Performance of advanced water treatment plant for removing Fe, Mn and organic pollutants from raw water

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ABSTRACT

In the case of treating a source water containing higher concentrations of Fe^{2+}, Mn^{2+} and organic pollutants, the Fe^{2+} was partially removed by pretreatment steps of aeration-sand filtration, while Mn^{2+} and organics were removed mainly by an ozonation-BAC process. The performance of the advanced treatment plant and removal mechanisms are studied in this paper. The optimal O_3 dosage and residual O_3 were found to be 4 mg l^{-1} and 0.4 mg l^{-1}, respectively, for which the Fe^{2+}, Mn^{2+} and COD_{Mn} removals reached 98%, 95% and 85.5% respectively.

GC/MS analytical results showed that the advanced water treatment plant was very efficient in micro-organic pollutant removal. The total species decreased from 59 in the raw water to 50, 40 and 26 in the effluents of the sand filter, ozonation column and BAC filter, respectively. The priority and potentially hazardous pollutant species decreased from 16 in the raw water to 10, 8 and 5 in the corresponding effluents, respectively.

Key words | advanced treatment, biological activated carbon, iron, manganese, organic pollutants, ozonation

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INTRODUCTION

The advanced purification system, consisting mainly of ozonation and biological activated carbon for removing organic pollutants in drinking water, has been widely employed for high quality drinking water production (Wang *et al*. 1985*a*,*b*, 1986*b*, 1999; Wang and Wang 2000). When the iron, manganese and organic pollutants co-exist in raw water, the treatment flow-sheet, its unit treatment processes and their parameters are different from those for removing organic pollutants only. Usually the pre-aeration and then sand filtration for iron removal and partial manganese removal are required (Wang *et al*. 1986*a*; Stumn and Lee 1960; Stumn and Singer 1966), which is then followed by ozonation for manganese and partial organic removal. By means of strong oxidation with ozonation, the residual dissolved bivalent iron and manganese are oxidized to trivalent iron in the form of insoluble $Fe(OH)_3$, tetravalent manganese in the form of $MnO(OH)_2$ and heptavalent manganese in the form of permanganate. At the same time, the large molecular organic pollutants are oxidized to small ones by ozonation at an optimal dosage; these are easily degraded and adsorbed by biological activated carbon (Wang *et al*. 1985*a*,*b*, 1986*b*, 1999; Wang and Wang 2000). A full-scale study on an advanced treatment facility for removing higher concentration of Fe, Mn and organic pollutants simultaneously was carried out at the Moon Bay Holiday Villa in Harbin, Heilongjiang.

RAW WATER QUALITY

The Moon Bay Holiday Villa is situated on the Sun Island of Harbin, Heilongjiang. Raw water is taken from Qianjin Water Treatment Plant for domestic and industrial use. The raw water quality is shown in Table 1. As shown, the

Table 1 | Raw water quality

Sample No.	Colour (NCU)	COD_{Mn} (mg l^{-1})	Iron (mg l^{-1})	Manganese (mg l^{-1})	pH	Turbidity (NTU)	Total hardness (mg $CaCO_3$ l^{-1})
1	28	3.52	2.13	0.85	7.45	3.8	147
2	15	2.4	2.11	0.76	7.25	1.8	140
3	5.5	3.44	—	—	7.42	1.5	143
4	17	1 .76	1.11	0.62	7.32	2.6	142
5	16	3.6	1.68	0.64	7.51	3.7	150
6	18	3.6	1.40	0.57	7.32	3.5	141
7	17	3.2	1.105	0.38	7.14	4.2	142
8	15	3.36	1.145	0.48	7.28	2.9	148
9	10	3.04	1.07	0.44	7.38	2.7	143
10	17	2.4	1.04	0.37	7.43	2.5	154
11	16	2.16	1.05	0.36	7.35	2.6	145
Average	15.86	2.95	1.26	0.55	7.34	2.89	145

