Riverbank filtration: removal of iron, manganese and hardness

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ABSTRACT

This research selects water treatment process that suitable to use by industrial and drinking water to remove high hardness, iron and manganese (Mn) included in bankfiltrate. In hardness removal experiment by membrane, flux of UTC-20 in permeate flux and total hardness removal $0.069 \text{m}^3/\text{m}^2/\text{hr}$ that was median value and 93% of removal efficiency was shown, therefore UTC-20 was considered as optimal membrane. After adding manganese dioxide (MnO$_2$) slurry to bankfiltrate containing manganese 4.0 mg/L and adsorption, conclusion of Mn oxidation by potassium permanganate (KMnO$_4$) are as follows; Mn adsorption experiment of MnO$_2$ slurry at $20^\circ\text{C}$, pH 7.0, $0.28 \text{mol-Mn}^{2+}/\text{mol-MnO}_2$ of maximum adsorption amounts by Langmuir isotherm was shown. The reason of decreasing equivalent values after MnO$_2$ slurry addition and adsorption of Mn was the less consuming amounts of KMnO$_4$ in generated MnO$_2$ particle from KMnO$_4$ and Mn reaction and MnO$_2$ slurry added by autocatalytic reaction. Calcium (Ca) and magnesium (Mg) which was contained in bankfiltrate in Mn adsorption by MnO$_2$ slurry showed positive effect in Mn adsorption.

Keywords: hardness; manganese; manganese dioxide; magnesium; riverbank filtration

INTRODUCTION

In many countries alluvial aquifers hydraulically connected to a water course are preferred sites for drinking water production. Since these aquifers are relatively easy to exploit (shallow), generally highly productive and located close to the consumers. In France, for instance, the proportion of bankfiltrate amounts to 50% of the total drinking water production.

The Nakdong river watershed, which has about 10 million inhabitants, has 20 industrial complexes in the area with a total of 6,783 industrial plants. Approximately 53% of these plants are located in the middle reach of the river. The Nakdong river watershed generates 2.79 million m$^3$/d of domestic or industrial wastewater and the middle reach of the river accounts for 62% of the total amount of wastewater. The river water is repeatedly used for irrigation and domestic or industrial purposes during its travel. During the dry season, the
river has little amount of flowing water, which mostly consists of used irrigation water and the effluents from treated domestic or industrial wastewater.

Cities in the lower part of the Nakdong river depend on the surface water of the river for their source of tap water. Waterworks in this area use the purification processes, i.e., coagulation, sedimentation, rapid sand filtration, ozonation, biological activated carbon filtration and disinfection. Despite the advanced purification method, a majority of the people in the lower part of the river is dissatisfied with the quality of tap water. Moreover, in case of accidental spill of pollutant, the distribution of water should be discontinued.

In order to supply safe drinking water, reservoir water and bankfiltrate are being discussed as alternative water resources. However, constructing a new reservoir dam may damage the natural ecology and upset the balance in nature. In the meantime, the Nakdong river has well-developed natural alluviums in the lower reach of its flow, and it has many prospective sites for large amounts of the riverbank filtrate.

This research selects water treatment process that suitable to use by industrial and drinking water to remove high hardness and iron, manganese that is included in bankfiltrate.

**MATERIALS AND METHODS**

*Development areas of bankfiltrate*

Figure 1 shows development areas of bankfiltrate. Sampling point is located downstream from junction of the Nakdong river and the Kumho river. Production well is located 150 m away from the Nakdong river and the depth is 18.5 m with a daily production of - 2000 m$^3$ of water.

![Fig. 1 Development areas of bankfiltrate](image-url)
Nanofiltration to hardness removal

Nanofiltration experiment installs flat type membrane on cross-flow filtration cell and conducted in semi-batch operation. A schematic diagram of the experimental setup is shown in Fig. 2. The feed water was forced through the filtration cell (outside-in) under nitrogen pressure of 3, 6 and 9 atm. The water flux was measured as a function of permeate throughput using an analytical balance signal. Concentrated water fed into to control tank and become recycling by pump.

