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OPTIMUM COMBINATION OF EXISTING TREATMENT PROCESSES IS ESSENTIAL FOR ELEVATION OF DRINKING WATER QUALITY

OPTYMALNE POŁĄCZENIE ISTNIEJĄCYCH PROCESÓW UZDATNIANIA JEST NIEZBĘDNE DLA POPRAWY JAKOŚCI WODY PITNEJ.

Some experiment results on biological filtration, activated carbon adsorption and membrane filtration are presented. By demonstrating the strengths and weaknesses of these processes in dealing with various known and emerging contaminants present in source water, the consideration for the need to build new drinking water supply systems through optimum combination of existing treatment processes and/or newer treatment technologies for realizing the expected elevation of drinking water quality is supported.

1. Introduction

Slow sand filtration system (SSF) and rapid sand filtration system (RSF), both have an application history for over 100 years, are widely used for drinking water production though the quality of the major source water (i.e., rivers and lakes) has experienced great changes: in most cases, it is getting more complicated regarding the number of contaminants originated from enhanced agricultural, industrial and social activities [1]. The major attractive side-effects of SSF are its capability to decompose some trace organic contaminants (pharmaceuticals & endocrine disrupters) that cannot be eliminated by conventional RSF, and also its capability to oxidize ammonium to nitrate and hence reduce the chlorine demand for disinfection [2,3]. For RSF, however, the relatively higher tolerance capability to raw water quality variations and higher removal efficiency for THM precursors, bacterial and viral agents are its major advantages.

With people's living styles getting more and more diversified and living standards upgraded, in future tens of years the source water quality in most countries may become more complicated by many known and emerging chemical compounds and microbial and viral agents of health and taste concerns. On the other hand, another important fact that may affect the existence and sustainable development of public water supply systems is the trend of people's escaping from waterworks seen in many countries. Such a trend may continue and, most probably, may get intensified due to people's increasing concerns on the quality of water not only for drinking but also for other usages (e.g., bath, washing and kitchen). Home users' pursuing for tap water with higher quality will never stop; instead, it will continue to increase. To ensure higher tap water quality along the trend with the source water quality getting increasingly complicated, to build or assembly new treatment systems on the basis of the core processes of the conventional SSF and RSF systems, and the existing advanced treatment processes or newer treatment technologies (including biological filtration, activated carbon adsorption, membrane filtration, advanced oxidation, UV disinfection, and even such technologies as ion exchange and nanofiltration adopted for pure water production) is the likely direction for future drinking water production.

In this paper, some recent research results of the authors on biological filtration, activated carbon adsorption and membrane filtration will be presented to demonstrate the strengths and weaknesses of these core treatment processes; and therefore to support the consideration on the need to combine existing treatment processes and/or newer treatment technologies for realizing drinking water quality elevations.

2. Biological filtration

Slow sand filtration (SSF) is the most representative biological filtration process used in the field of drinking water treatment. The biofilm developed on the sand medium can help detain most suspended impurities and contaminants (including bacterial and viral pathogens) contained in the water to be treated and, at the same time, can decompose some trace organic compounds that cannot be removed by physical and chemical processes adopted in the conventional rapid sand filtration system [2,3]. The biofilm developed on granular activated carbon (GAC) during adsorption also possesses the capability to degrade certain known or unknown trace organic compounds existed in the source water or those that have already been adsorbed inside the macropores of the well-recognized adsorbent.

The decomposition function of the biofilm should be recognized and reasonably evaluated when a new water treatment system is to be considered, in which a biological filtration process can be integrated either as a core process like the one used in the conventional SSF system or as a pretreatment or posttreatment process for dealing with some known or unknown organic compounds present in current or future water sources. Meanwhile, the limitations of biological filtration should also be recognized since not all organic contaminants are biodegradable and the development of biofilm may enhance the biological risk of the water after treatment. In addition, many factors may affect the performance of the biofiltration process, such as filtration rates, temperatures, and the microbial density and structure inside the biofilm developed.