organic pollutants measured as COD_{Mn} in raw water were higher than the domestic standard of 2.5 mg l^{-1} for the third class of surface water. These pollutants consist mainly of humic substances that can be effectively treated by ozonation and BAC processes (Wang 1987; Langlais *et al.* 1991*a*; McCann 1999). The iron and manganese exceeded the national standard (0.3 mg l^{-1} for Fe^{2+} and 0.1 mg l^{-1} for Mn^{2+}) significantly as well. These both exist as bivalent ions in water at low dissolved oxygen concentration. The manganese is difficult to remove from the raw water simultaneously with iron, because the standard electrode potential of manganese is 1.23 V, higher than 0.77 V for iron. Oxidation and reduction reactions will occur; the bivalent iron acting as reductant prevents the bivalent manganese from being oxidized to a high valency state and resists the manganese removal.

Iron can be removed effectively by the aeration method (Stumm and Lee 1960; Stumm and Singer 1966). Removal efficiency increases with dissolved oxygen and pH, but is obstructed by dissolved organic matter, which can react with dissolved iron to form complexing compounds and prevents bivalent iron from being oxidized to trivalent iron. Although the manganese can be removed by the aeration method, according to thermodynamics theory, the reaction velocity is slow in an alkaline medium (pH>9.2–9.5) and removal efficiency is low. Therefore, in order to remove the iron, manganese and organics in an integrated treatment facility, it is very important to choose a suitable treatment flow-sheet, unit processes and their parameters.

TREATMENT FLOW-SHEET AND UNIT PROCESSES

According to the raw water quality, the advanced treatment plant with a capacity of 10 m^3 h^{-1} was designed as follows:

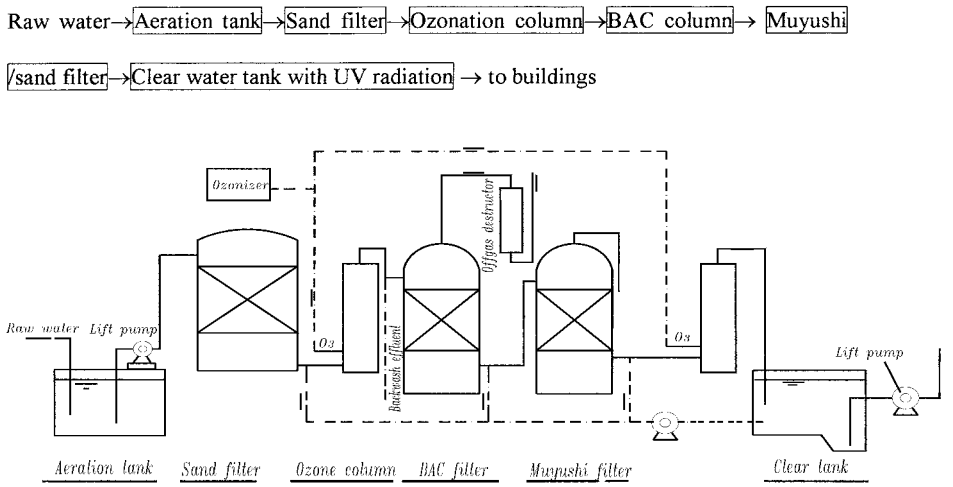

Figure 1 | Flowchart of the advanced drinking water treatment plant at Moon Bay Holiday Villa, Harbin, Heilongjiang.

The flow-sheet of the treatment system is shown in Figure 1, and the ozone contact column, BAC filter and Muyushi/sand filter are shown in Figure 2.

The parameters of each treatment unit are described as follows:

Aeration tank: 2 m × 2 m, made of steel with anti-corrosive lining by epoxy resin, HRT = 50 min, dissolved oxygen concentration = 8–9 mg l^{-1} maintained by an ejector installed in the tank above the top water level.

Figure 2 | Ozone contact column (left), BAC filter (middle) and Muyushi/sand filter (right).

Sand filter: 1.2 m diameter × 2.5 m height, steel with anticorrosive lining by epoxy resin, filtration velocity 6 m h^{-1}, HRT = 10 min.

Ozonation column: 0.5 m diameter × 3.4 m height, stainless steel, countercurrent contact pattern with upflow of O_3 containing air; package: polyethylene multi-surface hollow ball Φ50, HRT = 10 min.

