Charcoal produced from excess sludge appeared to be useful for removing SMP (soluble microbial products) in MBR (membrane bioreactors) and therefore for reducing membrane fouling. Batch experiments and long-term MBR experiments were performed by using charcoal made of actual excess sludge. In the batch experiments, SMP was removed effectively through charcoal addition. This approach proved especially effective for the removal of carbohydrate. Charcoal would serve as an absorbent and coagulant in SMP removal. High BOD (biochemical oxygen demand) removal efficiencies produced no negative effects on biological activity in the reactors during the long-term MBR experiments involving charcoal addition. The decrease of humic substances and COD (chemical oxygen demand) through charcoal addition suggested that this approach effectively enhanced the performance of activated sludge treatment. A charcoal addition of more than 0.1% in long-term MBR experiments effectively decreased the membrane fouling frequency. The use of charcoal therefore served to mitigate membrane fouling. A decrease in carbohydrate, corresponding to the increase in the mean fouling period, suggested that a charcoal addition of more than 0.1% effectively removed SMP, especially carbohydrate. A charcoal cyclic reuse system is also proposed. This system would involve charcoal production and charcoal addition to MBR.

**Key Words:** charcoal, excess sludge, fouling, membrane bioreactors (MBR), recycling of excess sludge

1. INTRODUCTION

Excess sludge reduction is one of the most important problems associated with wastewater treatment plants\(^1\)-\(^3\). Increased amounts of excess sludge are being produced worldwide. Moreover, the excess sludge contains certain undesirable components, including organic, inorganic and toxic substances as well as pathogenic or disease-causing microorganisms\(^4\). The sludge would pose a serious ecological threat to environment if it were treated improperly. In addition, the treatment and disposal of excess sludge in a biological wastewater treatment system involves extremely high costs\(^4\), \(^5\). These costs can reach approximately half of the entire cost of operating a domestic wastewater treatment facility\(^5\). The treatment and disposal of excess sludge constitute an increasing environmental challenge. A number of methods have been employed over the years to mitigate this problem. These methods include the use of sludge as fertilizer, as landfill material, dumping at sea and incineration\(^4\), \(^6\)-\(^9\). These methods either cause secondary pollution or consume a large amount of energy\(^9\). However, techniques are now available to control gaseous emissions, and incineration is becoming much more cost-competitive with other disposal options\(^4\). Therefore, the use of the incineration method is expected to increase in the future. For example, in the European Community the use of the incineration method has increased rapidly. The use of the incineration method has increased from 10% in 1985 to approximately 38% in 2005, whereas
the use of other methods has decreased or has increased slightly\(^9\). It is worth noting that charcoal production has also been introduced as a means of reducing the amount of excess sludge\(^9, 10\). Charcoal is used as an adsorbent, an energy source and a means of improving the soil\(^11-13\). Moreover, the application of charcoal has long been well known to represent a very effective absorption method for treating wastewater by enhancing biodegradation and sludge dewaterability, and for reducing membrane fouling\(^14-16\).

We have therefore proposed a recycling system that uses previously deodorized charcoal added to the aeration tank of a wastewater treatment plant. The principal features of this system are as follows. The biodegradable organic odor materials adsorbed on the charcoal would be released to the water phase in the aeration tank and be biologically decomposed. COD (chemical oxygen demand) materials and humic substances present in wastewater would then be absorbed on the surface of the charcoal. Thereafter, new charcoal would be produced by collecting, dewatering and burning the excess sludge from this reactor. However, it has proven difficult to separate charcoal from effluent water using an aeration tank. A membrane bioreactor (MBR) was therefore introduced in the current study. The MBR system has been considered as an innovative technology for wastewater treatment industry over the world\(^17-20\). However, the high rate of fouling of the membrane filter is one of the most serious problems affecting MBR systems\(^21, 22\). According to Drews et al. (2008), several factors have been found to affect membrane fouling. These factors include floc size, the viscosity of the mixed liquor and especially soluble microbial products (SMP)\(^19, 23\). SMP are compounds of microbial origin derived during biological processes of wastewater treatment\(^19\). They play an important role in creating high resistance on the membrane, and they lead to a reduction of permeate flux or an increase of TMP (transmembrane pressure)\(^18, 20\).

Many studies have stated that activated carbon is well suited for the removal of dissolved organics by adsorption and for the removal of SMP by heterogeneous coagulation\(^24, 25\). Moreover, the use of activated carbon can reduce the frequency of fouling in MBR\(^26\). Charcoal produced from excess sludge seems to play the same role as activated carbon\(^27, 28\). Therefore, the effects of charcoal addition on SMP removal and on the mitigation of membrane fouling were investigated in this study by using batch experiments and long-term MBR experiments. Moreover, a system involving the cyclic reuse of charcoal was also proposed to serve as a useful model.

