presence of bacteria (Exp. 5) was not significantly different from that in the presence of Mn(II) (Exp. 4). However, a significant difference was observed with Mn(II) removal efficiency in the presence or absence of bacteria, i.e. Mn(II) removal efficiency (Exp. 5) was 20% higher than that of Exp. 4. This result can be explained as follows. Functional groups on the cell surface of *E. coli* can contribute to the enhancement of Mn(II) removal because of interaction between bacteria and metal ions [34]. It has been reported that lipopolysaccharide, which constitutes the outer membrane of gram-negative bacteria such as *E. coli*, interacts with metals [35].

The BTCs for simultaneous removal of Fe(II), Mn(II), and bacteria are presented in Fig. 5. Fe(II) concentration in the effluent was as low as that observed in other experiments conducted in this study. The behavior of Mn(II) in Exp. 7 was similar to that in Exp. 6, showing that Mn(II) concentration increased gradually, with BTCs showing a lower slope than that in other experiments in the absence of bacteria (Exps. 1–4). The bacterial concentration in Exp. 7 sharply increased up to 0.690 C/C_0 and slightly decreased to 0.548 C/C_0 at 22 h. After 24 h, the bacterial concentration ranged from 0.110 to 0.271 C/C_0. The BTCs for bacteria in the presence of Fe(II), Mn(II), and Fe(II) + Mn(II) were compared with BTCs for bacteria obtained from previous studies conducted under the same conditions ($Q = 2$ mL/min, $C_0 = 0.15$ OD_{600}) [15]. In the absence of any metals, the BTC for bacteria in IMCS increased to 0.8 C/C_0 at 5 h. By comparison, the BTC for bacteria with Mn(II) approached 0.8 C/C_0 at 17 h. When bacteria were combined with Fe(II) or Fe(II) + Mn(II), BTCs for bacteria were always below 0.8 C/C_0. In the presence of Fe(II), the slope of the BTC for bacteria was more gradual than when Mn(II) was present. This result can be attributed to enhanced adsorption of bacteria to IMCS when Fe(II) is present. It was observed that divalent cations improve the adsorption of bacteria to filter media by creating a bridge between adsorbed bacteria on filter media and free bacteria in the aqueous phase [36,37]. Oxidized Fe, i.e. Fe(III), which is a commonly used inorganic coagulant, may be an additional reason for higher bacterial removal in the presence of Fe(II).

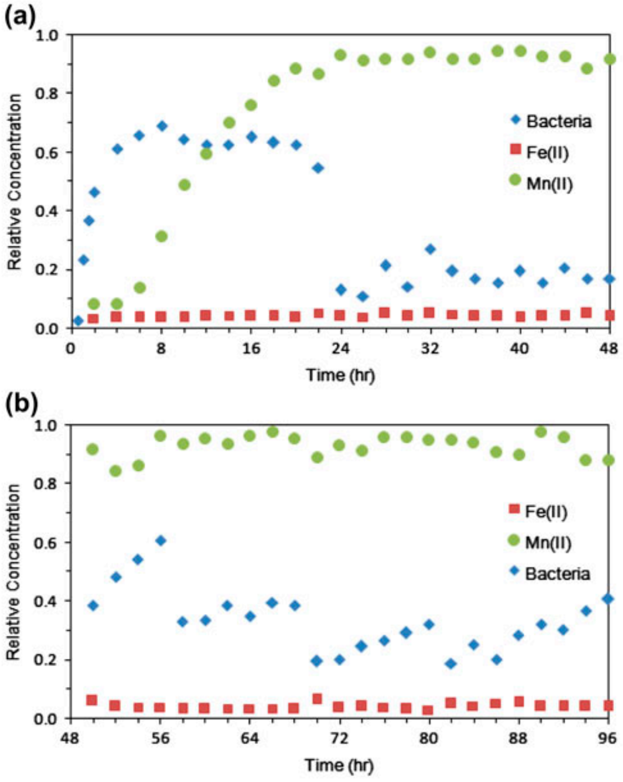

Fig. 5. Breakthrough curves of Fe(II), Mn(II), and bacteria obtained from small-scale column experiments with IMCS (a) before backwashing (Exp. 7), and (b) after backwashing (Exp. 7B).

