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Manganese removal using an aerated granular filter

Bong-Yeon Cho†

Department of Civil & Environmental Engineering, College of Engineering,
Dongguk University, 26, 3ga, Pildong, Jung-gu, Seoul 100-714, Korea

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Abstract−Experiments on manganese removal using an aerated granular filter with mean particle size of 3.68 mm and 5.21 mm anthracite were conducted at a filtration rate of 100 m d^{-1}. Air, with a rate of 0 to 366 m d^{-1}, was supplied through nozzles positioned 100 mm above the filter column bottom. From the experiments that were conducted, it was found that manganese removal is completed at a pH of 9.6 or above. In addition, the oxidation and removal rate of dissolved manganese were expressed as a first-order reaction. The smaller the filter media particles were, the higher the manganese removal efficiency was. The aeration rate of dissolved oxygen in raw water is sufficient for the manganese removal process. The manganese removal rate increased with time due to the catalytic effect of manganese dioxide (MnO_2) attached to the media. The x-ray diffraction analysis showed that the solids attached to the filter media were not crystalline but amorphous manganese.

Key words: Aerated Filter, Manganese Removal, Aeration, Oxidation, X-Ray Diffraction, Amorphous

INTRODUCTION

Since the presence of heavy metals in water brings about an offensive smell and taste, produces a yellow-brown stain on white clothing, and causes defects in industrial products, an excessive amount of heavy metals in water is undesirable. Since the early 1960s, the water supply has contained increasing amounts of manganese. Some say that this is caused by the excessive use of chemical fertilizers, but the exact causal relationship between the two has not been established. When lake or dam water is used, even if the water near the surface does not contain any metal, iron and manganese treatment will nevertheless be needed when the water near the bottom is used during periods of water shortage.

Manganese dissolved in water can be removed by contact filtration with manganese sand (catalytic sand coated with oxidized manganese) [1-4]. Other ways to remove manganese are the methods using Ozone oxidation [5-7], Potassium permanganate ($KMNO_4$) [8], Chlorination [9] and Biological filters [10-16]. But when using raw water containing organic matter, chlorine treatment causes the formation of organic chlorine compounds, and if not oxidized by chlorine, the second manganese treatment can become a problem. To remove manganese without creating organic chlorine compounds, oxidation by oxygen is needed.

In this paper, the performance of a biological filter [10,11], which has been known as a nitrification filter, on the removal of manganese is studied.

MATERIALS AND METHODS

Fig. 1 shows the experimental setup. The reactor is a circular column with a height of about 114 cm, and filled with anthracite media, with sizes varying from 3.36 to 4.00 mm (geometrical mean of 3.68 mm) and from 4.76 to 5.66 (geometrical mean of 5.21 mm) for filtration vessels A and B, respectively. Raw water containing sulfate manganese (3 to 6 mg-Mn l^{-1}) was fed to the column from the top of the reactor. Sodium hydrosulfite was added to remove the residual chlorine in raw water. Air was supplied through an aerator located at about 100 mm from the bottom column. The water level was controlled by the head loss.

The sampling ports were located at 10 to 20 cm intervals, and the water samples were taken from the center of the cross-section with the use of a stainless steel tube with an inner diameter of 3 mm. The dissolved oxygen, total and dissolved manganese, alkalinity, pH, temperature, and head loss were monitored.

Filtration was done on the downward flow, and the amount of the flow was controlled at the entry point. The filtration vessel that was used was a cylindrical tube made of transparent acryl with an inner diameter of 100 mm and a height of 2,200 mm.

Media were deposited at a filtration depth of 1,140 mm. As for the experiment method, about 3 mg l^{-1} of $Na_2S_2O_3$ was added to tap water to remove the remaining chlorine, and $MnSO_4$ (3-6 mg-Mn l^{-1}) was added as the source of manganese. Since the pH level plays a big role in removing manganese, the alkaline level was kept higher to mitigate the variance of the pH level in the direction of the filtration flow. A heater with an automatic temperature controller was added to the mixing tank to control the water temperature.

A manganese removal experiment was performed to study the effects of the particle diameter of filtration media, the aeration rate, the filtration rate, and the pH. X-ray diffraction, on the other hand, was performed to analyze the crystalline structure of oxidized manganese extracted from the surface of filter media. Table 1 shows the measuring items and methods.