2.1 Behavior of 17ß estradiol in biological sand filtration

Figures 1-3 show the effluent concentration profiles of 17ß estradiol (E2) in a continuous flow filtration experiment using columns packed with the sliced 0-6 cm, 6-12 cm and 12-18 cm sand layers of a practical SSF filter under the filtration rate of 2.4, 4.8, 12 and 24 m/d, respectively. The spiked E2 concentration in the influent was controlled at 30 µg/L. As shown, E2 in the effluent increased with time over the initial running period, with the period length being found equivalent to the designated filtration rate. After the initial period, apparent changes in the effluent concentration were not observed, indicating the biological reaction had reached the steady state.

For the column with the sand layer of 0-6 cm (Fig. 1), the average effluent concentrations of E2 in the steady state under the filtration rate of 2.4, 4.8, 12 and 24 m/d were 3.88, 8.66, 19.92 and 25.80 µg/L, representing a removal efficiency of 81, 71, 34, and 14%, respectively. Similar trends were also obtained for the filtration experiments with the sand layers of 6-12 (Fig. 2) and 12-18 (Fig. 3).

For all runs, estrone (E1), a well-known biotransformation product of E2, was observed, as shown in **Figure 4** as an example. This verified there were microbial species in the biofilm of the practical sand filter that could degrade E2.
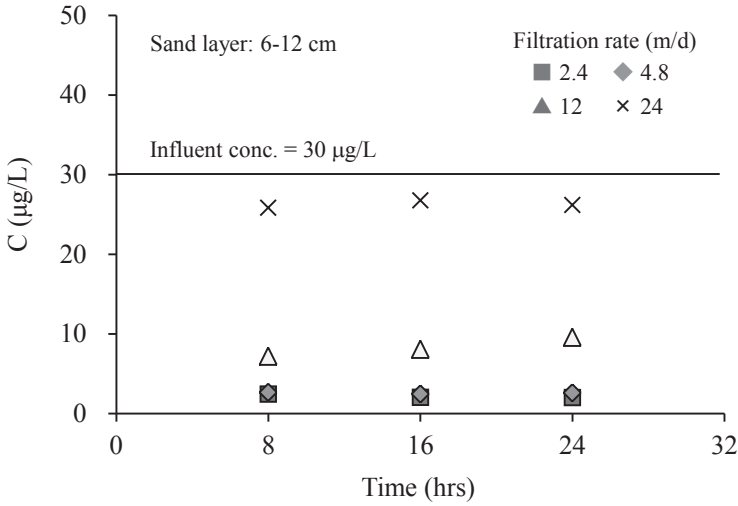
Fig 1. Effluent concentration profiles of E2 under different filtration rates from the column packed with 0-6 cm sand layer of a practical SSF filter in a drinking water treatment plant with river water as the so-urce water. The influent E2 concentration was 30 µg/L and the running temperature was 20ºC.
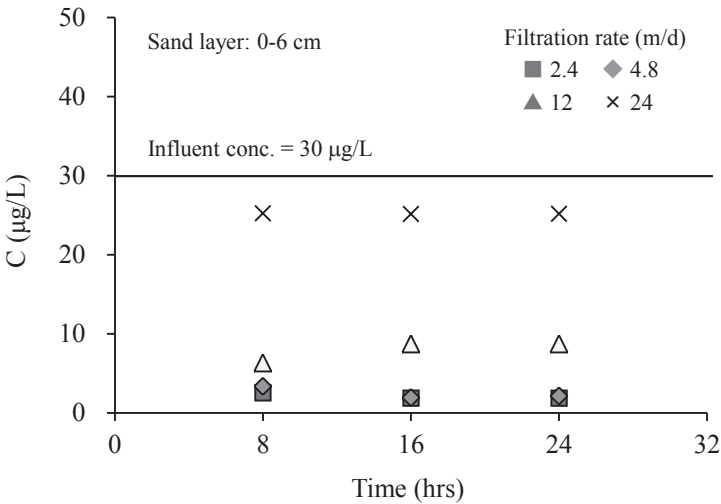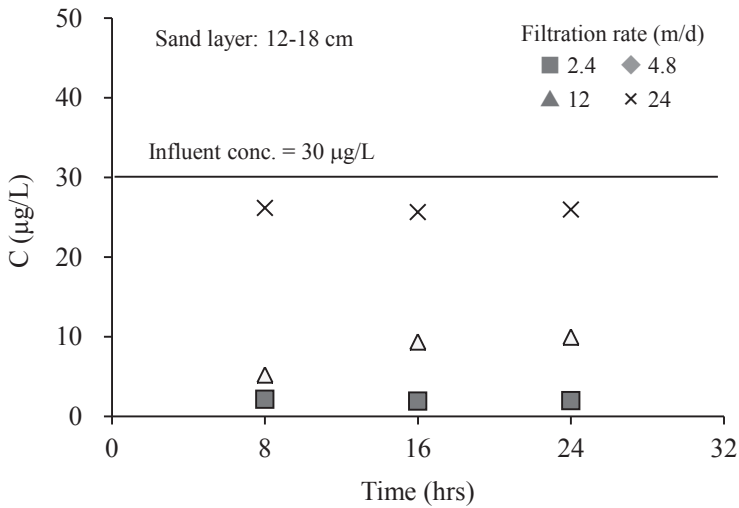