The BTCs for IMCS obtained from small-scale column experiments after the backwashing process with 0.1 mM HCl are shown in Fig. 5. It was found that the adsorption capacity of IMCS for Mn(II) was not recovered by the backwashing process. The Mn(II) concentration in the column effluent after backwashing was persistently around 0.90. The Fe(II) concentration was very stable, and its concentration was maintained even after backwashing. The average Fe(II) concentration after backwashing was 0.04. From the beginning of the operation and through the entire experiment, the Fe(II) removal efficiency was over than 95%. After backwashing, bacterial concentrations ranged from 0.187 to 0.606, and high variability was observed. The increased bacterial concentrations right after backwashing might be attributed to the detachment of attached bacteria by backwashing. It can be derived from these results that backwashing with low concentrations of HCl produced only a poor recovery of IMCS adsorption capacity for Fe(II), Mn(II), and bacteria.

3.3. Long-term performance of IMCS for simultaneous removal of Fe(II), Mn(II), and bacteria

The applicability of IMCS for the removal of Fe(II), Mn(II), and bacteria was assessed under pilot-scale conditions. The depth of the column and the linear velocity of flow through the column were determined following a review of the relevant literature [38]. In the literature, the depth of the filter media and flow rate of slow sand filtration range from 0.8 to1.2 m and 2.4 to 7.2 m^3 m^{-2} day^{-1}, respectively. The filter depth and flow rate in the present study were within the ranges reported in the literature, indicating that our experiments adequately replicated the actual conditions of slow sand filtration. The bacterial concentration (4.2×10^6 CFU mL^{-1}) in the pilot-scale column experiment was set to simulate microbe-contaminated water when wastewater and contaminated groundwater were used as sources. Fe(II) and Mn(II) concentrations for pilot-scale experiments were 1 and 3 mg L^{-1}, respectively—the same concentrations used in the small-scale column experiments. Pilot-scale column experiments were conducted using a column with five sampling points at different filter depths for 46 days. This enabled the monitoring of Fe(II), Mn(II), and bacterial concentrations in relation to the bed depth and the empty bed contact time in the column (Table 3).

Fig. 6 shows representative concentration profiles for each species. Fe(II), Mn(II), and bacterial concentration at different filter depths throughout the pilot-scale experiment were plotted with two *y*-axes. Mn(II) concentration was represented by a linear scale on the left *y*-axis, and Fe(II) and bacterial concentration were plotted using a logarithmic ($\log_{10}$) scale on the right *y*-axis. As shown in Fig. 6, Fe(II) concentrations at all positions were around −2 $\log_{10}$ C/C_0, ranging from 0.001 to 0.129. Mean total Fe(II) concentrations at all sampling points were 0.011 (20 cm), 0.008 (40 cm), 0.006 (60 cm), 0.007 (80 cm), and 0.011 mg L^{-1} (outlet). Iron concentration in the effluent was below the drinking water guideline value (0.3 mg/L) of the US EPA over the entire period after start-up. The monitoring of concentration profiles showed that Fe(II) concentrations fell below the drinking water standards even at a filter depth of less than 0.2 m.

