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Removal of iron and manganese in steel industry drainage by biological activated carbon

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ABSTRACT

The present paper studied the removal effect of iron and manganese in steel industry drainage by biological activated carbon (BAC) and discussed the removal mechanism. The results indicated that the removal rates of total Fe and Mn with concentrations of 0.62 and 0.55 mg/L in raw water could reach 71.9% and 75.4%, respectively. The total Fe and Mn was considered to be removed through combined effect of active carbon adsorption, biological oxidation and filtration, and the removal law could be described by the model of apparent first-order kinetics. Meanwhile, backwash could remove more than 50% of total Fe and Mn in the filter column, which was a significant procedure for the stability of BAC. Besides, the removal of turbidity and NH_3-N was also obvious, and the removal rates could reach 77.8% and 71.9%, respectively.

Keywords: Biological activated carbon; Removal mechanism; Steel industry drainage

1. Introduction

Steel industry is one of the high energy, high water consumption and high pollution industries with its drainage containing large amounts of metal contaminant [1], such as iron (Fe), manganese (Mn), etc. Excess amount of Fe and Mn will also bring great harms to human health and industrial production. Washing water or the production of raw materials containing Fe and Mn will reduce the quality of luster and colour of the products in the textile, printing and dyeing, knitting, paper and other industries. In the boiler water, Fe and Mn are one of the components of scale forming and tank mud, often cause blockage and corrosion. With the increasingly stringent water standards, conventional water treatment process can hardly guarantee the safety of water [2–4]. The application technology of Fe and Mn removal in micro polluted water has developed from air oxidation, contact oxidation to the biological fixation removal stage.

Biological activated carbon (BAC), developed in 1970s, is a main trend treatment of metal contamination [5]. Compared to quartz sand, BAC has huge surface area and developed pore structure, thus it has strong adsorption properties on the organic matter, dissolved oxygen, heavy metals and other pollutants. BAC has the advantages of high efficiency, strong stability, high purity and strong ability of biodegradation [6,7], and the adsorbed organics can be biodegraded later, which retains the adsorption ability of BAC in a steady range [8]. And, as a carrier, activated carbon

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can play a synergistic effect of adsorption and microbial degradation, achieving good removal effect on wastewater under the condition of suitable temperature and nutrient. In recent years, BAC has been increasingly used in the purification of water source, the treatment of industrial wastewater and the advanced cleansing of city sewage [9–11], and it has been proved that BAC has strong removal efficiency for COD, turbidity, chroma and phenol of organic pollutant [12]. Besides, by the capillary model of filter layer, Wang set up an equation between dissolved organics and empty bed contact time [13].

Recently, BAC was found to possess prominent removal effect on some metals [14–16]. As for removal of Mn and Fe by BAC, the biological removal effect always varied with reaction conditions, including selection of filter material, filter column structures, strain and inoculation, and the process parameters to the actual operation such as dissolved oxygen, pH, temperature, empty bed contact time, etc. For example, Pacini found that dissolved oxygen and pH needed to be strictly controlled in order to limit abiotic iron oxidation [17]; Mondal proved that the reaction time, temperature and pH law of iron and manganese had a prominent impact on the removal of iron and manganese [18]; Fu found a certain linear relationship between pH value and manganese removal rate [19]. Besides, there were also some kinetic researches on the dynamics of biological removal for iron and manganese [20]. Katsoyiannis analyzed the process with simple first-order reaction [21], and Stembal established a dynamic model based on mass transfer limit dynamic model [22].

Nevertheless, few researches have focused on the treatment of steel industry wastewater by BAC. In the present paper, BAC is used in the advanced treatment of total Fe and Mn in steel industry drainage. The removal effect of Fe, Mn, turbidity, COD, NH_3-N and total P under different operating conditions is investigated, and the removal mechanism of Fe and Mn is discussed. The purpose of the present study is to evaluate the removal effect and mechanism of BAC on steel industry drainage and to find new approaches to the reuse of steel industry drainage.

2. Materials and methods

2.1. Raw water quality and source

The raw water was sampled at the No. 2 pumping station of the river around the factory in Baosteel Engineering & Technology Co. Ltd. (Shanghai, China), which mainly collected the treated wastewater, sewage and rainwater. The raw water quality during the experiment was denoted as shown in Table 1.

