The study on chemical adsorption of dissolved oxygen on naturally formed co-oxides filter film in aqueous solution: combined characterization of XPS and TPD
Tinglin Huang, Xin Cao, Gang Wen and Yingming Guo

ABSTRACT
The chemical adsorption of dissolved oxygen (DO) by co-oxide filter film-coated sands, formed through the filtration of ground water containing high concentrations of ammonia, manganese and iron, were studied. The results showed that the filter film consisted of silicates, carbonates, manganese and iron oxides and was constructed in a three-layer porous structure. The specific area of film-coated sands was 6.5 m²/g. The chemical adsorption sites of DO are composed of silicates, iron and manganese atoms, and the adsorption was a weak chemical effect. The O₂ is the adsorbed species of DO.

INTRODUCTION
Dissolved oxygen (DO) is one of the important operating conditions in both waste and drinking water treatment. Especially in drinking water treatment, the DO, which is considered to be an economical oxidant, has been focused on in both chemical and biological processes. The use of DO as oxidant may avoid the negative effects caused by additional oxidants used in traditional oxidation treatment processes, making it one of the developing directions in the modern drinking water treatment area (Qu 2014).

It is reported that the simultaneous removal performance of chemical oxygen demand (COD), NH₄⁺-N and Mn²⁺ in a biologically aerated filter system was obviously affected by the concentration of DO. A greater contamination with COD, NH₄⁺-N and Mn²⁺ in drinking water require that a higher aeration rate be supplied (Hassimi et al. 2015). The simultaneous NH₄⁺-N and Mn²⁺ removal from drinking water in both high and low pollutant strengths were studied in a biologically aerated filter system, and the optimized DO concentrations were determined for each condition (Hassimi et al. 2014). In a fixed-bed bioreactor, the DO concentration was changed by air-assisted back-washing, and the experimental results indicate that the denitrifying and arsenate-reducing microbes have a tolerance to DO, while the activities of sulfate-reducing microbes decreased noticeably as the concentration of DO increased (Upadhyaya et al. 2012). The physical and chemical properties of active carbon have been characterized in an oxygen adsorption process and the kinetics and equilibrium of the process were determined by batch experiments (Matsis & Grigoropoulou 2008). It was also reported that the adsorption rate of DO on the active carbon surface generally conforms to a model of adsorption limited by intra-particle diffusion, and at least 10–50% of the amount of adsorbed oxygen can be accounted for by an increase in the prevalence of carboxylic acid groups (Prober et al. 1998). In fixed-bed biofilm reactors, the decreased capacity of DO chemical adsorption on granular active carbon reduced the removal of perchlorate in a long-term operation (Young et al. 2008).

The adsorption of DO occurs in most water treatment processes. The properties of adsorption sites existing on liquid-solid interfaces determine the adsorption capabilities and the adsorption states of DO, which plays an important role in the removal of pollutants. However, both chemical adsorption sites and the adsorption species of DO exist on
water-solid interfaces were rarely under discussion and the adsorption of DO on the oxide–water interface was less reported.

In the filtration of ground water, which contains high levels of ammonia, manganese and iron, on the sand surface coating the co-oxide filter film. The present study aims to determine the chemical adsorption sites of DO on co-oxide filter films, and the bonding affinities between each site and the oxygen atoms. The morphologies and the elemental composition of film-coated sands were characterized by Brunauer–Emmett–Teller (BET), scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) methods. The chemical properties of filter films before and after the DO adsorption were characterized by using the X-ray photoelectron spectroscopy (XPS) method. When combined with temperature programmed desorption (TPD) methods, the amount of chemically adsorbed oxygen and the desorption activation energies on each chemisorb site were determined.

**MATERIALS AND METHODS**

**Formation of the co-oxide filter film**

The initial concentrations of ammonia, manganese and iron in ground water pumped from a depth of 50 m were between 2.0 and 2.8, 1.2 and 1.7 and 0.9–2 mg/L, respectively. The concentration of DO was increased from between 2.5 and 3.5 mg/L to a value of nearly 7.8 mg/L by aeration as well as the water fall method. Then the raw water was filtered through a filter bed with a depth of 1.5 m; the bed was filled by quartz sand with diameters ranging between 1 and 2 mm. The filtration loading rate was 8 m³/m² h, and the intensity of the air and water backwash were 13–17 and 3–4 L/s m², respectively. After 3 months of operation, the surface of the quartz sand was naturally coated by the co-oxide filter film in a dark color, and the removal of ammonia, manganese and iron was noticeably improved (Huang et al. 2014).