BAC column: 1.2 m diameter × 3.0 m height, stainless steel, downflow, HRT = 20 min. The domestic granular carbon GH-16 was packed with mesh size of 14 × 40 and specific surface area of 1,150 m^2 g^{-1}, the biological activity appeared after 4 weeks' operation from start-up and increased with operation time.

Muyushi/sand dual media filter: 1.2 m diameter × 2.5 m height, stainless steel, downflow pattern, size of Muyushi mineral granules 1–3 mm and sand 0.8–1.2 mm; mainly used for the increase of mineral and micro-element contents in filtrate through leaching from the mineral.

As shown in Figure 1, the aeration tank and sand filter were employed to remove iron, but were ineffective for removing manganese and organics, which are mainly removed by the post-positioned ozone contact column and BAC filter. The ozone dosage was calculated in reference to chemical formulae (Langlais *et al*. 1991*b*) shown in Table 2.

At low ozone dosage, the ozone reacts with iron first at high speed until a very low residual concentration of

Table 2 | Reaction equations and theoretical stoichiometric amounts of oxygen and ozone for Fe^{2+} and Mn^{2+} removal (Langlais *et al. 1991b*)

Metal/Oxidants	Reaction equations	Chemical metering
1. $Fe^{2+}/O_2(aq)$	$2Fe^{2+} + 1/2O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 4H^+$	0.14 mg O_2/mg Fe^{2+}
or $O_3(aq) \rightarrow O_2(aq)$	$2Fe^{2+} + O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + O_2 + 4H^+$	0.43 mg O_3/mg Fe^{2+}
2. $Mn^{2+}/O_2(aq)$	$Mn^{2+} + 1/2O_2 + H_2O \rightarrow MnO_2 + 2H^+$	0.29 mg O_2/mg Mn^{2+}
or $O_3(aq) \rightarrow O_2(aq)$	$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + O_2 + 2H^+$	0.88 mg O_3/mg Mn^{2+}
	$Mn^{2+} + 2O_3 + H_2O \rightarrow MnO_4^- + O_2 + H_2O$	2.2 mg O_2/mg Mn^{2+}

iron is reached; then it starts to react with manganese. As shown in Table 2, 0.43 mg l^{-1} and 0.88 mg l^{-1} O_3 was needed to oxidize 1 mg l^{-1} bivalent iron and 1 mg l^{-1} manganese, respectively. The oxidation efficiency of Mn^{2+} to MnO_2 increased with ozone dosage and reached 85% for 1 mg l^{-1} ozone dosage. The optimum ozone dosage is about 3–4 mg l^{-1} for simultaneous organics removal. However, it is very difficult to control the removal efficiency by adjusting the ozonation dosage, for the influent quality varied with operation time. Hence, the 0.4 mg l^{-1} residual ozone concentration was employed as an effective measure to control the ozonation dosage, which ensured that the manganese was not only oxidized into MnO_2 or $MnO(OH)_2$, but also partially into MnO_4^-, with a light purple colour in the effluent from the ozonation column. Then MnO_2 or MnO(OH) and MnO_4^- were reduced to $MnO(OH)_2$ by catalytic reduction on the surface of the biological activated carbon in the post-positioned BAC filter.

RESULTS AND DISCUSSION

COD_{Mn}, iron and manganese removal

The variation of iron, manganese and COD_{Mn} in the effluent of different treatment units with operation time is shown in Figures 2, 3 and 4, respectively.

As shown in Figure 3, the COD_{Mn} was removed mainly in the ozonation column and BAC filter (35 and 48% of removal, respectively); removal in the sand filter was negligible, with an additional removal of some 5% in

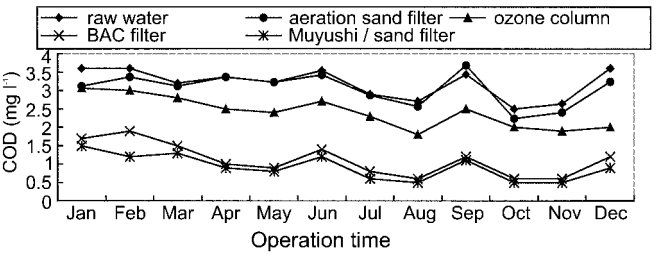

Figure 3 | Variation of COD_{Mn} in the effluent of different treatment units with operation time.