The raw water quality varied greatly in which the average concentrations of turbidity, total Fe and Mn failed to meet the requirement of GB/T 19923-2005 Standards (turbidity ≤ 5 NTU, total Fe ≤ 0.3 mg/L and Mn ≤ 0.1 mg/L).

2.2. Equipment for test

Activated carbon (AC, using coal columnar activated carbon with specification of Φ 2 mm × 4 mm, specific surface area ≥ 900 m^2/g and pore volume ≥ 0.65 cm^3/g) was obtained from Shanghai Activated Carbon Factory (Shanghai, China). The filter column was made from polymethyl methacrylate plastic with a diameter of 150 mm and a height of 2,400 mm (Fig. 1). Gravel was stowed at the bottom to 100 mm high as the supporting layer, on which AC of 1,200 mm high was then filled in. Sample collections were set every 20 cm along the AC column wall.

The raw water was regulated in a barrel, and then lifted to the top of the filter column by a peristaltic pump. After that, it fell into the filter column and was aerated by a miniature aerator at the same time. At the bottom of the filtering cylinder, a back washing pipeline was arranged, and the recoil of backwash water was excluded from the top of the overflow filter column. Empty bed contact time was altered through adjusting the flux of the peristaltic pump. By altering dissolved oxygen concentration, the aeration quantity could be adjusted, and temperature could change with the natural changes. Referring to the pipeline pressure loss, the head loss of pipeline is less than 4.5×10^{-4} m.

Table 1
Raw water quality in the river around the factory

Items	pH	Turbidity (NTU)	COD (mg/L)	NH_3-N (mg/L)	Total P (mg/L)	Total Fe (mg/L)	Mn (mg/L)
Range	7.0–8.8	4.56–50.3	8.04–21.7	0.11–2.86	0.10–0.50	0.12–1.42	0.09–1.66
Average	7.5	17.6	13.83	0.77	0.2	0.62	0.55

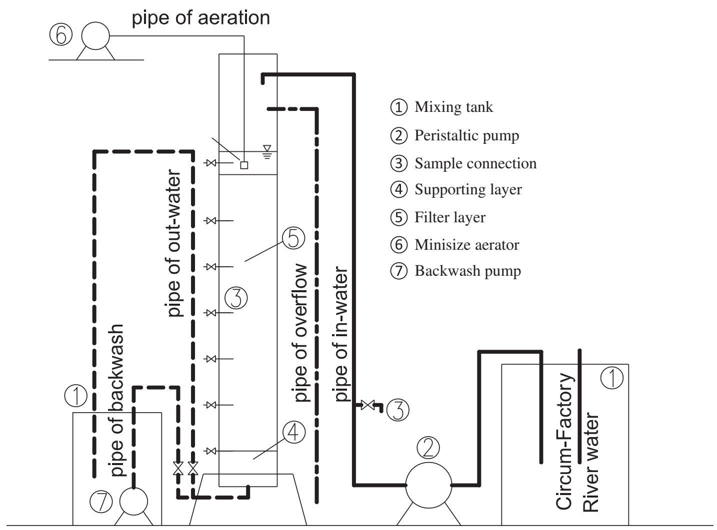

Fig. 1. Experimental set up.

2.3. Test methods

2.3.1. BAC field experiment in Baosteel

The test was started in July and the water temperature was about 30℃, which was propitious for the biofilm development, so the bacteria were bred naturally [23]. During the biofilm growth, relatively longer empty bed contact time and weaker backwash intensity were selected as 60 min and 25% expansion ratio, respectively.

After successful biofilm development, the filter column was run under empty bed contact time of 60, 45 and 30 min, respectively. The concentrations of Fe and Mn in influent, effluent and different depths of filter layer were measured every 36 h.

2.3.2. Backwash condition research

Backwash parameters were set as follows: backwash speed ranged from 0.033 to 0.039 m/h, filter layer expansion degree was 20–30%, backwash time lasted for 6–8 min and the interval of backwash was 3–4 d.