2. MATERIALS AND METHODS

(1) Materials

Powder-type charcoal made from excess sludge from a municipal wastewater treatment plant in Shiga prefecture, Japan was used in this study. The excess sludge was burnt at 600°C after dewatering and drying and was then ground. The mean diameter of the charcoal was 60 µm. Its specific surface area adsorption was 62.8 m²/g. The charcoal was mixed with pure water, namely mixed charcoal-containing liquor, before all experiments. Commercial albumin (from eggs) and glycogen (from oysters) were used as the biopolymer in the batch experiments to represent standard SMP materials. They were dissolved in pure water, and their pH was adjusted to 7 before the experiments. A flat sheet membrane made of chlorinated polyethylene (0.4µm nominal pore size and 0.04 m² filtration area, Kubota) and mixed liquor taken from actual MBR facilities treating domestic wastewater (1000 p.e.) in Kusatsu City was used in the long-term MBR experiments.

(2) Batch experiments

First, the albumin or glycogen solution and mixed charcoal-containing liquor were put in a 1000 mL beaker. The concentrations of the SMP and of the charcoal and the pH were adjusted to 100 mg/L (as albumin or glucose concentration), 0.25 % and 7, respectively. The contents of the beaker were mixed using a jar test apparatus at 100 rpm and 25°C. After mixing intervals of 15 minutes and 6, 12, 24, 36 and 48 hours, the mixed liquor was filtered through filter paper (1µm pore size, Advantec 5C), and the protein and carbohydrate concentrations of the filtrate were measured.

Next, a mixture of 100 mg/L of biopolymer and mixed liquor of charcoal at various concentrations (0 %, 0.01 %, 0.05 %, 0.1 %, 0.25 %, 0.5 %, 0.75 %, 1.0 %) were mixed in a 1000 mL beaker using the same jar test conditions. After 24 hours, the mixed liquor was also filtered, and protein and carbohydrate concentrations of the filtrate were measured. Duplicate tests were conducted for each batch condition.

(3) Long-term MBR experiments

A flat sheet membrane was submerged in a reactor filled with 10 L of mixed liquor (Fig. 1). Filtration was performed intermittently (1.5 hours on and 0.5 hour off) at 25°C with a flux of 0.25 m³/m²/day by using a suction pump to obtain the effluent. Synthetic wastewater (Table 1) was fed into the reactor at 10 L/day (HRT 24 hours) to keep the volume of the mixed liquor at 10 L. The experiments were conducted at a SRT of 33 days and an average MLSS (of activated sludge) of 1500 mg/L.
Fig. 1 Schematic diagram of the long-term MBR experiment.

Table 1 Components of synthetic wastewater.

<table>
<thead>
<tr>
<th>Components</th>
<th>Conc. (g/L)</th>
<th>Influent water quality</th>
<th>Conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>74</td>
<td>BOD</td>
<td>1000*,750**</td>
</tr>
<tr>
<td>Sodium</td>
<td>40.1</td>
<td>COD</td>
<td>700*, 530**</td>
</tr>
<tr>
<td>L(+)-glutamate monohydrate</td>
<td>1.0</td>
<td>Nitrogen</td>
<td>50</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.66</td>
<td>Phosphorus</td>
<td>25</td>
</tr>
<tr>
<td>CaCl2</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgSO4</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K2HPO4</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH2PO4</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Run A, B, C, D, E
** Run F, G, H, I

Table 2 Conditions of charcoals in long-term MBR experiments.

<table>
<thead>
<tr>
<th>Run</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (%)</td>
<td>0</td>
<td>0.05</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.5</td>
<td>0.7</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Period (days)</td>
<td>39</td>
<td>40</td>
<td>40</td>
<td>119</td>
<td>40</td>
<td>48</td>
<td>39</td>
<td>57</td>
<td>41</td>
</tr>
</tbody>
</table>

Air was supplied intermittently from an aeration pipe below the membrane module at 3 L/min (1.5 hours on and 0.5 hour off). The membranes were washed (physical washing in tap water while wiping the membrane by hand, or chemical washing by submerging the membrane in 0.25% NaOCl solution for 1 to 2 hours) if TMP increased by more than 0.03 MPa. The concentration of the charcoal was maintained at 0 % – 1.5 % during each run (Table 2) through daily addition of the mixed charcoal containing liquor. The runs were conducted almost 40 days or more.