the Muyushi filter. As shown in Figure 4, nearly 60% of the iron was removed in the aeration oxidation-sand filter. The residual part was removed in the ozone column and BAC filter with a total of 95–100% (mean 98%) removal, when the residual ozone in the effluent of the ozonation column was 0.2 mg l^{-1}. At the start of operation of the Muyushi sand filter, the iron concentration in the filter effluent increased because of the small amount of iron dissolved from the Muyushi mineral, and reached 0.44 mg l^{-1}. However, after a short period, this phenomenon did not recur and there was almost complete iron removal.

As shown in Figure 5, there was insignificant manganese removal through the aeration tank and sand filter. Only part of the manganese was removed in the ozone contact column, with 20–30% removal of the insoluble MnO_2 and $MnO(OH)_2$ forms. The residual parts were oxidized into the soluble MnO_4^- form at an effluent

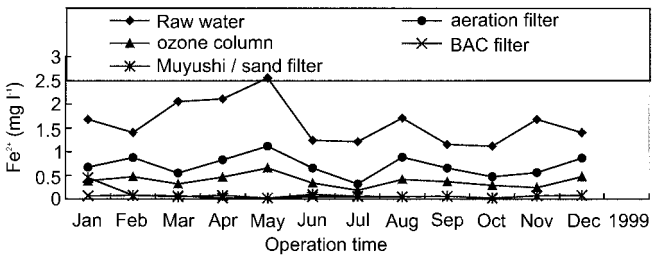

Figure 4 | Variation of iron in the effluent of different treatment units with operation time.

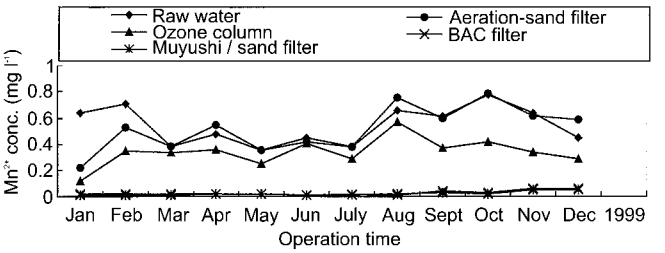

Figure 5 | Variation of manganese in the effluent of different treatment units with operation time.

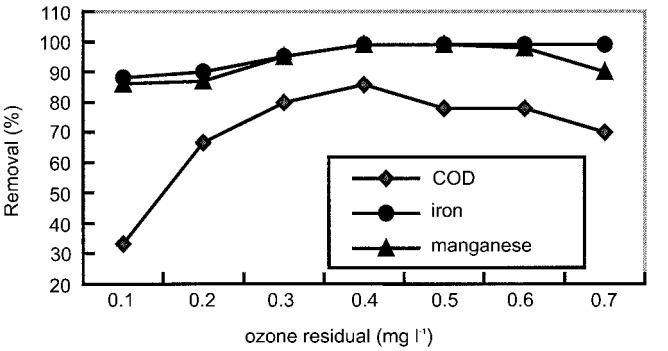

Figure 6 | Relationship between residual ozone content and COD_{Mn}, iron and manganese removal.

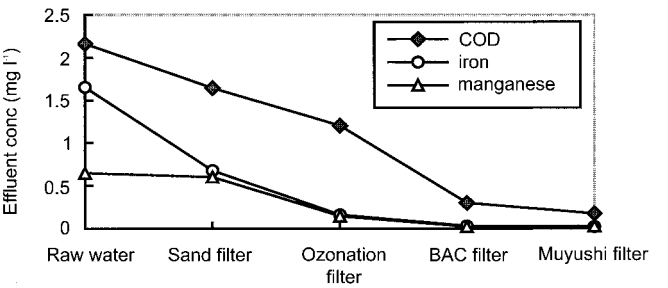

Figure 7 | Variation of COD_{Mn}, iron and manganese removal in the effluent of different treatment units at optimum ozone dosage (4.0 mg l^{-1}).