2.3.3. BAC removal mechanism research by shake flask experiments in the laboratory

Contrast experiments were carried out between BAC and AC on the removal of dissolved Fe and Mn. Take unused AC, soaked with 5% hydrochloric acid to desorb the adsorbed substance overnight, dipped in pure water. Take a small amount of BAC from the filter column, and gently rinse the surface. During the experiment, add $FeSO_4$, $Fe_2(SO_4)_3$ and $MnSO_4$ to the factory moat which was already cleaned with Fe and Mn, which results 2 mg/L Fe^{2+}, Fe^{3+} and Mn^{2+} water. Twenty grams of pretreated AC and BAC was added to 1,000 mL prepared water, respectively. The dispersion was then slowly stirred using a magnetic stirrer and the concentrations of Fe and Mn in the solution at regular intervals were analyzed. When it came to the biological removal of Mn^{2+}, BAC sterilized for 30 min at 120℃ was also used to treat the mixed water as a control group.

2.4. Analysis methods

The concentrations of Fe, Mn, NH_3-N and total P in supernatant fluid were determined by a UV–visible spectrophotometer (SPECORD 200, Analytik Jena AG, Germany) at 505, 525, 420 and 700 nm, respectively, corresponding to their respective maximum absorption wavelength. All measurements were undertaken in triplicate with errors below 5% of average values that were reported.

Turbidity was analyzed by turbidimetric apparatus (HACH 2100 Q, Portable turbidimeter, Hach), and COD was determined by potassium dichromate method.

3. Results and discussion

3.1. Biofilm colonization phase

After the filter column ran for 15 d, the organic matter and ammonia nitrogen removal effect was stable, and micro-organism immobilized on the activated carbon, forming a layer completely wrapped the mature biofilm carrier, which were the symbol of successful and mature biofilm [23]. Meanwhile, the removal rate of COD remained steady in 60–80%, which also indicated that biofilm development was successful. During the period of biofilm development, the concentrations of non-dissolved Fe and Mn in raw water were high, but total Fe and Mn of out-water quickly reached the standard, which were below 0.3 mg/L at 5 d and 0.1 mg/L at 6 d, respectively.

3.2. The result of running

After biofilm development, the BAC filter column ran for five months and the removal effects of total Fe and Mn were shown in Figs. 2 and 3, respectively.

It can be seen that the concentrations of total Fe and Mn of in-water both vary largely, and the total Fe and Mn concentrations of out-water were below 0.37 and 0.30 mg/L, which mean the great average removal rates of 71.9% and 75.4%, respectively. Having been rich in iron, biome with the core of iron, manganese oxidizing bacteria gradually increase on the carbon surface, and by catalytic oxidation of bacterial extracellular enzyme, Mn^{2+} in wastewater can be oxidized to Mn^{4+} deposition, which adheres to the surface of filter. Thus, the BAC process has the ability to remove iron and manganese.

As the reduction of empty bed contact time and the decrease of water temperature, the concentrations of total Fe and Mn of out-water rise and the average removal rate reduces. Under empty bed contact time of 30 min, the concentration of Mn in out-water surpasses the standard of reuse water (0.1 mg/L) at most of the time, so proper empty bed contact time should be no less than 45 min.

In addition, the average removal rates of turbidity, COD, NH_3-N and total P of BAC filter column can reach 77.8, 46.5, 71.9 and 26.5%, respectively, which all meet the standard of reuse water.

3.3. Backwash research

When steel wastewater flows through the BAC layer, the dissolved Fe and Mn are oxidized to the non-dissolved state. Together with non-dissolved Fe and Mn in the raw water, they are captured in filter layer through adsorption of AC and filtration of the layer. With the extension of time, the accumulation of biotic and abiotic particles in the filter layer increases, resulting in carbon particle clearance reduction, the adsorption material and the growth of biofilm on BAC surface are growing more and more, to a certain extent, which will affect the water quality of effluent filtration, so reasonable backwash is a key process in normal operation of filter column. At this time, taking an appropriate time, intensity and period of backwashing can improve the hardening phenomenon of filtration column and meanwhile make the entrapped particles out of the filter layer then recover the activity.

In the present paper, backwash water was collected, and the concentrations of total Fe and Mn were measured and compared with total removal quantity of Fe and Mn by BAC in a backwash cycle. As Table 2 illustrates, backwash can remove more than 50% of solid Fe and Mn in the filter column and renew the removal activity of BAC for total Fe and Mn. It is indeed an important procedure for the stability of BAC.