RESULTS AND DISCUSSION

1. Manganese Removal in Strong and Weak-alkalinity

The measurements of manganese concentration in the filtered

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†To whom correspondence should be addressed.
E-mail: bycho@dongguk.edu

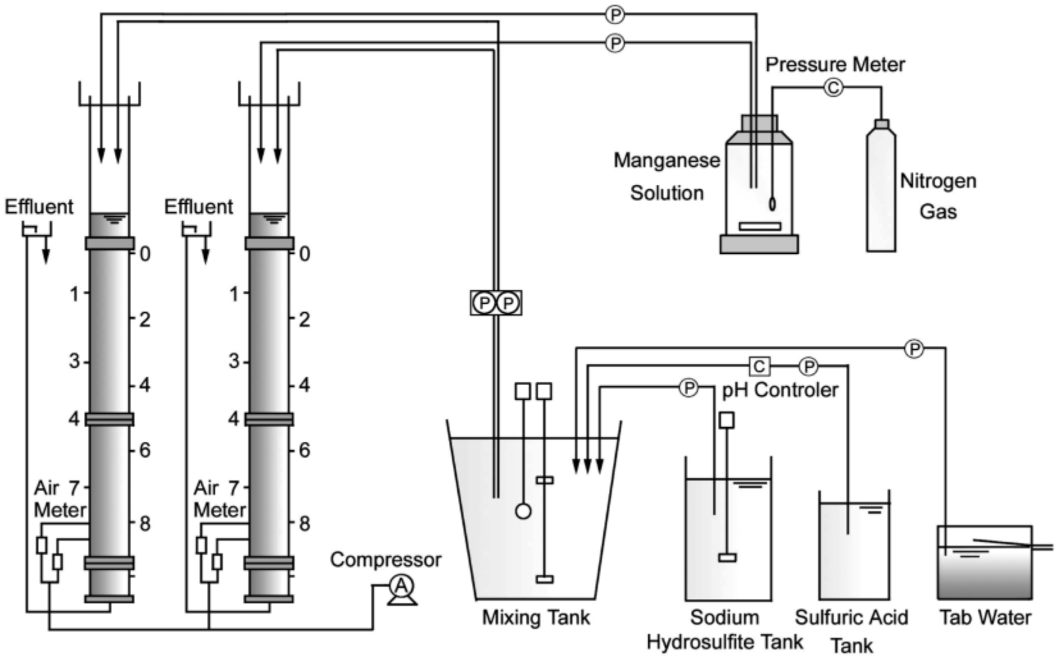

Fig. 1. Experiment set up.

Table 1. Measuring items and methods

Items	Measurement methods
Total manganese (T-Mn)	Standard methods (AA)
Dissolved manganese (Mn^{2+})	Standard methods (AA)
Dissolved oxygen (DO)	Permanganate modification
Alkalinity	Standard methods
pH	pH meter
Temperature	Temperature meter

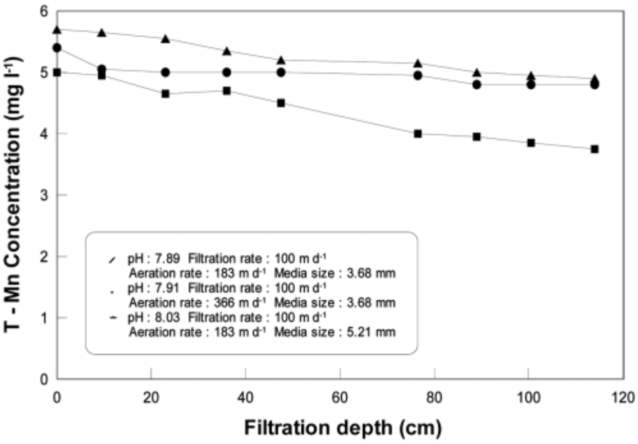

Fig. 2. Total manganese concentration with pH of 7.89-8.03 in raw water.

water 4 days after the start of filtration are shown in Fig. 2. Here, the filtration rate was set at 100 m d^{-1}, the aeration rate at 183 m d^{-1}, and the pH level of raw water at a weak alkalinity of about 8. The amount of manganese was not reduced in any of these experiments, and the total and dissolved manganese concentrations were almost the same (both concentrations plot almost the same graphs in the figure). Moreover, Mn^{2+} was not at all oxidized. No change in the filtration head loss was detected as well during the experiment.