**Morphology and elements**

The samples of co-oxides filter film-coated sands were cleaned by ultrapure water, and then vacuum freeze-dried for 1 h. Then the samples were kept in sealed plastic bags for the characterization of morphology and elements. The specific area and pore properties of the co-oxide film-coated sand were characterized by the BET method (Quantachrome-AUTOSORB-1C). The morphologies and chemical constituents of the co-oxide film were characterized by SEM (JEOL-JSM6360LV) combined with energy-dispersive X-ray spectroscopy (Thermo Fisher Scientific-Noran System six).

**The XPS characterization**

In XPS characterization (Thermo Scientific K-Alpha), the samples before and after DO saturation sorptions were vacuum-dried and kept in sealed vacuum tubes (Zhao et al. 2003). A conventional Al Kα anode radiation source was used as the excitation source for XPS. The binding energies were calibrated by the C1s peak at 284.6 eV. The XPS spectra of the elements of O, Mn, Fe and Si were analyzed and peak fitted by bundled software (Avantage).

**The TPD characterization**

**The adsorption of DO**

The washed and weighed sample (10 g) was introduced into a batch reactor. The volume of the reactor, which was filled by ultrapure water, was 0.5 L. The concentration of DO in the reactor was maintained at approximately 8.0 mg/L for a sufficiently long time with aeration to ensure that the sand reached DO saturation sorption. The blank samples were prepared in a similar process, in which the nitrogen, not oxygen, was aerated to keep the concentration of DO less than 0.02 mg/L. Both the DO-adsorbed and the blank samples were vacuum freeze-dried for 30 min and kept in sealed plastic bags. The extra air in the bag was discharged by vacuum pump after the loading of samples for TPD characterization.

**Tests**

The temperature programmed desorption was carried out in a quartz reactor with sample loadings of approximately 0.5 g. The samples were initially vacuumed at 298.15 K for
12 h, and then N₂ (30 mL/min) was passed through for approximately 20–30 min until the output signal was stable. Then the samples were heated in the stream of flowing N₂ at certain heating rates to obtain the desorption spectra, which were recorded by a thermal conductivity detector. The detector was calibrated by the desorption of 1 mg of oxygen. The integral area of the correction spectrum was 44.54.

RESULTS AND DISCUSSION

Morphology and elements

Figure 1 illustrates the surface and the section images of the co-oxide filter film. The surface of the filter film was completely covered by irregular lamellar oxides with sizes around 0.5 micron (Figure 1(a)). The rough structure provided substantial surface area for the adsorption of DO. As for the growth of co-oxides, the molecules of oxides formed and gathered firstly in the cracks on the surface, which are the best acceptance sites for atoms or ions (Scheel & Fukuda 2003). The filter film was scraped off from the sand surface by external force and the section images (Figure 1(b)) showed that the filter film consisted of three layers. The inner layer of the film, referred to as Point 1, had a compact structure and was nearly 20–30 μm thick, whereas the middle and outer layers, referred to as Point 3 and Point 5, respectively, had a loose and porous structure and were approximately 60–70 μm and 20–30 μm thick, respectively.

Figure 2 illustrates the EDS spectra of the five points enumerated in Figure 1(b). At Point 1, the detected elements were C, Mn, Ca, Mg and O, implying that the inner layer of the filter film consists of manganese oxides as well as carbonate. In the middle and outer layers, different elements were detected, including Si, Al and Fe, indicating the existence of silicates.

Specific areas and pore properties

The specific areas and pore properties of the original sand before treatment and for the co-oxide film-coated sands are illustrated in Table 1. It was shown that the specific area increased by nearly 60 times (from 0.11 to 6.5 m²/g), and the pore volume increased from $2.803 \times 10^{-4}$ to $1.565 \times 10^{-2}$ cm³/g. Coincident with the results of SEM, the increased specific area may due to the inner walls of pores and the cluster of oxides formed on the surface of filter film; thus, more adsorption site of DO was provided. Combined with the surface images of the filter film, the small volume of the pores indicated that the adsorption of DO could be considered as a surface process.