3.4. Removal of Fe and Mn in filter layer and apparent kinetics

The composition of raw water is quite complex, including various amount of COD, NH_3-N, P, Fe and Mn

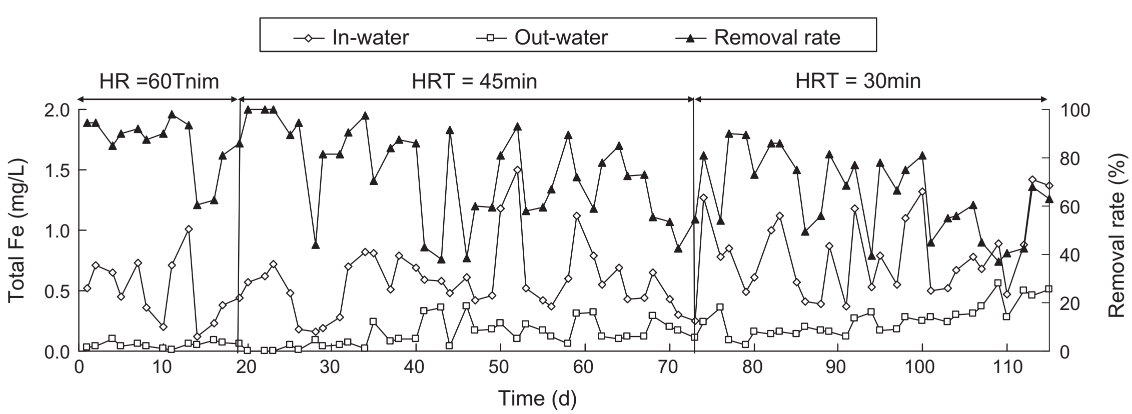

Fig. 2. Removal effect of total Fe by BAC.

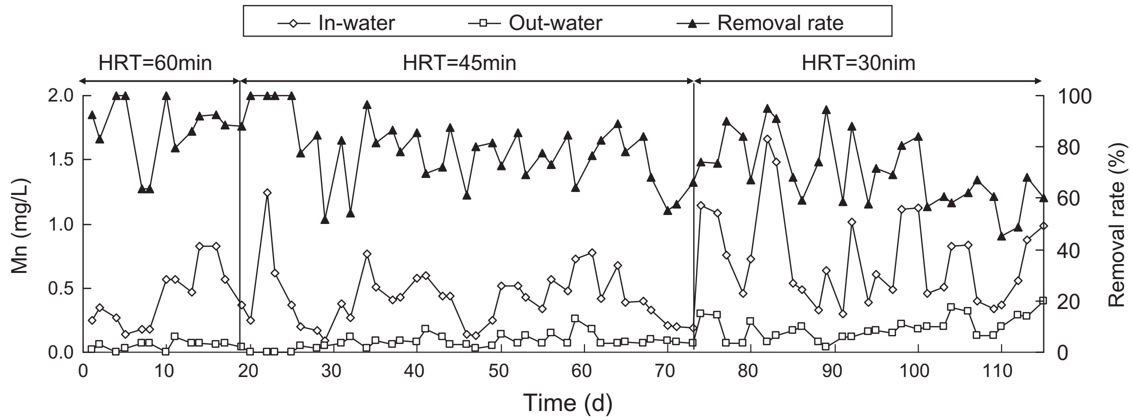

Fig. 3. Removal effect of total Mn by BAC.

Table 2
Removal research of Fe and Mn by backwash

	The first test		The second test		The third test	
	Total Fe	Mn	Total Fe	Mn	Total Fe	Mn
Removal quantity by backwash/mg	906.8	1,078.3	840.8	691.3	497.8	384.2
Removal quantity by BAC/mg	1,241	1,523	1,592	1,265	928.4	674.4
Ratio	0.73	0.71	0.53	0.55	0.54	0.57

(see Table 1), and the removal of iron and manganese is a combination of a variety of mechanisms, which cannot be fitted by a simple diffusion model. However, we find that the removal of iron and manganese along the filter depth of filter columns at Baosteel is regular. Fig. 4 illustrates the change of removal effect with filter layer depth when the empty bed contact time is 60 min. It can be seen that the removal of total Fe and Mn is mainly in the top 20 cm of the filter layer, and the curve becomes smoother in later filter layer. This may be because there are some amount of non-dissolved Fe and Mn in raw water, and these Fe and Mn are mainly filtrated in the top of the layer, which lead to the higher DO and microbe mass in the top of filter column.

