Comparisons of the film peeling from the composite oxides of quartz sand filters using ozone, hydrogen peroxide and chlorine dioxide

Yingming Guo, Tinglin Huang*, Gang Wen, Xin Cao

School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China

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ABSTRACT

To solve the problem of shortened backwashing intervals in groundwater plants, several disinfectants including ozone (O_3), hydrogen peroxide (H_2O_2) and chlorine dioxide (ClO_2) were examined to peel off the film from the quartz sand surface in four pilot-scale columns. An optimized oxidant dosage and oxidation time were determined by batch tests. Subsequently, the optimized conditions were tested in the four pilot-scale columns. The results demonstrated that the backwashing intervals increased from 35.17 to 54.33 (H_2O_2) and to 53.67 hr (ClO_2) after the oxidation treatments, and the increase of backwashing interval after treatment by O_3 was much less than for the other two treatments. Interestingly, the treatment efficiency of filters was not affected by O_3 or H_2O_2 oxidation; but after oxidation by ClO_2, the treatment efficiency was deteriorated, especially the ammonia removal (from 96.96% to 24.95%). The filter sands before and after the oxidation were characterized by scanning electron microscopy and X-ray photoelectron spectroscopy. Compared with the oxidation by O_3 and H_2O_2, the structures on the surface of filter sands were seriously damaged after oxidation by ClO_2. The chemical states of manganese on the surfaces of those treated sands were only changed by ClO_2. The damage of the structures and the change of the chemical states of manganese might have a negative effect on the ammonia removal. In summary, H_2O_2 is a suitable agent for film peeling.

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Introduction

As some water plants apply quartz sands as filter materials (Al-Gabr et al., 2014), a layer of black film tends to gradually be formed on the surface of the materials, and its components are manganese, silicon, magnesium, aluminum, iron and other elements (Guo et al., 2003). The particle size of the quartz sands increases and the surface of the film becomes smooth. The film tends to be overgrown after one to two years' continuous operation, and the resistance of the filter bed gradually increases under the same hydraulic loading, which shortens the backwashing interval and decreases the water production period.

Ozone (O_3), hydrogen peroxide (H_2O_2), chlorine dioxide (ClO_2) and chlorine are some of the types of disinfectants commonly used in water treatment (Li et al., 2013; Chhetri et al., 2014; Tachikawa and Yamanaka, 2014; Zhang et al., 2014). The hydroxyl radical generated by O_3 oxidation has strong oxidation capability, and it can deal with many water pollution problems and will not pollute the environment (El-Araby et al., 2009). H_2O_2 is used as an efficient oxidant, especially in the removal of organic materials (Pottage et al., 2010), and at high

concentration it can generate excessive hydroxyl radicals, which can directly oxidize the organic pollutants in water. ClO_2 has been reported to be effective in pathogenic organisms' inactivation, including the inactivation of *Cryptosporidium parvum*. The oxidation capacity of ClO_2 is mainly determined by reaction time and pH of the water (Zhu et al., 1998), and it shows almost no reactivity with humic substances to form trihalomethanes (Korn et al., 2002). All the disinfectants have strong oxidation capability, so that it was reasonable to use them to oxidize and peel off the overgrown filter film from filter sand surfaces.

The aim of the present work was to select a suitable disinfectant for oxidation treatment of the overgrown filter film on the surface of the filter sands, which could not only increase the bed voidage and recover the backwashing interval of the filter, but also ensure that the water quality of effluent should be within the permitted limits. A series of batch tests were operated to determine the optimized dosage of oxidants and the oxidation time. Four pilot-scale columns were used to test the recovery of backwashing interval and the influence of the three kinds of disinfectants on the water quality of effluent.

1. Materials and methods

1.1. Pollution loading and pilot-scale columns

The raw water was pumped from the depth of 40 m by submersible pump in the northwest area of Xi'an City, China. As summarized in Table 1, the main pollutants in raw water were ammonia, iron and manganese.