The XPS analysis

The XPS method was used to characterize the binding energies of each element of the samples before and after the DO saturation sorption. Figure 3 illustrates the XPS spectra of O1s of the co-oxide film before and after the DO saturation sorption and it is shown that each spectrum consists of three peaks. The binding energies of peaks in the spectrum of O1s before DO adsorption were in the positions of 532.07, 531.28 and 529.57 eV, and the area percentages of each peak were 24.64, 38.94 and 36.39%, respectively. After the adsorption of DO, the area percentages of each peak changed noticeably to 11.36, 65.37 and 23.26%, and the binding energies of the three peaks increased to 532.55, 532.02 and 529.57 eV, implying the formation of adsorbed oxygen in three adsorbed sites (Li et al. 2000). The areas of the three peaks have a proportional ratio of about 1:6:2, representing the surface distribution of adsorbed oxygen on different kinds of sites. It has been proved that the adsorption of DO on the filter film was a molecular adsorption process (Zheng
since the binding energies of adsorbed oxygen are in the ranges of 529–533 eV, according to the reports in former relevant studies (Seiyama et al. 1985; Kharus & Lunsford 1989; Borman et al. 1994), the adsorption states of oxygen could be O$_2$. As the chemical adsorption occurred, the formation of chemical bonds changed

Figure 2 | The EDS spectra of co-oxide films at different depths: (a) Point 1, (b) Point 2, (c) Point 3, (d) Point 4, (e) Point 5.
the chemical environment of inner electrons of the atoms in adsorption sites and the binding energies changed. However, as for physical adsorption, the interactions between molecules of oxygen and the atoms on surface were too weak to change the binding energies (Hüfner 2003). The XPS spectra of the elements Si, Fe and Mn before and after the DO saturation sorption are also depicted in Figures 4–6. As shown in Figure 4, the binding energy of Si2p before DO saturation sorption was 101.97 eV, indicating the existence of silicates. Owing to the higher electron negativity of O atoms than of Si atoms, after the adsorption of DO, the binding energy of Si2p increased to 102.81 eV, indicating the chemical bonding effect between atoms of oxygen and silicon.

Similarly, the binding energies of Fe3/2p and Mn3/2p were also changed due to the DO saturation sorption. As shown in Figures 5 and 6, the chemical states of iron and manganese were FeO (710.04 eV), Fe2O3 (711.24 eV), Ca3Fe9 (SiO4)z (715.18 eV) and MnO (640.94 eV), Mn2O3 (641.91 eV) and MnO2 (642.77 eV), respectively. Since the electron negativity of Fe and Mn atoms are lower than that of O atoms, after the DO saturation sorption, all the binding energies of iron and manganese atoms in each kind of states increased obviously. The binding energies of Fe3/2p and Mn3/2p were FeO (710.04 eV), Fe2O3 (711.24 eV), Ca3Fe9 (SiO4)z (715.18 eV) and MnO (640.94 eV), Mn2O3 (641.91 eV) and MnO2 (642.77 eV), respectively, indicating the formation of chemical bonds between O and Fe, as well as O and Mn atoms. To sum up, the DO was chemically adsorbed on filter film in the state of O2 and the atoms of Si, Fe and Mn were the adsorption sites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
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<tr>
<td>Fresh sand</td>
<td>0.11</td>
<td>2.8 × 10⁻⁴</td>
<td>10.5</td>
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<tr>
<td>Co-oxide film-coated sands</td>
<td>6.5</td>
<td>1.57 × 10⁻²</td>
<td>13.91</td>
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Figure 3 | The XPS spectra of O1 s of the co-oxide filter film.

Figure 4 | The XPS spectra of Si2p of the co-oxide filter film.

Figure 5 | The XPS spectra of Fe3/2p of the co-oxide filter film.
The TPD analysis

Figure 7 illustrates the TPD spectra of blank samples with the desorption peak fitted at different heating rates. It is shown that there exists an output signal for the blank samples. The TPD spectra were fitted by six peaks. As the heating rate increased, the fitted peaks in each spectrum shifted towards the high temperature area (Leary et al. 1988). The signals were generated by the release of surface matters in the heating processes of blank DO adsorption samples. The composition of the gas which characterized the natural properties of the filter film might include the carbon dioxide generated from the resolved carbonates as well as the water vapor released by resolved silicates, carbonates and the surface hydroxyl existing on the surfaces of manganese and iron oxides.
The species of adsorbed oxygen could be identified by
the positions of desorption peaks fitted with the TPD spectra
as well as the analysis of desorption activation energy of
each peak (Tokoro & Misuo 1978). The TPD spectra of
DO-saturated-adsorbed samples at different heating rates
were peak fitted and are shown in Figure 8. Compared
with the TPD spectra of the blank samples with the same
heating rate, TPD spectra of the DO-saturated-adsorbed
samples changed noticeably in shape and area. Desorption
temperatures of fitted peaks in the blank and the DO-
adsorbed samples are summarized in Tables 2 and 3,
respectively.