No breakthrough of bacteria was observed in any of the samples over the 14-day study. Bacteria detected in all sampling ports were found in concentrations ranging from −7 $\log_{10}$ C/C_0 to −3 $\log_{10}$ C/C_0. A bacterial concentration of less than −4 $\log_{10}$ C/C_0 was monitored at effluent during overall pilot-scale experiments (46 days). The average bacterial removal efficiency was 99.994 (20 cm), 99.998 (40 cm), 99.998 (60 cm), 99.997 (80 cm), and 99.999% (outlet). The bacterial removal by IMCS observed was higher than reported values of other metal oxide-coated sands in the literature. Lukasik et al. [17] showed that columns packed with aluminum- and ferric hydroxide-coated sand removed more than 99% of *E. coli* and *Vibrio cholerae* from dechlorinated tap water. Similarly, Ahammed and Chaudhuri [16] reported that >99% of total coliforms were removed in column tests with a MCS and iron hydroxide-coated sand dual-media filter. Other research of Ahammed's group [10] reported that iron hydroxide-coated sand removed 97 to >99% of the total and fecal coliforms from rainwater.

Bacterial removal in the pilot-scale experiment was quite different compared to the small-scale study. It is evident that the higher removal efficiency in the pilot-scale column experiments can be attributed to the low inlet concentration of bacteria, which was 10 times lower than that in the small-scale columns. The increased contact time for bacterial adhesion may be an additional reason for the higher removal efficiency in the pilot-scale column experiments. In our previous study [15], flow rate played a dominant role in bacterial removal in columns packed with IMCS.

Each of the BTCs for Mn(II) showed a characteristic S-shape, demonstrating that the solute concentration in the effluent increased as inlet water passed through, because of the saturation of the adsorption capacity of the filter media (Fig. 6). Mn(II) concentration at sampling ports S1, S2, S3, and S4 increased linearly, and the time required to reach 1.0 C/C_0 was delayed as the filter depth increased. After 8 days from the beginning of injection, manganese concentration in the effluent appeared to be above 0.4 mg L^{-1}, which is the limit recommended by the WHO guidelines [4]. Our removal percentage (Re) of Mn(II) by IMCS was ranged from 18.2% to 38.0%, which was lower than the literature value of Tiwari et al. [39] who observed Mn(II) removal of 40–80% by MCS at pH 6–7. This discrepancy can be attributed to experimental conditions they used in the experiments (i.e. batch condition, low Mn(II) concentration, and different filter media). Knocke et al. [40] also observed that Mn(II) removal MCS in the presence of free chlorine was higher than that in the absence of it. Potentially, the Mn(II) removal capacity of IMCS could be enhanced by the use of an oxidizing agent. Lee et al. [2] reported that the presence of NaClO oxidized soluble Mn(II) to manganese oxide Mn(IV), resulting in aggregation of Mn(IV) on the solid surface and improving Mn removal. This increased the Mn(II) removal capacity of manganese-coated sand from 10.93 to 20.21 mg g^{-1}. Manganese cannot be removed effectively by IMCS filtration only. Based on these data, chemical oxidation will be required to achieve safe levels of Mn(II) in drinking water within reasonable periods and at neutral pH values.