Fig. 2 Schematic diagram of the experimental setup

Removal of iron and manganese

The method we select to remove manganese was potassium permanganate (KMnO₄) oxidation. Characteristics of oxidation with KMnO₄ are followed Eq. 1 and Eq. 2. Oxidation of manganese is very fast with potassium permanganate, according to literature, and this reaction is finished at the second round. Mogan and stumm finds that the potassium permanganate demand to oxidize manganese is less than the stoichiometric equivalent owing to the autocatalytic reaction of manganese particles produced in the reaction. So if we used this property for manganese removal, we save demand potassium permanganate.

\[
3\text{Mn}^{2+} + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \leftrightarrow 5\text{MnO}_2 + 2\text{K}^+ + 4\text{H}^+ \]  
\[
3\text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}_2\text{O} \leftrightarrow 2\text{MnO}_2 + 8\text{H}^+ \]
Preparation of MnO$_2$ slurry

Manganese dioxide (MnO$_2$) slurry concocted manganese chloride (MnCl$_2$) and KMnO$_4$ by stoichiometrical reaction (Ref. Eq. 1). Adsorbability of MnO$_2$ slurry for Mn was evaluated by Langmuir isotherm. Thirty milliliters MnO$_2$ slurry of each concentration was placed into 500 ml glass beaker containing 350 ml of bankfiltrate. The mixed solutions were stirred on a magnetic stirrer for 1 day at 20°C to have adsorption equilibrium. It was confirmed that equilibrium was achieved at 1 day.

RESULTS AND DISCUSSION

Nanofiltration of hardness removal

Three types of nanofiltration membrane such as UTC-60(TORAY), NTR729-HF(NITTO DENTCO) and UTC-20(TORAY) was used. The characteristics of membrane were shown in Table 1.

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>Charge</th>
<th>Percent removal of NaCl at 25°C</th>
<th>Percent removal of MgSO$_4$ at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTR-729HF</td>
<td>Polyvinyl alcohol Negative</td>
<td>93</td>
<td>(at 1.5Mpa 0.15%)</td>
<td>99 (at 1.0Mpa 0.15%)</td>
</tr>
<tr>
<td>UTC-60</td>
<td>Polyamide     Negative</td>
<td>55</td>
<td>(at 0.35Mpa 0.05%)</td>
<td>97.3 (at 0.3Mpa 0.05%)</td>
</tr>
<tr>
<td>UTC-20</td>
<td>Polyamide     Positive</td>
<td>60</td>
<td>(at 0.75Mpa 0.05%)</td>
<td>99.5 (at 1.0Mpa 0.05%)</td>
</tr>
</tbody>
</table>

The comparison of water flux and total hardness removal by pressure to select optimal membrane were shown in Fig. 3 and Fig. 4. Flux was increased with pressure increases in three kind of NF film. UTC-60 showed the highest value in 0.043 - 0.144 m$^3$/m$^2$/hr and NTR729-HF is the lowest flux value 0.024 - 0.069 m$^3$/m$^2$/hr. Removal of total hardness was about 93% for UTC-20, 25% for UTC-60. Chose water flux and senior superintendent to optimum film to hardness removal because UTC-20 fluxes displays intermediate value by 0.069 m$^3$/m$^2$/hr but removal is the highest by 93% in removal.
Water quality of NF permeate

Nanofiltration that was UTC-20 group achieved enough drinking water criteria but UTC-60 and NTR29-HF incongruent in the standard in manganese and total hardness. Also UTC-20, NTR729-HF membrane could possible magnesium hardness 40 mg/L that is industrial water guideline. Table 2 showed the water quality permeates in chosen NF.