residual ozone concentration of 0.4 mg l^{-1}, corresponding to a 4 mg l^{-1} ozone dosage. This made the effluent of the ozone column change from an orange-yellow colour to a light purple-red colour and was removed in the BAC

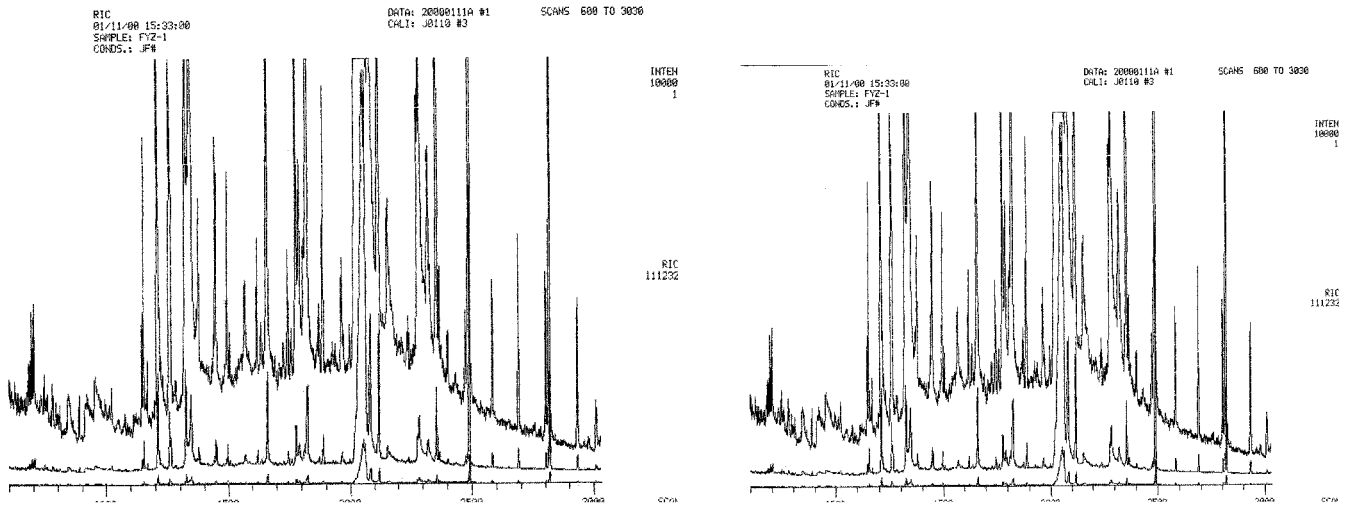

Figure 8 | GC/MS of raw water (left) and sand filter effluent (right).