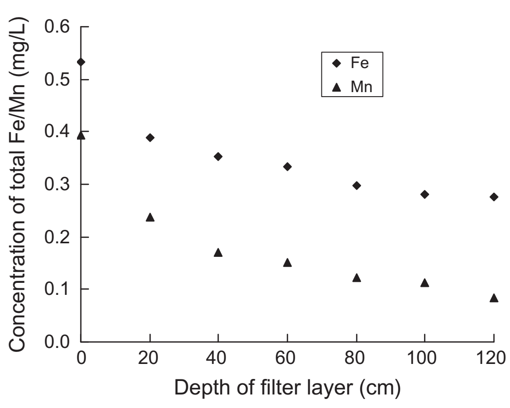

Fig. 4. Removal laws of total Fe and Mn in different depth of filter layer.

Dealing with the data of Fig. 4 by the model of apparent first-order kinetics, equations can be obtained as below:

$$\frac{dC}{dt} = -kC \tag{1}$$

or

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{2}$$

where k denotes the velocity constant and C denotes the concentration of Fe or Mn (mg/L). The linear least-squares fitting of ln (C_0/C) vs t is shown in Fig. 5, and k can be determined by the slope coefficient.

Significance test shows that the removal process of Fe or Mn can be described by the above model, and when the confidence is set as 95% (α = 0.05), the removal of Fe and Mn shows a close linear relationship.

3.5. The mechanism research of removal of Fe and Mn by BAC

3.5.1. Iron

The results of removal mechanism research of Fe were show in Figs. 6 and 7. As shown in Figs. 6 and 7, the removal rates of Fe by BAC and AC can both reach 60% in 6 h. Besides, it can be noticed that the removal rate of Fe^{3+} is higher than that of Fe^{2+} for the same treating time, which may be attributed to the different features of Fe^{2+} and Fe^{3+} in the raw water. Compared to Fe^{2+}, Fe^{3+} can be adsorbed by AC more easily in forms of ion and complex compound [24], and the deposition and separation of Fe^{3+} from water is much easier owing to its small solubility, so the removal of Fe^{3+} is faster than Fe^{2+}. Furthermore, BAC performs a better removal of Fe than AC does, which indicates that BAC gains the Fe-removing activity through long time of running. As the catalytic oxidant, the bacteria in BAC can continuously oxidize Fe^{2+} into Fe^{3+}, and bring about the deposition of Fe^{3+} [25].

3.5.2. Manganese

Similar to the Fe-removing experiment, the removal rates of Mn^{2+} by BAC and AC were both measured. Besides, another two experiments were added, one of which was BAC together with Mn^{2+} sample prepared by raw water (from the river round the factory), and the other was BAC together with Mn^{2+} sample prepared by distilled water.

Fig. 8 shows the results of all the above experiments. It can be seen that Mn^{2+} can hardly be removed by AC, while BAC has a good removal effect. The adsorption of Mn^{2+} is strongly pH dependent [26], and under the experiment condition of pH 6, AC almost has no adsorption effect on Mn^{2+}. Meanwhile, Mn^{2+} cannot be oxidized by air under neutrality condition. So the concentration of Mn^{2+} in the water is basically unchanged during the running process. However, as for BAC, it has gained the ability

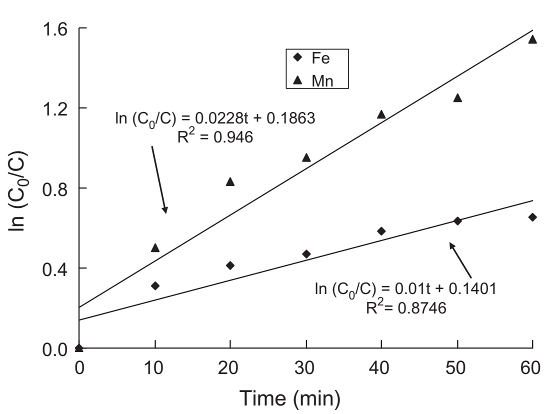

Fig. 5. The diagram of ln $(C_0/C)-t$.