The pilot-scale column was constructed of Plexiglas tubes with internal diameter of 0.1 m and height of 3.8 m, and the filter bed in the tube was filled to a height of 1.1 m. At the bottom of each tube was a support layer of 0.3 m depth. The filtration velocity of all pilot-scale columns was 7 m/hr. All pipes for water transport were made of random polypropylene, an important class of plastic resins. All pilot-scale columns were backwashed when the water reached a preset

overflow location, about 1.6 m above the bed layer. When the water quality of the effluent was deteriorated, the filter was backwashed as well. Backwashing was conducted *via* the following steps: air flow intensity = 50.8–72 $m^3/(m^2 \cdot hr)$, water flow intensity = 15.1–36 $m^3/(m^2 \cdot hr)$: (1) air scouring for 3 min at the bottom of column, (2) simultaneous air and water scouring for 4 min, and finally (3) water scouring for 3 min.

A daily analysis of water samples taken from certain positions of the pilot-scale columns was carried out to determine the concentrations of each pollutant in the filter. A schematic of the pilot-scale filter system is presented in Fig. 1.

1.2. Batch tests and the voidage

To determine the optimized oxidant dosage and oxidation time, a series of batch tests were performed as follows: The weighed filter sand (650 g, diameter of about 1–1.5 mm, and the mass of film was about 650 g × 6.3% = 40.95 g) was introduced into a basket made of stainless steel wire mesh with the pore size of 1 mm (Fig. 2), then the baskets were settled in polyethylene bottles (1 L). The oxidant solution (0.4 L) was added into the bottles. After a certain reaction time, the liquid sample was separated from solid sample in the bottom of the bottles, and the oxidized filter was washed by clean water until the wash water was clear. All the wash water was filtered through a 0.45 μm membrane, and the solid sample was collected in a sand core funnel and the amount of peeled film was weighed; the solids were dried (120°C, 60 min) before being weighed. The batch experiments were performed for different reaction times of 5, 10, 20, 40, 80 min.

The oxidants of O_3, H_2O_2 and ClO_2 were used in batch tests. O_3 was generated from an ozone generator (CF-G-3-10G, Qingdao Guo Lin Industry Co., Ltd., China), and its production was in the range of 1.17–5.27 g/hr. H_2O_2 was made from 30% analytical grade solution (Tianjin Tian Li Chemical Reagent Co., China), and ClO_2 was made from chlorine dioxide effervescent tablets (Beijing Xinli World Environment Technology Co., Ltd., China). The initial concentration of O_3 was controlled by adjusting the current intensity of an ozonizer (I = 0.2, 0.3, 0.6, 0.9) and the initial concentrations of the other two oxidants (H_2O_2 and ClO_2) in the solution were 0.1, 0.2, 0.4, 0.6, 1.2 g/L, respectively.

The procedure of determining the voidage was as follows: as the backwashing finished, all the water of the column was emptied. Clean water was introduced into the filter column, and the water level was controlled to submerge the media exactly. After that, the clean water introduced into the column was drained and collected, the volume of collected water was measured and defined as V_1. The packing volume of the filter bed was calculated from the diameter and the height of the filter bed and was defined as V. So the voidage was V_1/V.

1.3. Analytical methods

Concentrations of ammonia, iron and manganese were determined by conventional spectrophotometric methods (China E. P. B. O., 2002) (HACH, DR5000, USA). Dissolved oxygen and pH were determined by a portable instrument (HACH, HQ30d, USA). The concentration of O_3 was determined by indigo spectrophotometry (Bader and Hoigné, 1981). The concentration of H_2O_2