(4) Analytical methods

Protein and carbohydrate concentrations were measured using Lowry’s methods and the anthrone-sulfuric acid reaction, respectively. Aluminum, iron and silicate were determined by inductively coupled plasma-emission spectrometry (SPS 4000, Seiko) after the digestion of organics using nitric acid and hydrogen peroxide. The amounts of protein and carbohydrate in the effluent and mixed liquor filtered by filter paper (1 μm pore size, Advantec 5C) were measured as SMP of < 0.4 μm and 0.4–1 μm, respectively. COD was measured using KMnO4 oxidization. Quantitative analyses of other parameters were conducted according to JIS K0102. Humic substances were measured using a spectrophotometer at wavelengths of 260 nm and 400 nm (E260 or E400).

3. RESULTS AND DISCUSSIONS

(1) Batch experiments

The changes in SMP removal rates as a function of the mixing time in the batch experiments are shown in Fig. 2. The removal rates of carbohydrate were apparently larger than those of protein. These rates increased moderately at the beginning of the experiment and then remained stable after 24 hours. Therefore, a value of 24 hours was chosen as the minimum required time for further batch experiments involving changes in the charcoal concentrations. The results of these experiments are also shown in Fig. 2. The carbohydrate removal rates increased rapidly from 0 % to 97 % with an increase of charcoal concentration from 0 % to 0.5 %. It remained
at almost 100% in a range of charcoal concentrations from 0.5% to 1.0%. The protein removal rate rose gradually and reached 65% at 1.0% charcoal concentration.

These results indicate that protein and carbohydrate were removed effectively through the addition of charcoal. The removal of carbohydrate appeared to be especially effective. Activated carbon adsorbed soluble organic matter as well as coagulated organic colloids, e.g., SMP\(^{14,24}\). The characteristics of activated carbon are almost the same as those of charcoal because both substances are produced from the same carbonaceous materials\(^\text{12, 24}\). Charcoal would therefore serve as an absorbent and coagulant to decrease the concentrations of SMP.

(2) Long-term MBR experiments

a) Effluent water quality

The BOD (biochemical oxygen demand) removal efficiencies of Run A – Run I with and without charcoal addition were more than 99.8% and showed no significant differences (p = 0.05). This result showed that addition of charcoal in concentrations below 1.5% had no negative effects on the biological activities in the reactors. The COD removal efficiency in Run A was 98.4%, lower than the BOD removal. However, charcoal addition seemed to increase this value to 99.3% or 99.5% in Run C or Run E, but the significance of this difference was not clear. Moreover, \(E_{260}\) in the effluent decreased gradually from 0.09 (Run A) to 0.01 (Run G – Run I) through charcoal addition. \(E_{400}\) also decreased from 0.01 to 0.002. The adsorption of humic substances by activated carbon or charcoal is well known. These substances were detected as COD and by absorbance (\(E_{260}\) or \(E_{400}\))\(^{15}\). The decrease of the absorbance as well as that of COD suggested that humic substances in the reactors would be adsorbed by the added charcoal. Therefore, the charcoal addition enhanced the performance of conventional activated sludge and furnished a hybrid method including both biological and physicochemical components. This hybrid approach therefore resembles a biological activated-carbon process\(^29\).

b) Decrease of membrane fouling by charcoal addition

The membrane fouling frequency (fouling times per unit period) was decreased by the addition of charcoal (Fig. 3). Because the reactors were operated in the condition that membrane fouling easily occurred, the membrane fouling frequency exhibited quite higher than practical MBR operations. The fouling frequencies observed in the three MBR systems were considerably different over the entire experimental period. Specifically, the fouling frequencies for runs A, D, and G (corresponding to 0%, 0.2% and 0.7% charcoal addition) were 39 times in 39 days, 8 times in 119 days, and 7 times in 39 days, respectively.

Moreover, Fig. 4 also illustrates the mean periods and standard deviations associated with one fouling event in all runs. The figure suggests that a charcoal addition of more than 0.1% increased the fouling intervals period considerably (mitigated membrane fouling). However, the addition of 0.05% charcoal was not sufficient to affect the fouling intervals. The difference between the 0% – 0.05% and 0.1% – 1.5% runs was statistically significant (p <
0.0001). On the contrary the difference among 0.1 % – 1.5 % runs was not clear because of the large deviations. It suggested that the effect of 0.1 % charcoal addition was enough to mitigate the membrane fouling. As shown in the previous section, the charcoal addition removed SMP and was especially effective for carbohydrate removal. These substances are known to cause membrane fouling\(^ {18)}\), \(^ {20)}\), \(^ {26)}\). The mitigation of fouling seemed to be a result of the decrease of SMP caused by the charcoal addition, as will be discussed in the next section.