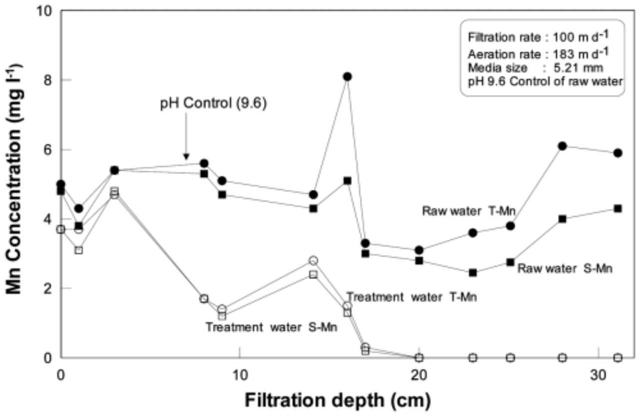

Fig. 3. Total and dissolved manganese concentration with a pH of 9.6.

Since manganese was neither oxidized nor removed in the weak-alkalinity area, as described above, the experiment was continued, this time using raw water with a pH level of 9.6 [1]. The change in the manganese concentration in the filtered water after the pH in raw water was changed is shown in Fig. 3. The manganese concentration in the filtered water started to go down slowly on the 7*th* day after the pH was set at 9.6, and it was determined to be almost 0 after 20 days. During the experiment, the manganese concentration in the filtered water went down on the 9*th* day and started to go up again on the 14*th* day. The pH level was then slightly over 9.6 (<9.6). After backwashing, no change in the manganese concentration in the filtered water was detected at the initial stage of the experiment.

Examples of the measurements of water quality indicators at various filter level depths are shown in Fig. 4. In the figure, the total and the dissolved manganese concentrations approach 0 mg l^{-1} as the filtration depth increases. When the pH level of the raw water was set at over 9.6, manganese was oxidized and was rapidly removed.

The time that it took the filter layer to stop was 17-18 days when using filtration media with a diameter of 3.68 mm, and 26 days for filtration media with a diameter of 5.21 mm.

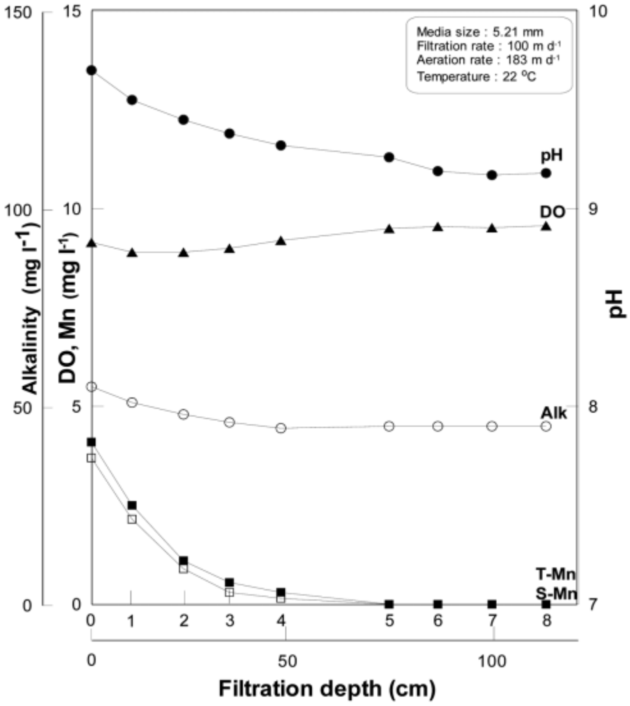

Fig. 4. Water index with various points of filtration depth for a pH of 9.6 in raw water.