| Table 1 – Water quality of raw water used in pilot-scale filter system.		
Parameters	Value	Quality standard for groundwater of China (GB/T 14848-9)
pH	7.2 ± 0.3	6.5–8.5
Temperature (°C)	15.0 ± 0.5	NG
Dissolved oxygen (mg/L)	1.45 ± 0.56	NG
Ammonium (mg/L)	1.30 ± 0.25	0.50
Ferrous Fe (mg/L)	0.85 ± 0.05	NG
Total Fe (mg/L)	1.25 ± 0.25	0.30
Manganese (mg/L)	1.15 ± 0.25	0.10
Total phosphorus (mg/L)	0.06 ± 0.01	NG
Total nitrogen (mg/L)	3.95 ± 0.85	NG
Turbidity (NTU)	1.45 ± 0.55	3.00
NG—not given.		
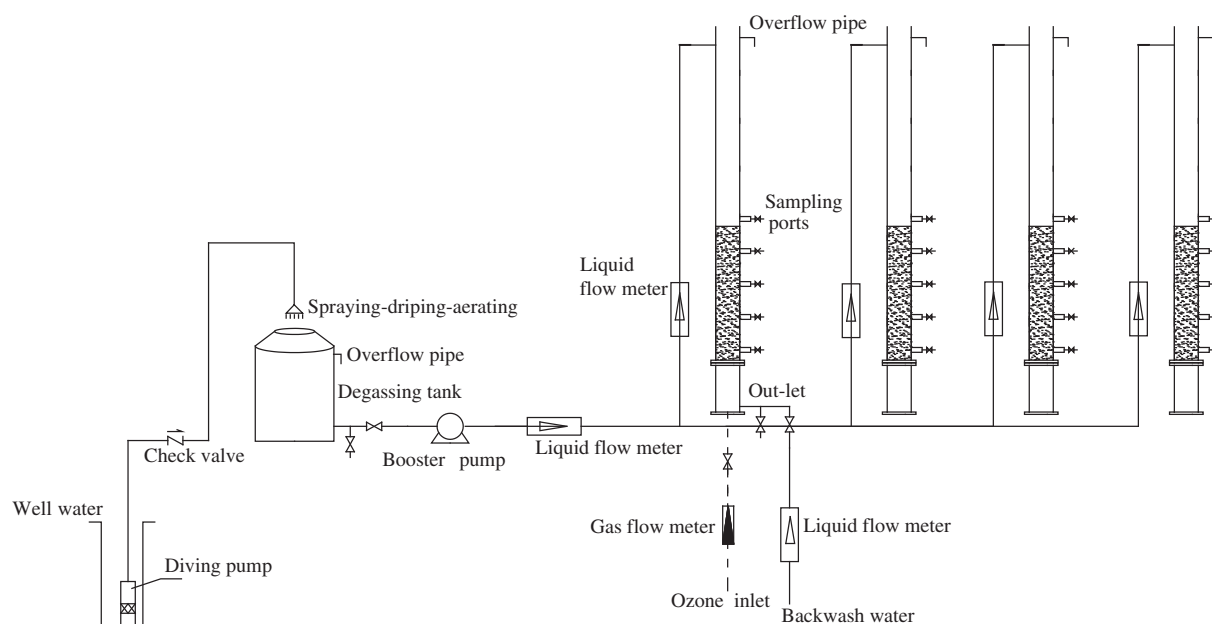
Fig. 1 – Schematic of pilot-scale filter system.

was determined by the potassium permanganate titration method. The reagents were of analytical grade in the experiment, and solutions were prepared using deionized water.

1.4. Characterization methods

The quartz sand filters were frozen and vacuum-dried (FD-1D-50, Beijing Medical Kang Bo Experimental Instrument Co., China), and then kept in sealed vacuum tubes (Zhao et al., 2003). The morphologies of each kind of filter sand were characterized by scanning electron microscopy (SEM, JEOL-JSM6360LV, Japan). The binding energies of selected elements on the sand surface before and after the

oxidation treatment were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific-Noran System Six, USA), and the XPS spectra of the elements Fe and Mn were analyzed and peak fitted by bundled software (Avantage).

2. Results and discussion

2.1. Change of backwashing interval with operation time

As shown in Fig. 3, the backwashing interval decreased from 65 hr to less than 35 hr after two years, which might be attributed to the overgrown filter film. Backwashing is a commonly used method to reduce the resistance of the filter bed (Rittmann et al., 2002). However, increasing the backwashing intensity in the present study had negligible effect on the recovery of backwashing interval, since it could not destroy the structure of the filter film. Thus strong oxidants such as O_3, H_2O_2 and ClO_2 were used to peel off the overgrown filter film from the sand surface so that the backwashing interval of the filter bed could be recovered.

2.2. Film peeling efficiency of batch tests

The amount of peeled film in different oxidation conditions was studied by batch tests, and the results are shown in Fig. 4. In each oxidation condition, the film peeling amount of the filter materials increased sharply at first and then became stable in about 40 min, while the optimized dosage of different oxidants was distinct. Taking account of both cost and treatment efficiency, the optimized dosage and oxidation time for O_3 were found to be 85.8 mg/(g film·hr) and 40 min,