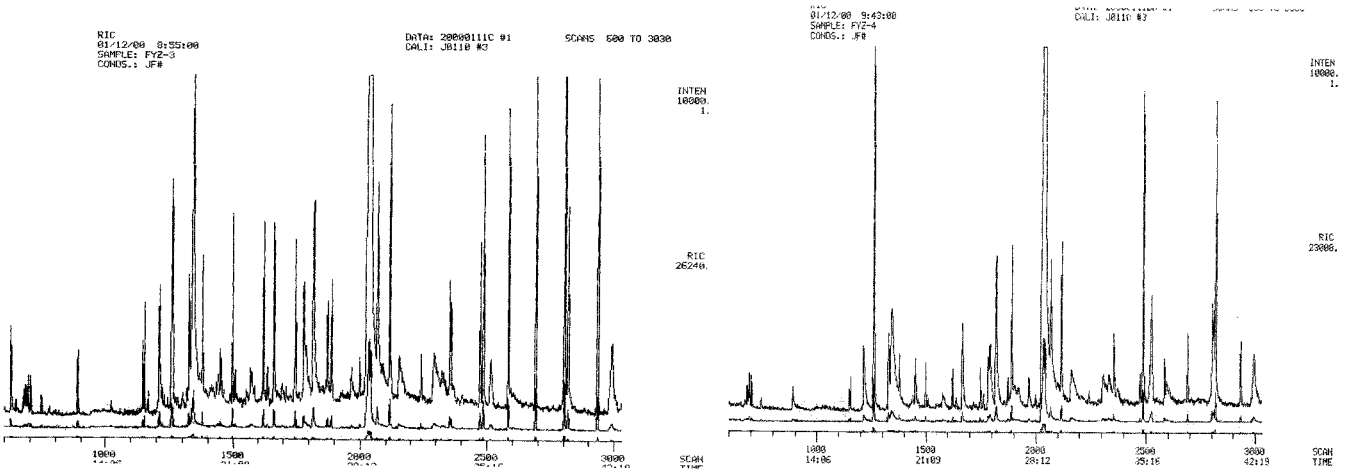

Figure 9 | GC/MS of ozone column effluent (left) and BAC filtrate (right).

filter by catalytic reduction without any colour in the filtrate. The mechanism of manganese removal is as follows: the MnO_4^- is catalytically reduced on the BAC surface into insoluble MnO_2 and $MnO(OH)_2$ and then removed. Furthermore, a small residual amount of Mn^{2+} reacts with MnO_4^- in the alkaline medium to form Mn_2O_3, which can be oxidized into MnO_2 or $MnO(OH)_2$ by strong oxidation with O_3 and/or MnO_4^- and then removed by the BAC filter through adsorption with over 90% removal.

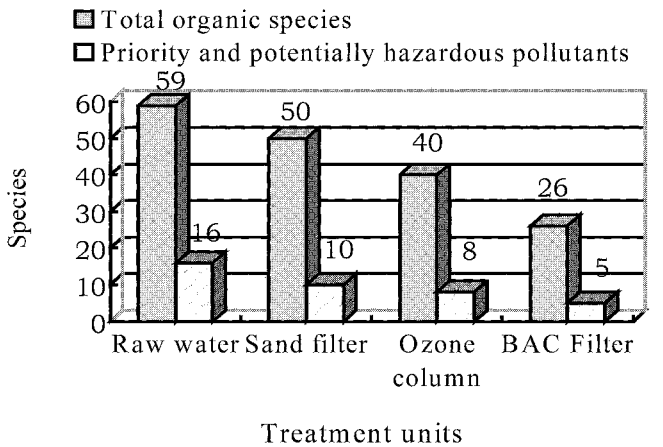

Figure 10 | Numbers of organic pollutant species.

Relationship between ozone dosage and COD_{Mn}, iron and manganese removal

In order to observe the effect of ozone dosage on COD_{Mn}, iron and manganese removal and to determine the optimum ozone dosage, their removal efficiencies were noted at different ozone dosage. An experiment was carried out (results shown in Figures 6 and 7), from which it was found that the ozone dosage of 4.0 mg l^{-1} (with the corresponding residual ozone concentration of 0.4 mg l^{-1}) is the optimum dosage for COD_{Mn}, iron and manganese removal. At this dosage, the removal efficiencies were 85.8%, 98% and 95%, respectively, of which the COD_{Mn} was removed with very high efficiency because of the synergetic effect of the co-existing O_3 and MnO_4^-. However, when the ozone dosage increased, even though the removal of iron and manganese was maintained at 98% and 95% or more, respectively, the removal of COD_{Mn} dropped sharply. This was due to excessive ozone dosage, at which large molecular organic pollutants were oxidized into very small molecular compounds with strong polarity; these were hardly adsorbed by GAC and resulted in effluent containing a higher COD_{Mn}. Therefore, the optimum ozone dosage for removing iron, manganese and COD was above 4 mg l^{-1} and the residual ozone was 0.4 mg l^{-1} for the raw water at Moon Bay Holiday Villa.