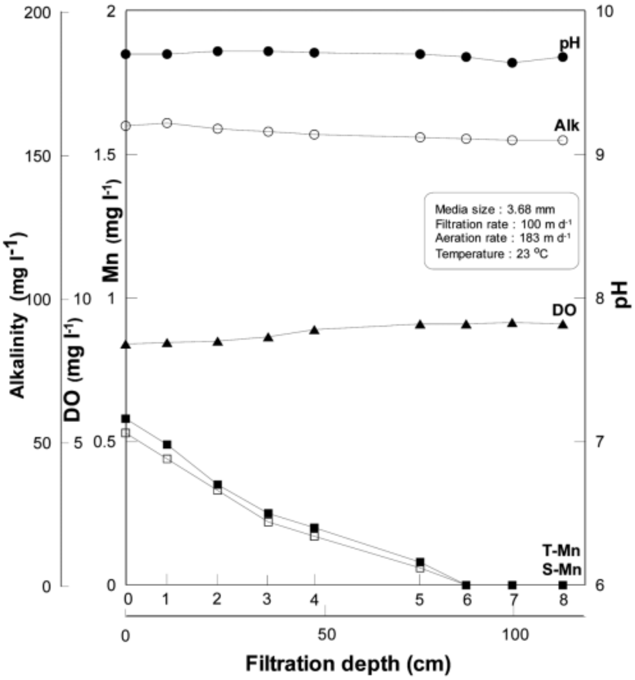

Fig. 5. Water index with various points of filtration depth for low manganese concentration in raw water.

2. Characteristics of the Removal of Low Manganese Concentrations

The experiments above were performed using raw water with a relatively high manganese concentration (about 5 mg l^{-1}).

Another filtration experiment was performed, with the manganese concentration in raw water set at a lower level of about 0.5 mg l^{-1}, closer to that in river water. The filtration rate was set at 100 m d^{-1}, and the aeration rate at 183 m d^{-1}.

Examples of the measurements of water quality indicators at various filter level depths are shown in Fig. 5. As can be deduced from this figure, when the pH level was set at above 9.6, the total and dissolved manganese concentrations were determined to be 0 mg l^{-1}, but when the pH level was set at below 9.4, the manganese concentration in the filtered water was not 0 mg l^{-1}. This result is the same as that of the former experiment, where the raw water that was used had a high manganese concentration. Based on these results, it can be concluded that manganese cannot be removed from water without raising the pH level, even when the manganese concentration is considerably low.

3. Mechanism of Manganese Removal

The result of each experiment was plotted on a semi log graph, with the dissolved manganese concentration as the Y-axis and the filter layer depth as the X-axis. The data points nearly make up a straight line. For the filter layer depth z, the total and dissolved manganese concentrations can be described by the following equations:

$$\ln\frac{M_s}{M_{so}} = -\alpha' z \tag{1}$$

$$\ln\frac{M_T}{M_{To}} = -\beta' z \tag{2}$$

Eqs. (1) and (2) can be also written as follows:

$$\frac{dM_s}{dz} = -\alpha' M_s \tag{3}$$

$$\frac{dM_T}{dz} = -\beta' M_T \tag{4}$$

The relation between the oxidation rate and the removal rate with respect to the time of flow in the filter layer can be written as follows:

$$\frac{dM_s}{dt} = -\alpha' v M_s = -\alpha M_s \tag{5}$$

$$\frac{dM_T}{dt} = -\beta' v M_T = -\beta M_T \tag{6}$$

The values of α' and β' are given as the slope of the straight line in the semilog graph of z-M_s or z-M_T, and the values of α and β can be obtained from these. Fig. 6 shows the plotting of the α and β values obtained from each experiment. The graph is a straight line, with a slope of about 45 degrees. Hence, the α and β values are almost the same. That is, in the case of manganese removal using aeration filter paper, the amounts of manganese oxidized and removed are almost the same.