As listed in Table 2, six peaks were fitted to the TPD
spectra of the blank samples at different heating rates. How-
ever, as listed in Table 3, the number of fitted peaks in the
TPD spectra of DO-saturated-adsorbed samples increased
to nine, and six of them, at the same heating rate, had
nearly the same desorption temperatures as the fitted
peaks for the blank spectra. This result indicates that these
six peaks fitted in both kinds of spectra represent the natural
bulk-phase properties of co-oxide filter-film-coated sand.

As for the TPD spectra of DO-saturated-adsorbed
samples, there were three peaks of adsorbed oxygen at
different desorption temperatures. As the heating rates
increased, the peaks moved towards the high temperature
area. The increased spectra integral areas caused by the
adsorption of DO had a value of about 12, indicating that
the amount of adsorbed oxygen was nearly 0.5 mg/g. The
area proportions of the three adsorbed oxygen peaks is
nearly 1:6:2, which coincides with the surface properties

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**Figure 8** The TPD spectra of DO-saturated-adsorbed samples at different heating rates. Experimental conditions: mass of the sample: 0.5 g, vacuum time: 12 h, nitrogen flow rate: 30 mL/min, initial temperature: 25 °C, heating rate (°C/min): 5, 10, 15 and 20.
characterized by XPS, indicating that the three peaks represent the oxygen chemically adsorbed on silicate, iron atom and manganese atom sites respectively. The three desorption peaks were located in the regions 100°C/C20°C - 150°C/C20°C, 200°C/C20°C - 250°C/C20°C and 350°C/C20°C - 600°C/C20°C, respectively, indicating that the adsorption state of DO could be chemically adsorbed O2 (Zhao et al. 1999; Wei et al. 1999). Coincident with the results of the XPS characterization, the adsorption state of DO, which is O2, could finally be determined.

The interaction strength between adsorbent and adsorbate could be determined by the analysis of TPD spectra. Generally speaking, the lower the desorption activation energy, the weaker the adsorption interaction effect. The desorption activation energy of adsorbed oxygen on each kind of site can be calculated from Equation (1) (Wang & Xie 1980). The linear fitting of $2 \log T_m - \log b$ to $1/T_m$ of each desorption peak is shown in Figure 9, and the desorption activation energies are listed in Table 4. As shown in Table 4, the $E_d$ of oxygen on silicates, iron atoms and manganese atoms are 19.84 kJ mol$^{-1}$, 38.89 kJ/mol and 29.35 kJ/mol, respectively. Compared to the desorption active energies of oxygen chemically adsorbed on gas–solid interface of other kinds of oxide surfaces, such as TiO$_2$ (111) (94 kJ/mol) (Gopel et al. 1985) and SmMnO$_3$ (67.0 and 93.9 kJ/mol) (Chen et al. 1995), on the surface of co-oxides filter film, the DO is adsorbed on each site by a weak

<table>
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<th>Desorption temperatures of fitted peaks of spectra of blank samples</th>
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<td>Blank sample</td>
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<th>Desorption temperatures of fitted peaks of spectra of dissolved oxygen adsorbed samples</th>
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<td>DO saturated-adsorbed sample</td>
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effect. Combined with the results of XPS characterization, the adsorption of DO is kind of weak chemical adsorption

\[
2 \log T_m - \log b = \frac{E_d}{2.303R} \cdot \frac{1}{T_m} + \log \frac{E_d}{A_n R n \theta_m} \tag{1}
\]

where \( T_m \) is the desorption temperature (K); \( b \) is the heating rate (K/min); \( E_d \) is the desorption active energy (J/mol); \( R \) is gas constant (J/mol K); \( A_n \) are pre-exponential factors; \( \theta_m \) is the coverage degree in adsorption peak; and \( n \) is the desorption degree.

### CONCLUSION

The co-oxide filter film formed in the filtration process of groundwater containing high levels of ammonia, iron and manganese was constructed in a three-layer porous structure. The formation of a filter film improved the surface properties of the filter sands. On the surface of the filter film, the chemical adsorption sites are silicates, iron and manganese atoms respectively. The \( O_2 \) was considered to be the adsorbed oxygen specie. The \( E_d \) values of adsorbed oxygen on three kinds of sites shows that the adsorptions were weak chemical effects.

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