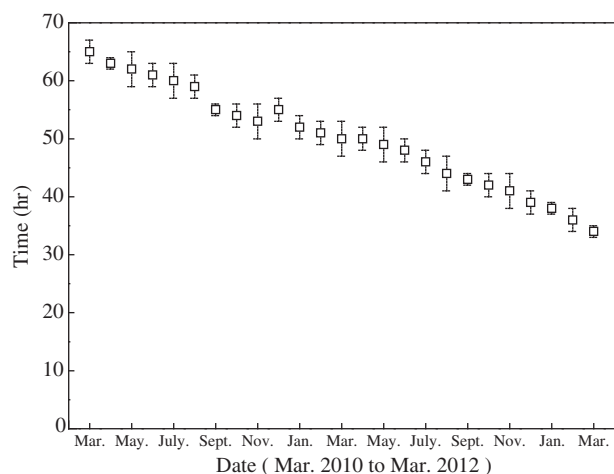**Fig. 2 – Schematic of batch apparatus.**

Fig. 3 – Change of backwashing interval over operation time. Data represents an average of five values.

and for both H_2O_2 and ClO_2 they were 11.7 mg/g film and 40 min.

2.3. Recovery of backwashing interval in the pilot-scale columns

Experiments for treatment by different oxidants in each one's optimized condition as well as a control experiment without oxidation were conducted, and the bed voidages and backwashing intervals of the pilot-scale columns are shown in Fig. 5.

The voidage of the clean sand before the tests was about 38.4%, and after the oxidation treatment by H_2O_2 and ClO_2, the bed voidages increased obviously from 28.1% to 36.7% and 39.8%, respectively. Correspondingly, the backwashing intervals increased from 35.17 to 54.33 and 53.67 hr, respectively. Thus the backwashing interval could be well recovered after oxidation treatment by H_2O_2 and ClO_2. After the oxidation by O_3, the bed voidage and backwashing interval increased much less than that for the other two treatments.

2.4. Change of water quality

An experiment without oxidant and for treatment by different oxidants in each one's optimized condition was conducted (Fig. 6). After oxidation by O_3 (Fig. 6b) and H_2O_2 (Fig. 6c), the removal efficiencies of ammonia, iron and manganese were hardly changed. However, after oxidation by ClO_2 (Fig. 6d), the removal efficiencies of ammonia, iron and manganese were rapidly reduced from the initial 96.96% to 24.95%, 87.36% to 71.87%, and 94.56% to 72.97%, respectively. As the operation went on, the removal of iron and manganese was recovered after 24 hour operation, and the removal efficiency of ammonia was recovered to 95.81% after 288 hour operation.

The removal of ammonia in a filter bed was investigated in a former study, and it was indicated that the filter film had
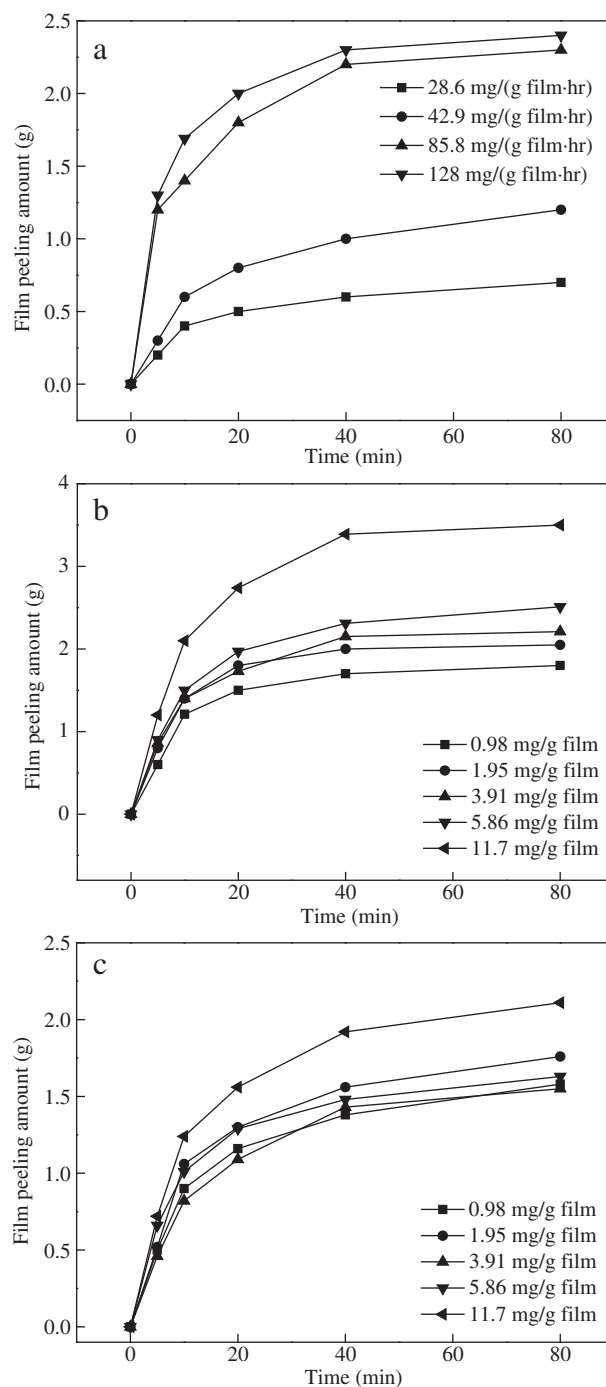