4. Effect of pH

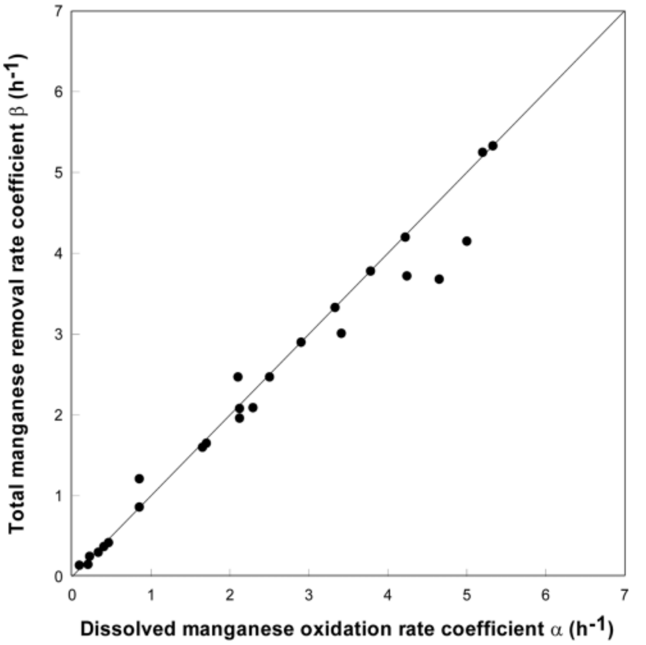

Fig. 6. Relationship between the dissolved manganese oxidation rate, α and the total manganese removal rate, β.

Since the removal and oxidation of manganese are greatly influenced by the pH level of influent water, an experiment on the effect of pH was performed in advance.

The initial pH level of raw water was set at 9.6 [1]. After the start of filtration, the pH was incrementally lowered by 0.3 to determine the lowest limit of the pH level. This was done to test the hypothesis that if the removal of manganese is begun at a high pH level, the oxidized manganese that is attached to the filter media may work as a catalyst, and the removal of manganese from a lower pH area may become possible. The result when each pH level returned to a normal state is shown in Fig. 7. In this figure, it is shown that even with the oxidized material attached to the filter media, to remove manganese effectively, the pH should be set at a level higher than 9.6. In the case of contact filtration using chlorine as a catalyst, manganese was removed from the neutral pH area. This, however, seems to have resulted from the fact that the oxidation-reduction potential of chlorine is 1.49 V, which is higher than the oxidation-reduction potential of oxygen, which is 1.23 V.

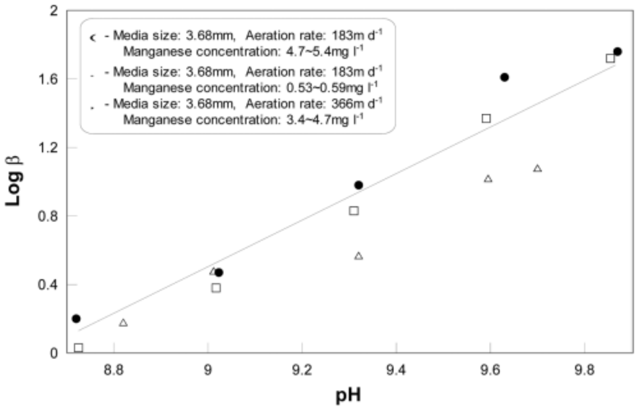

Fig. 8. Relationship between pH and the total manganese removal rate, β.

Fig. 8 shows the plotting of the total manganese removal rate coefficient vs. the pH level of influent water, using the data in Fig. 7. In this figure, the total manganese removal rate coefficient β can be represented as follows:

$$\ln\beta = 1.42\,\mathrm{pH} - 12.19 \tag{7}$$

5. Effect of Filtration Rate

Another experiment was performed, where the pH level of raw water was set at 9.8, the filtration rate at 50 and 100 m d^{-1}, and the aeration rate at 366 m d^{-1}.

The total manganese rate coefficient β was 17.2 h^{-1} when the filtration rate was 100 m d^{-1}, and β was 19.7 h^{-1} when the filtration rate was 50 m d^{-1}.

All the aforementioned were measured four days after the start of the filtration. Hence, they represent a normal state. The results show that the effect of the filtration rate on the removal rate coefficient is minimal.

6. Effect of Aeration Rate

Another filtration experiment was performed with an aeration rate of 0, 10, 46, 91.5, and 183 m d^{-1}, and with the other conditions the same as in the previous experiments - that is, the diameter of

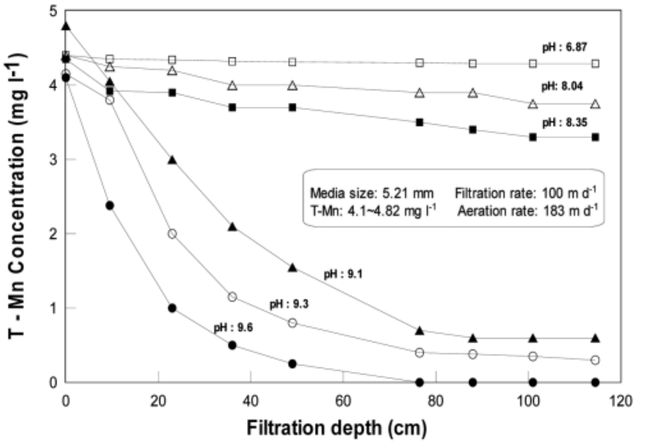

Fig. 7. Removal characteristics of pH and total manganese.