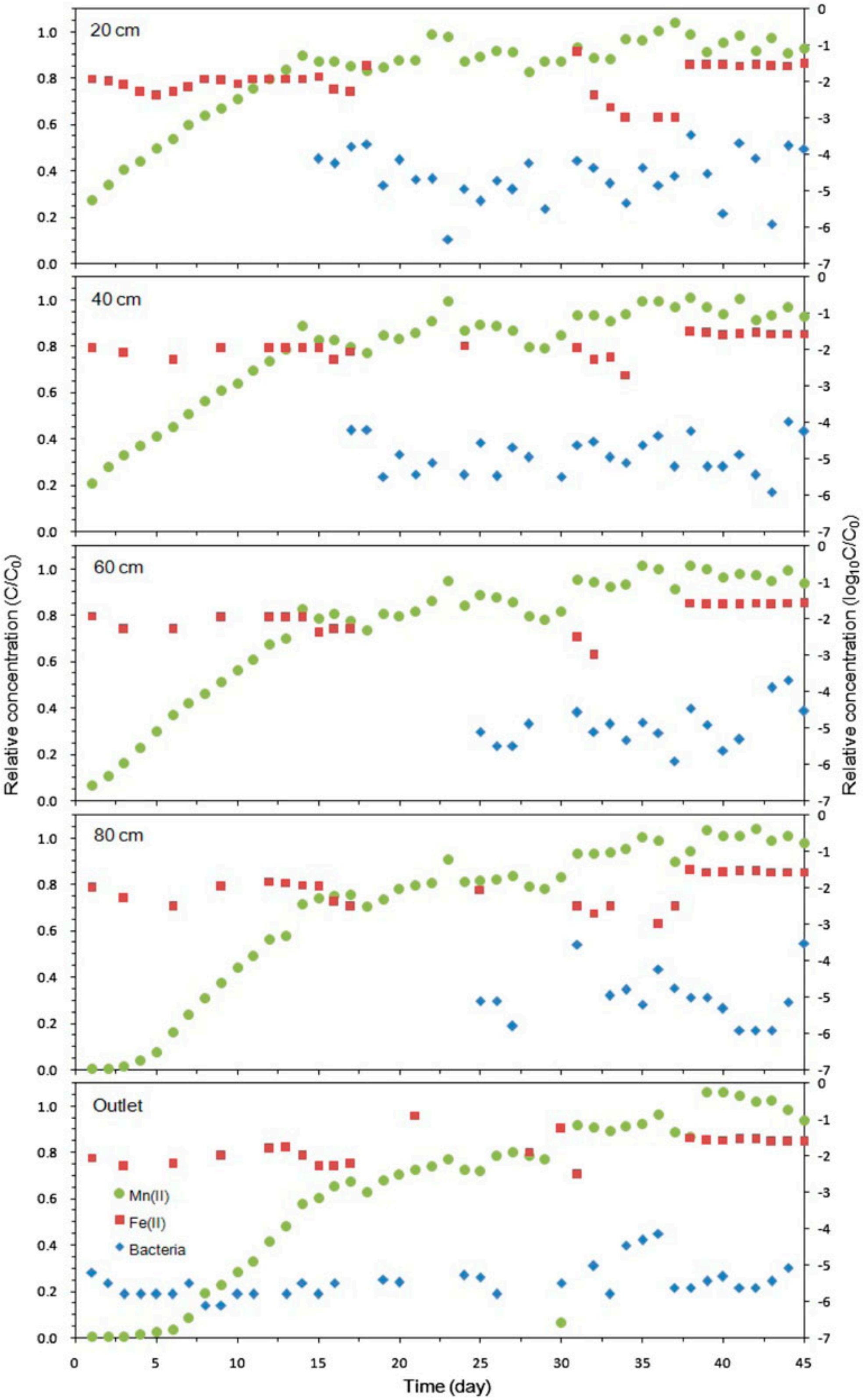

Fig. 6. Breakthrough curves of Fe(II), Mn(II), and bacteria obtained from long-term pilot-scale column experiments at various sampling positions: (a) 20 cm, (b) 40 cm, (c) 60 cm, (d) 80 cm, (e) outlet.

4. Conclusions

The performance of IMCS for the removal of Fe(II), Mn(II), and bacteria was examined using small- and pilot-scale column experiments. Small-scale column experiments showed that the Mn(II) removal capacity of IMCS was greater than that of ICS, MCS, and ICS/MCS. The Fe(II) removal capacity of IMCS was similar to that of ICS, MCS, and ICS/MCS. Simultaneous removal experiments indicated that the bacterial removal capacity of IMCS in Fe(II) and bacteria was greater than that in Mn(II) and bacteria. In addition, when Fe(II), Mn(II), and bacteria were combined, the bacterial removal capacity of IMCS was greater than that of Mn(II) and bacteria. These results indicated that bacterial removal capacity was improved in the presence of Fe(II). The pilot-scale column experiment demonstrated that IMCS was effective as an adsorptive filter medium for simultaneous removal of Fe(II) and bacteria. However, chemical addition might be required for Mn(II) removal to meet the water quality limit.

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