Fig. 4 – (a) Curves of film peeling amount with time at different electric current intensities for O_3 oxidation of the quartz sands. (b) Curves of film peeling amount with time at different concentrations of H_2O_2 for oxidation of the quartz sands. (c) Curves of film peeling amount with time at different concentrations of ClO_2 for oxidation of the quartz sands.

a catalytic effect on ammonia oxidation (Huang et al., 2014). The oxygen surface groups have a greater contribution to the removal of ammonia than the chlorine surface groups (Molina-Sabio et al., 2011). The active absorption sites on the
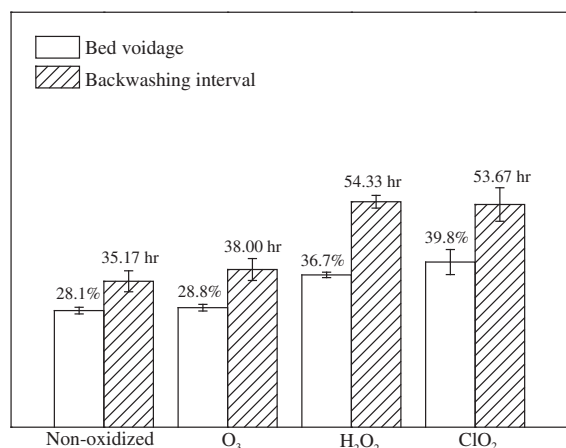
Fig. 5 – Effects of oxidation treatments by O₃, H₂O₂ and ClO₂ on the bed voidages and backwashing intervals of filter columns.

surface of the film were limited, if more active absorption sites were occupied by chloride ion instead of oxygen, which would certainly lead to the removal efficiency of ammonia being decreased. There are two possible reasons for the change in effluent water quality. First, as the oxidation occurred, the ClO₂ was decomposed to chloride ion, which might be competitive with the adsorption of dissolved oxygen or the ammonia on the surface of the film, so that

the catalytic oxidation process of ammonia was affected, leading to the reduction of ammonia removal. Second, the surface structures of the filter film were damaged by the oxidation process with ClO₂, reducing the number of catalytic active sites for ammonia oxidation and thus decreasing the removal efficiency of ammonia (Fig. 6d).

2.5. Microscopic characterization of the composite oxides of quartz sands before and after the film peeling

The morphology of the composite oxides of quartz sands before and after oxidation was characterized by SEM (Fig. 7). Before the oxidation treatment, the surface of the filter film was relatively uniform and integrated. After the oxidation treatment by O₃ and H₂O₂, the morphologies of the filter-film-coated sands were barely changed, which was consistent with the results of experiments in pilot-scale columns. Compared with the oxidation by O₃ and H₂O₂, the structure of the filter film was obviously damaged by ClO₂, the surface of the film became smooth, and the structures of the oxide particles were obviously damaged. So the removal efficiency of ammonia was reduced seriously, and it took a long time to recover.