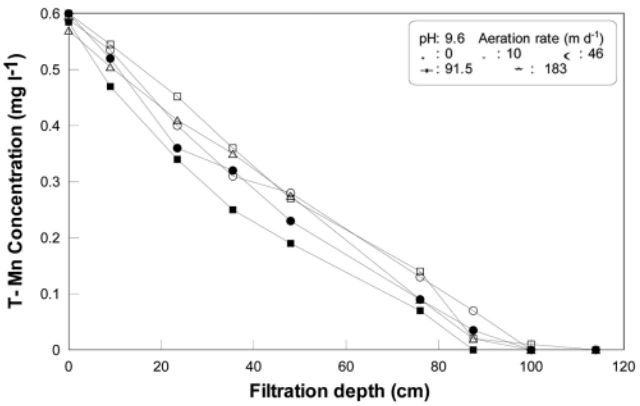

Fig. 9. Characteristics of aeration rate and manganese removal with a pH of 9.6 in raw water.

the filtration media was 3.68 mm, the filtration media rate was 100 m d^{-1}, and the water temperature was 23 °C. The result is shown in Fig. 9. There was no major change in the removal rate of the total manganese when the aeration rate was varied. If aeration were stopped, the oxygen that would be needed for oxidation would come only from the dissolved oxygen in raw water, and the oxidation would continue until such dissolved oxygen would have been consumed.

As indicated above, the total manganese removal rate does not depend on the change in the aeration rate. This is very different from the case of iron removal. Moreover, even when the usual rapid filtration paper is used, if the pH level is kept above 9.6, and if there is much dissolved oxygen, the removal of manganese may become possible.

7. Effect of Filter Media

The filtration media used in the experiment were two kinds of anthracite, with an average particle diameter of 3.68 mm and 5.21 mm, respectively. When their normal state was reached on the fourth day of the filtration experiment, the total manganese removal rate coefficient β for the two filtration media was 13.9 h^{-1} and 9.9 h^{-1}, respectively. The ratio of the two was 1.4, almost the same as the ratio of the specific surface area (the inverse of the ratio of the particle diameters) of the filtration media, which was 1.42. That is, the removal rate for a unit of the surface area was the same for each filtration media. Within the scope of this experiment, the manganese removal efficiency per unit volume was higher for the media with a smaller particle diameter.

8. Presence of Oxidized Manganese Coating on the Filter Media

The filter media with a particle diameter of 3.68 mm was washed with hydrochloric acid so that the effects of the former experiments on it could be removed. Another experiment was then performed, and 2 and 96 hours after the start of the filtration, and the characteristics of manganese removal were determined and then compared. Two hours after the start of the experiment, β=4.31 h^{-1} had a pH level of 9.75, and 96 hours after the start of the experiment, β=8.18 h^{-1} had a pH level of 9.6.

The removal rate, β, tells whether the media is covered with oxidation manganese that is working as a catalyst, or not. So, it varies with pH, oxidation manganese, and so on.

The removal rate of the manganese increased with time, compared with the removal rate at the start of the experiment.

The aforementioned result can be thought to show that oxidized manganese attaches itself to the filtration media and plays the role of a catalyst. It was already stated, however, that manganese could not be removed even with the presence of the coating of oxidized manganese if the pH of raw water was below a certain level. In any case, only with a sufficiently high pH level will the removal rate coefficient β increase with time and get closer to the normal value.

9. Removal of Manganese in the Presence of Iron

It was expected that the bacteria that oxidate manganese could grow in an environment where manganese is present. The water was thus kept flowing for a long time at several pH levels under 8, and the growth of the bacteria was awaited, but the manganese concentration in the filtered water did not change.