Table 3 | Species of priority and potentially hazardous pollutants in the raw water and effluent of different treatment units

Number	Priority and potentially hazardous pollutants	Raw water	Sand filter	Ozonation column	BAC filter
1	1,8-dimethyl naphthalene	✔	✔	✔	✔
2	(1,1-dimethyl)-4-methoxy phenol	✔			
3	2,6-bis(1,1-dimethylethyl)-4-methyl phenol	✔	✔	✔	✔
4	4,7-dimethyl undecane	✔			
5	Pentandioc acid dibutyl ester	✔			
6	Hexadecane*	✔	✔	✔	✔
7	2,6-bis(1,1-dimethylethyl)-4-ethyl phenol	✔			
8	2-methyl-N-phenyl-2-propenyl amide	✔		✔	
9	1,2-benzenedicarboxylic acid butyl-2-methylpropylester	✔	✔	✔	✔
10	5-hydroxy-2-methylbenzopyranyl-4-ketone	✔			
11	5-ethoxythiazole	✔	✔	✔	
12	1-methyl ethyl cyclopentane	✔			
13	docosane*	✔			
14	1-phenanthrene carboxylic acid	✔			
15	1,4-dimethyl cyclohexane	✔	✔		
16	1,2-benzenedicarboxylic acid diisooctyl ester	✔	✔	✔	✔
17	naphthalene*		✔		
18	1,2,3,4-H-6-methyl naphthalene		✔		
19	4,6-dihydroxy-2,3-dimethyl benzaldehyde		✔		
20	1,4-diethoxy cyclohexane			✔	

*Belongs to the 129 species of priority pollutants identified by US EPA.

Micro-organic pollutant removal with GC/MS analysis

The raw water and effluent from different treatment units were analysed by GC/MS, and the results are shown in Figures 8 and 9. The species numbers of organic micro-pollutants were reduced from 59 in the raw water to 50 in the sand filter effluent, 40 in the ozone column effluent and 26 in the BAC filter effluent (Figure 10).

Details of the species of priority and potentially hazardous pollutants contained in the raw water and effluent of different treatment units are shown in Table 3. The table shows that there existed 16 species of priority and

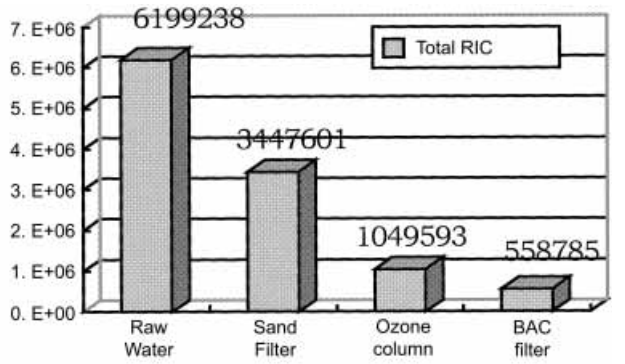

Figure 11 | Total GC/MS relative ionic currency intensity (RIC) in raw water and effluent from different treatment units.

potentially hazardous pollutants in the raw water, 10 in the sand filter effluent, 8 in that of the ozone contact column and 5 in the BAC filtrate. The GC/MS relative ionic currency intensity (RIC) was reduced from 6.2×10^6 in raw water to 5.59×10^5 in the BAC filter effluent, with 91% removal, as shown in Figure 11.

CONCLUSION

The advanced treatment plant at Moon Bay Holiday Villa, Harbin, employed for the efficient, simultaneous removal of Mn^{2+}, Fe^{2+} and organic pollutants, consists of aeration tank, sand filter, ozonation column, biological activated carbon filter, Muyushi mineral/sand filter, and clear water tank with UV disinfection, which operate in series.

- The iron was mainly removed in the pretreatment stage of aeration and sand filtration with a removal of over 60%; the rest was removed in ozonation and in the BAC filter.
- The Mn^{2+} and organic pollutants were mainly removed in ozonation, the BAC filter and the Muyushi mineral/sand dual media filter with high removal efficiencies.
- At the optimal ozone dosage of 4.0 mg l^{-1}, the Fe, Mn and COD_{Mn} removals were 98%, 95% and 85.7%, respectively.
- The priority and potentially hazardous micro-organic pollutants were effectively removed by the treatment system employed at Moon Bay Holiday Villa. Species number was reduced from 16 in the raw water to 5 in the BAC filtrate (68.7% species removal), with 91% removal of total RIC.

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