2.6. X-ray photoelectron spectroscopy

After the oxidation treatment by different oxidants, the changes of the filter film were characterized by XPS, and the spectra of Fe(3/2p) and Mn(3/2p) are shown in Fig. 8.
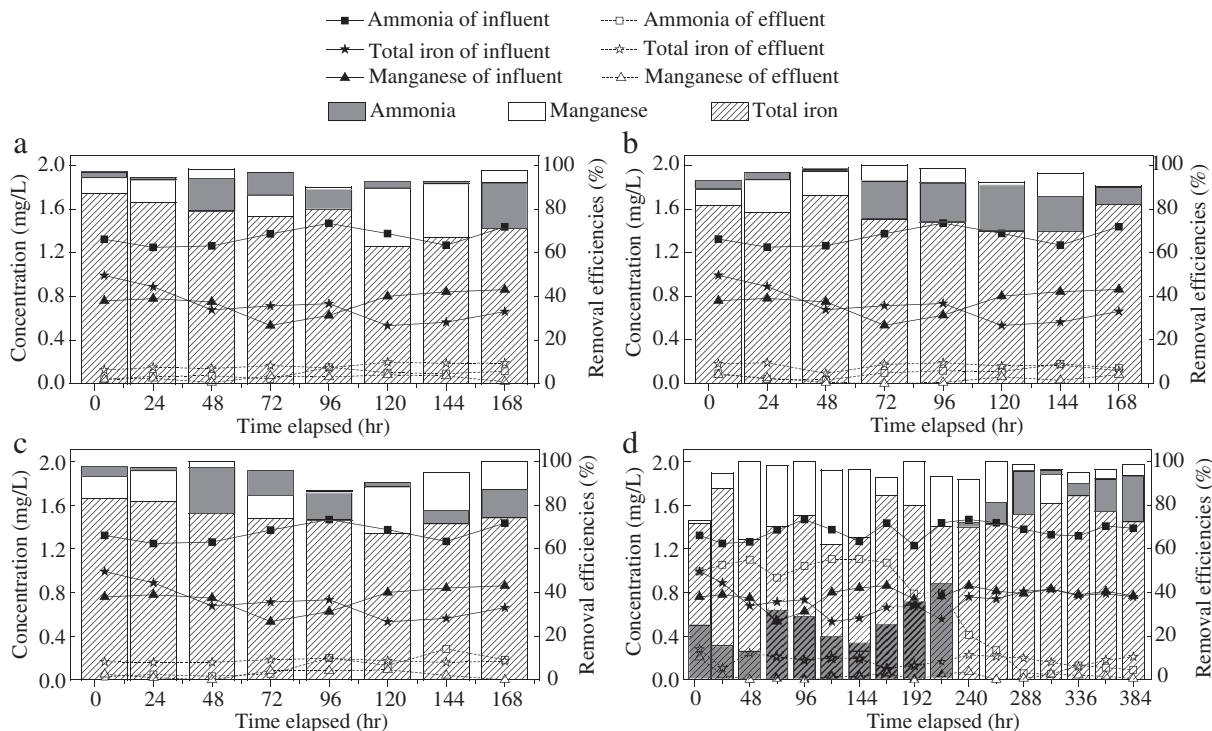

Fig. 6 – Effects of oxidation treatments on water quality of influents, effluents and the removal efficiencies of filter column. (a) Nonoxidized, (b) oxidized by O₃, (c) H₂O₂ and (d) ClO₂.
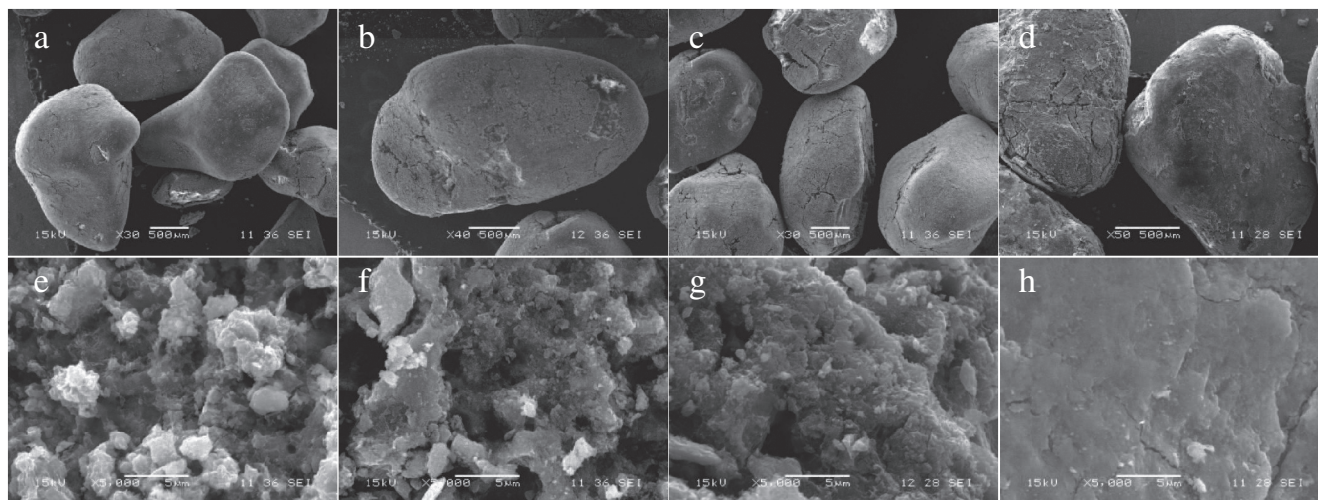
Fig. 7 – Scanning electron microscopy (SEM) images of the quartz sand surface amplified by (30–50) times. (a) Non-oxidized (30 times), (b) oxidized by O_3 (40 times), (c) oxidized by H_2O_2 (30 times), (d) oxidized by ClO_2 (50 times), (e) non-oxidized (5 K times), (f) oxidized by O_3 (5 K times), (g) oxidized by H_2O_2 (5 K times), (h) oxidized by ClO_2 (5 K times).