At this stage, manganese was removed under the condition where iron bacteria grew and where iron was completely removed at the low pH level of 6-6.5 [10]. Raw water was then made to flow through the aeration filtration vessel. When raw water was made to flow for a short time at a pH level of about 6.5, iron was completely oxidized or removed. Manganese, however, was neither oxidized nor removed.

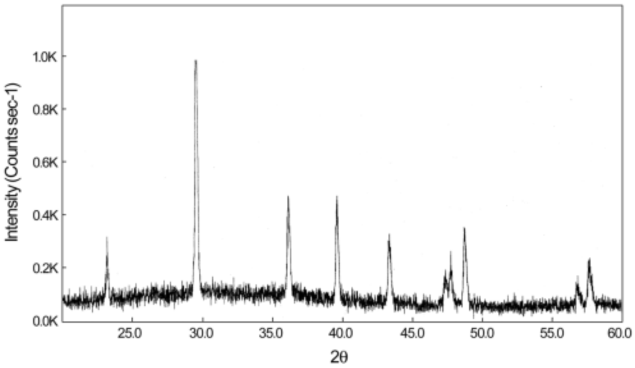

Fig. 10. X-ray diffraction of attached materials on the surface of the media with influent of pH 9.6.

As in the former experiments, a change in the manganese concentration appeared when the pH level went beyond 9.0, and the manganese was almost completely oxidized or removed when the pH level was 9.6. On the other hand, iron was oxidized, but the total iron was run off [10]. This result indicates the major effect that the pH level has on the removal of manganese and iron [10].

10. Crystalline Structure of the Solids Attached to the Surface of the Filter Media

The crystalline structure of the oxidized solids attached to the surface of the filter media was studied by using x-ray diffraction [10,17,18]. The sample was obtained from the solids attached to the filter media in the experiment system, filtered at a pH level of above 9.

The result of the x-ray diffraction is shown in Fig. 10. Most of the acute peaks in the figure are indications of $CaCO_3$, and natural peaks shaped like a plateau, with a 30 ° slope, are identified as MnO_2^{4+}. Since the crystalline structure of oxidized manganese is amorphous, it was not shown distinctly as peaks of spectacles.

CONCLUSIONS

Laboratory-scale experiments on manganese removal from artificial raw water by an aerated filter using anthracite as filtered media were conducted. The aeration rate from the bottom of the filter was 0-366 m d^{-1}. The filtration rate, on the other hand, was between 100 and 200 m d^{-1}. The following results were obtained:

Oxidation rate of dissolved manganese is proportional to dissolved manganese concentration, and the removal rate of the total manganese is proportional to the total manganese concentration.

The case where the pH level exceeds 8.7, β can be represented as follows:

$$\ln\beta=1.42\ \mathrm{pH}-12.19$$

The dissolved manganese oxidation rate coefficient α and the total manganese removal rate coefficient β were almost the same when the pH level of raw water was kept over 9.6. With a filtration rate of 100 m d^{-1} and a filtration depth of under 1 m, manganese was removed to an undetectable level.

Within the scope of this experiment, the values α and β were proportional to the specific surface area of the filter media. From this it can be concluded that filter media with a smaller particle diameter has a higher removal efficiency. Normally, the amount of aeration rate of dissolved oxygen in raw water is sufficient for the manganese removal process.

The attachment of oxidized manganese from oxidation to the filter media increases the removal efficiency due to its catalytic effect, and four days after the start of the filtration, it reaches a normal level. This effect does not appear unless the pH level is significantly high. The manganese extract that was attached to the filter media was amorphous MnO_2^{4+}.

NOMENCLATURE

M_s : dissolved manganese concentration [mg/l]
M_{so} : initial of dissolved manganese concentration [mg/l]
M_T : total manganese concentration [mg/l]
M_{To} : initial of total manganese concentration [mg/l]
α' : dissolved manganese oxidation coefficient [m^{-1}]
α : dissolved manganese oxidation rate coefficient [h^{-1}]$=\alpha' v$
β' : total manganese removal coefficient [m^{-1}]
β : total manganese removal rate coefficient [h^{-1}]$=\beta' v$
z : filtration depth [m]
t : filtration time [h]
v : filtration rate [m/h]

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