Table 2 Water qualities of nanofiltration permeates

<table>
<thead>
<tr>
<th>Items</th>
<th>UTC-60</th>
<th>NTR729-HF</th>
<th>UTC-20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percent removal (%)</td>
<td>Percent removal (%)</td>
<td>Percent removal (%)</td>
</tr>
<tr>
<td>Alkalinity, mg/L</td>
<td>31</td>
<td>66</td>
<td>59</td>
</tr>
<tr>
<td>Total hardness*, mg/L</td>
<td>37</td>
<td>84</td>
<td>92</td>
</tr>
<tr>
<td>Ca hardness*, mg/L</td>
<td>36</td>
<td>84</td>
<td>92</td>
</tr>
<tr>
<td>Mg hardness*, mg/L</td>
<td>39</td>
<td>84</td>
<td>91</td>
</tr>
<tr>
<td>DOC, mg/L</td>
<td>70</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>UV254, 1/m</td>
<td>100</td>
<td>N.D.**</td>
<td>100</td>
</tr>
<tr>
<td>Conductivity, µs/cm</td>
<td>24</td>
<td>73</td>
<td>90</td>
</tr>
</tbody>
</table>

* as CaCO3

** N.D. : Not detected

Adsorption of manganese by MnO2 slurry

The results using Lagmuir isotherms to investigate Mn adsorption amounts by MnO2 slurry was shown in Fig. 1. The slope is 1/qmax and calculated the value of the maximum Mn adsorption amounts per MnO2 slurry, which was 0.28 mol-Mn²⁺/mol-MnO2. Previous value of maximum Mn adsorption amounts per MnO2 slurry by Morgan and Jimbo were 0.3, and 0.02 - 0.15 mol-Mn²⁺/mol-MnO2, respectively.

Ca and Mg effect by MnO2 slurry in Mn adsorption

Bankfiltrate contained Ca 97 mg/L and Mg 27 mg/L as hardness. To investigate the effect on Mn ion adsorption to MnO2 slurry by those ions, 7 mg/L of MnO2 slurry was added to bankfiltrate and distilled water of which Mn concentration are same as bankfiltrate and variation of Mn concentration with adsorption time was shown in Fig.6. Ca and Mg showed positive effect in Mn adsorption because residual Mn concentration after 10 min of reaction time was 2.1
mg/L in bankfiltrate and 3.35 mg/L distilled water.

![Graph](image1)

**Fig. 5** Plot of isotherm data for the determination of Langmuir constants.

![Graph](image2)

**Fig. 6** Effect of dissolved Ca, Mg on Mn adsorption by MnO₂ slurry

**Mn adsorption by MnO₂ slurry and residual Mn oxidation by KMnO₄**

In case of oxidation of bankfiltrate containing Mn 4.0 mg/L by KMnO₄ and oxidation of residual 2 mg/L Mn by KMnO₄ after 15 mg/L MnO₂ slurry addition-20 min adsorption, consuming amounts as equivalent was shown in Fig 7.

The theoretical equivalents of bankfiltrate oxidation by KMnO₄ were shown in upper (dotted line) showed equivalents in oxidation. The theoretical addition amounts (i.e., equivalents) to
Mn 4.0 mg/L is 7.7 mg/L. However, the KMnO₄ consuming amounts is 0.87 equivalents. The reason of decreasing equivalent values after MnO₂ slurry addition and adsorption of Mn was the less consuming amounts of KMnO₄ in generated MnO₂ particle from KMnO₄ and Mn reaction and MnO₂ slurry added by autocatalytic reaction.

![Variations of KMnO₄ equivalent for the oxidation of Mn in bankfiltrate with or without MnO₂ slurry.](image)

4. Conclusion

In hardness removal experiment by membrane, flux of UTC-20 in permeate flux and total hardness removal 0.069 m³/m²/hr that was median value and 93% of removal efficiency was shown therefore UTC-20 was considered as optimal membrane.

After addition of MnO₂ slurry to bankfiltrate containing Mn 4.0 mg/L and adsorption, conclusion of Mn oxidation by KMnO₄ are as follows;

1) Mn ion adsorption experiment of MnO₂ slurry at 20°C, pH 7.0, 0.28 mol-Mn²⁺/mol-MnO₂ of maximum adsorption amounts by Langmuir isotherm was shown.

2) Ca and Mg which was contained in bankfiltrate in Mn adsorption by MnO₂ slurry showed positive effect in Mn adsorption.

3) The reason of decreasing equivalent values after MnO₂ slurry addition and adsorption of Mn was the less consuming amounts of KMnO₄ in generated MnO₂ particle from KMnO₄ and Mn reaction and MnO₂ slurry added by autocatalytic reaction.
References


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