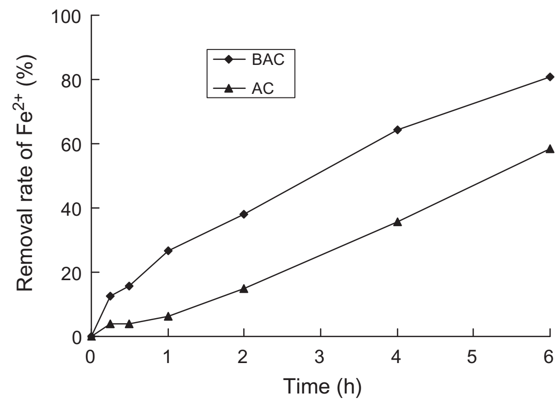

Fig. 6. Removal of Fe^{2+} by BAC and AC.

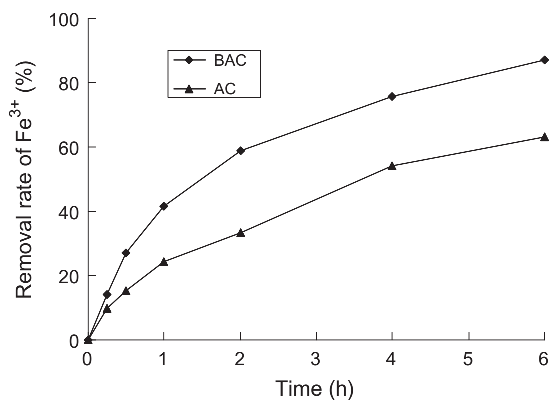

Fig. 7. Removal of Fe^{3+} by BAC and AC.

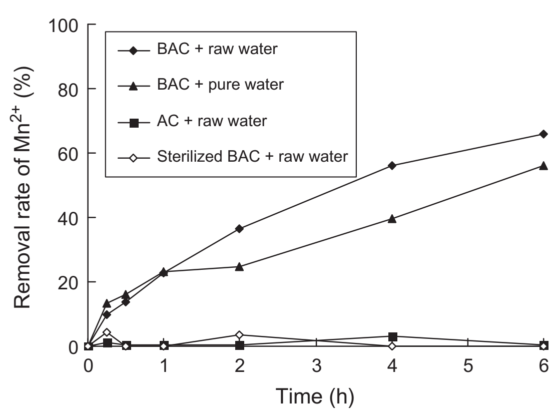

Fig. 8. Removal effect of Mn^{2+} by AC and BAC in different samples.

of removing Mn after long time of running, and the activated film for removing Mn has formed under the inducement of micro-organism, which can oxidize Mn^{2+} into $MnO_2{\cdot}mH_2O$ by virtue of iron bacteria using dissolved oxygen. After that, $MnO_2{\cdot}mH_2O$ can be removed from water through deposition [27].

For the tests of BAC together with Mn^{2+} sample prepared by raw water and distilled water, the removal rates are almost the same within 1 h, but after 1 h, the removal rate of the former is apparently better than that of the latter, reaching 66% at 6 h. In distilled water, total Fe and Mn bacillus cannot survive for long and the biomass reduces gradually, so the removal rate of Mn^{2+} just has a slow growth. While in raw water, there is abundant nutrient, and the Fe and Mn bacteria can function normally, which keeps the removal rate steady. In sterilized BAC, micro-organism is killed and no biological reaction would happen, so sterilized BAC cannot remove Mn^{2+} effectively, even in raw water, which indirectly indicates that removal of Mn^{2+} by BAC is by virtue of biological reaction.

4. Conclusions

In summary, the removal effect of iron and manganese in steel industry drainage by BAC was studied in the present paper, and some conclusions can be drawn as follows:

(1) BAC had a good removal effect towards contaminants in the river around the factory river, and the average removal rates of total Fe and Mn could reach 71.9% and 75.4%, respectively. The quality of out-water could reach the standard of industry water.

(2) Backwash could remove more than 50% of total Fe and Mn in the filter column and renew the removal activity of BAC for total Fe and Mn, which was an important procedure for the stability of BAC.

(3) The removal of total Fe and Mn was mainly in the top 20 cm of the filter layer, and it tended to become smaller in later filter layer. The removal rule could be described by the model of apparent first-order kinetics.

(4) The removal effect of Fe and Mn by BAC was much better than that of AC, and Fe and Mn were removed through combined effect of AC adsorption, biological oxidation and filtration.

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