Compared with the binding energies of Fe(3/2p) of untreated sands, the chemical states of O_3-, H_2O_2- and ClO_2-treated sands changed obviously. The binding energy of Fe(3/2p) on non-oxidized sand was 709.53 eV (FeO) (Mills and Sullivan, 1983) and 711.01 eV (Fe_2O_3) (Konno and Nagayama, 1980), respectively. After oxidation, the Fe atoms present as Fe(II) (709.53 eV) were oxidized to ferric states (710.69 eV, 710.75 eV and 710.74 eV) (Mathieu and Landolt, 1986), In addition, after the oxidation treatment, in the XPS spectra of Fe(3/2p) the presence of calcium iron silicate (712.49 eV, 712.53 eV and 712.54 eV) was indicated (Seyama and Soma, 1987); this might be attributable to exposure of inner layer materials caused by the peeling effects of oxidation.

Also, as shown in Fig. 8b, there were three kinds of manganese atoms in the filter film. Their binding energies were 642.41 eV (MnO_2) (Di-Castro and Polzonetti, 1989), 641.17 eV (Mn_3O_4) (Oku and Hirokawa, 1976) and 640.02 eV (MnO) (Ivanov-Emin et al., 1982), respectively. After oxidation by O_3 and H_2O_2, the binding energies of the fitted peaks of Mn(3/2p) were all increased, but the chemical states of manganese on the surfaces of the treated sands were not changed by the oxidation processes. This might explain the capabilities of removal of ammonia by O_3- and H_2O_2-treated sands. After oxidation by ClO_2, the binding energy of manganese atoms increased to 643.32 eV (MnO_2) (Dzhurinskii et al., 1975), 642.04 eV (Mn_2O_3) (Tan et al., 1991) and 640.76 eV (MnO) (Di-Castro and Polzonetti, 1989), respectively, and the Mn atoms present as Mn_3O_4 (641.17 eV) were changed to Mn_2O_3 (642.04 eV). The differences of binding energies of manganese between O_3- and H_2O_2-treated and ClO_2-treated sand were obvious. These differences in chemical states of manganese might be caused by the differences in oxidation capabilities of each oxidant, and further studies on this problem are needed.

The chemical states of manganese on the surfaces of the treated sands were only changed by ClO_2, such that the electro-negativity of the chemical environment of manganese

atoms was increased. The chemical states were changed by ClO_2 oxidation treatment, so that the active sites for catalytic oxidation of ammonia changed, thus the ammonia removal was obviously decreased. So it could be remarked that the ammonia removal efficiency was primarily affected by destruction of the surface structure and the change of catalytic oxidation active sites. Thus, ClO_2 treatment could not be proposed as a suitable method for film peeling.