**c) Change in SMP resulting from charcoal addition**

The effects of charcoal addition on SMP concentrations are shown in **Fig. 5**. As was the case in the batch experiments, the effect of the charcoal addition on carbohydrate removal was stronger and clearer than the corresponding effect on protein removal. Therefore, changes in carbohydrate removal will be considered in this section. The carbohydrate concentrations were strongly correlated with the mean fouling period. They were considerably higher in Run A and Run B than in Run C – Run I in both size fractions. These results correspond to the significant differences in the mean fouling period found for the runs. The carbohydrate concentrations exhibited significant differences (p < 0.001) as well. In the batch experiment, the carbohydrate concentration decreased much more as a result of charcoal addition than did the protein concentration. This finding supported the results above regarding SMP changes that occurred during the long-term MBR experiments.

The correspondence between the decrease in carbohydrate and the increase in the mean fouling period suggested that a charcoal addition of 0.1 % – 1.5 % removed SMP by adsorption and coagulation, thereby producing a decrease in membrane fouling frequency. However, SMP are composed of many micro-molecular and macro-molecular compounds. Therefore plural measures such as addition of mixture of coagulants and/or charcoals would be more effective in practice.

**d) Charcoal cyclic reused system combined with MBR**

The results from this study suggested that the addition of charcoal to MBR enhanced MBR performance. Charcoal could be retrieved from the excess sludge of the MBR and could then be added to MBR once again after utilization (e.g., deodorization). Therefore, the charcoal cyclic system model shown in **Fig. 6** could be proposed. This model includes the following stages: addition, MBR, excess sludge, production (burning), utilization (if necessary) and addition again (**Fig. 6**). The amount of charcoal to be added per day can be calculated as follows to compensate for the decrease of the amount of charcoal amount in the reactor that resulted from the removal of the excess sludge.

\[
a = \frac{(S \times MC)}{MLSS}
\]  

where \(a\) (g/d): mass of charcoal addition per day, \(MC\) (g/m\(^3\)): charcoal concentration in the reactor, \(MLSS\) (g/m\(^3\)): mixed-liquor suspended solids and \(S\) (g/d): mass of excess sludge withdrawn per day. \(S\) is written using SRT (d) and the reactor volume \(V\) (m\(^3\)) to obtain
Equation (2) shows that the amount of charcoal addition per unit volume of the reactor can be estimated using \( Mc \) and \( SRT \). It will be proportional to \( Mc \) and inversely proportional to \( SRT \).

The amount of charcoal production is assumed to be \( \gamma S \), where \( \gamma \) is the yield of charcoal production (0 – 1). To supply enough charcoal to the MBR through charcoal production, we require

\[
a < \gamma S
\]

Combining (1) with (3) gets,

\[
(S \times Mc) / MLSS < \gamma S
\]

which corresponds to

\[
Mc < \gamma \times MLSS
\]

Equation (5) suggests that the \( Mc \), the possible concentration of the added charcoal, depends on the yield of the charcoal produced by the cyclic system. If we assume that \( MLSS \) is 15000 mg/L and that \( \gamma \) is 0.4, \( Mc \) must be less than 6000 mg/L. The result obtained for this example is 0.6 %. This 0.6 % charcoal addition would be effective for decreasing the amount of fouling. It is clear that if \( Mc \) is equal to \( \gamma \times MLSS \) (0.6 % in the above example), no excess charcoal need be removed from the cycle. In other words, no emission system would be established.

4. CONCLUSIONS

This study investigated the effects of the addition of charcoal to MBR by conducting a number of batch experiments and long-term MBR experiments. The following results were obtained:

- In the batch experiment, SMP (protein and carbohydrate) was removed effectively by the charcoal addition. The removal of carbohydrate was especially effective. Therefore, charcoal would serve as an absorbent and coagulant in SMP removal.
- High BOD removal efficiencies were not associated with any negative effects on biological activities in the reactors in the long-term MBR experiment involving charcoal addition. The decrease of humic substances as well as COD as a result of the addition of charcoal suggested that charcoal addition effectively enhanced the performance of conventional activated sludge.
- The addition of more than 0.1 % charcoal in the long-term MBR experiments greatly increased the length of the fouling intervals. This result means that membrane fouling was mitigated.
- The decrease in carbohydrate corresponded to the increase in the mean fouling period. This result suggests that the addition of more than 0.1 % charcoal effectively removed SMP, especially carbohydrate.
- A charcoal cyclic reuse system was proposed and discussed. The consideration of this system produced some useful equations describing the relations linking the amount of charcoal addition, its concentration and SRT based on a simple model.

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REFERENCES


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