3. Conclusions

Oxidation by O_3 only had a slight effect on the recovery of backwashing interval. Compared with the treatments by O_3 and H_2O_2, the structures of the filter film were obviously damaged by ClO_2 treatment. The chemical states of Mn on the surface of ClO_2-treated sands were also changed, possibly leading to the sharp increase of the backwashing interval of filter column and rapid reduction of the removal efficiencies for the contaminants. The damaged structure of the filter film and the changed chemical states of manganese induced a long recovery time for the removal efficiency of ammonia. After the treatment by H_2O_2, the backwashing interval of the filter column increased from 35.17 to 54.33 hr and the removal efficiencies of contaminants were not obviously reduced. Thus, H_2O_2 is a suitable choice of oxidant for peeling off the filter film.
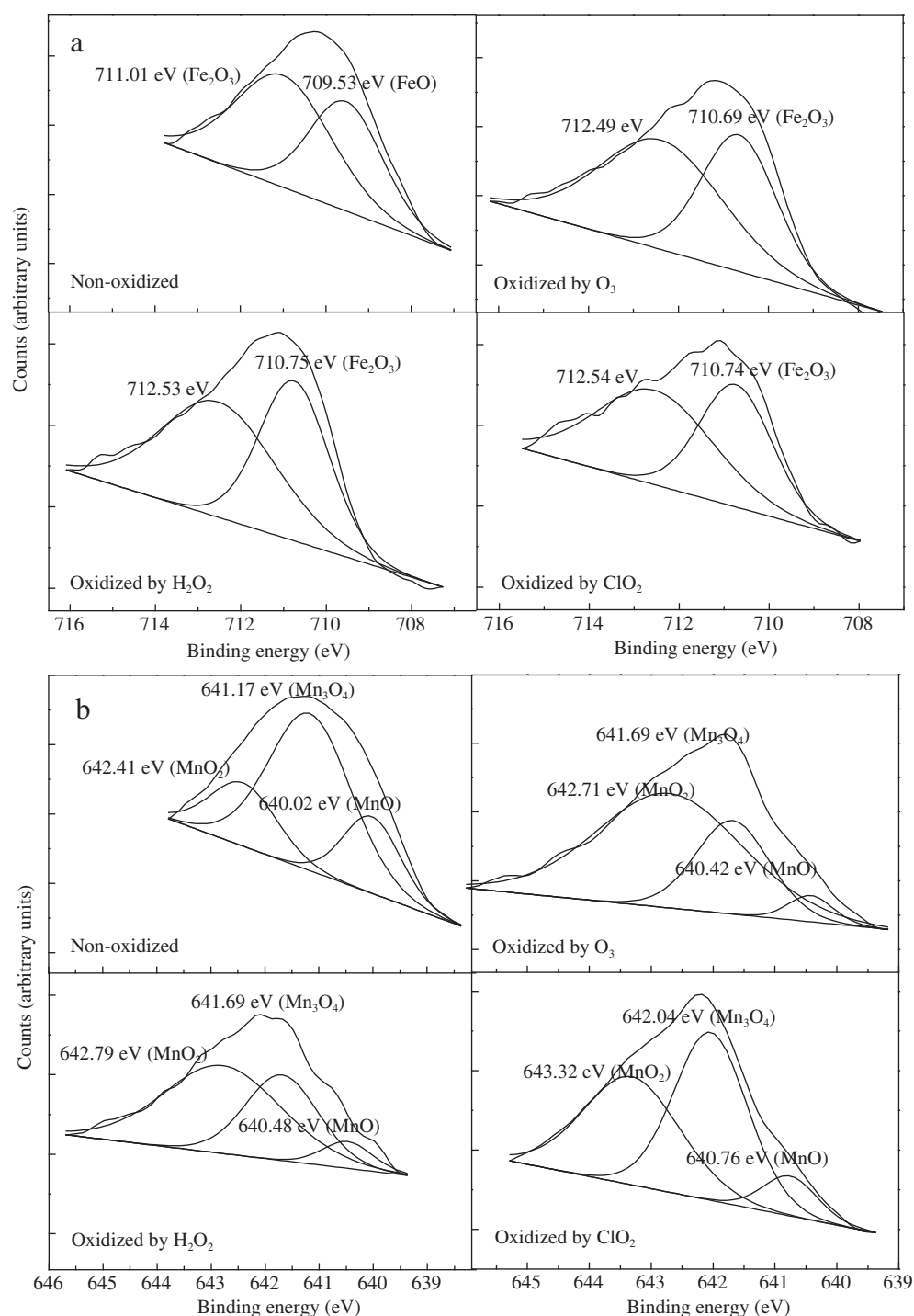
Fig. 8 – (a) Fe(3/2P) X-ray photoelectron spectroscopy (XPS) of the filter film non-oxidized and oxidized by O₃, H₂O₂ and ClO₂. (b) Mn(3/2P) XPS of the filter film non-oxidized and oxidized by O₃, H₂O₂ and ClO₂.

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