Fig 2. Effluent concentration profiles of E2 under different filtration rates from the column packed with 6-12 cm sand layer of a practical SSF filter in a drinking water treatment plant with river water as the source water. The influent E2 concentration was 30 µg/L and the running temperature was 20ºC.

Fig 3. Effluent concentration profiles of E2 under different filtration rates from the column packed with 12-18 cm sand layer of a practical SSF filter in a drinking water treatment plant with river water as the source water. The influent E2 concentration was 30 μg/L and the running temperature was 20°C.
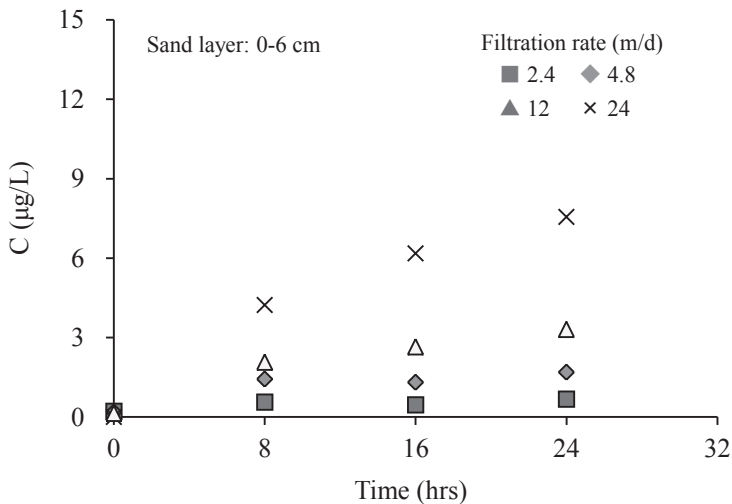

Fig 4. Concentration profiles of E1 transformed from the spiked E2 un-der different filtration rates in the column packed with 0-6 cm sand layer of a practical SSF filter in a drinking water treatment plant with river wter as the source water. The spiked E2 concentration in the influent was 30 μg/L and the running temperature was 20°C.

Assuming biological degradation was the major mechanism leading to the dissipation of E2 in the sand columns, the following mass balance equation could be used to describe the concentration profiles of this compound in the effluent:

$$V\frac{dC_{eff}}{dt} = QC_{inf} - QC_{eff} + V\left(-kC_{eff}\right) \quad (1)$$

where, V is the volume of the packed sand media, Cinf and Ceff is the concentration of E2 in the influent and effluent, respectively, t is the filtration time and k is the first-order degradation rate constant. Many biodegradation studies have confirmed that the degradation of E2 generally follows the first-order reaction model.

The rate constant k could be easily estimated from the above equation when the ef-fluent concentration reached the steady state, i.e., when $d_{Ceff}/dt = 0$. Then, from the estimated *k* values, the half-life of E2, $t_{1/2}$, under different filtration rates, temperatures and influent concentrations could be estimated according to the following:

$$t_{1/2} = \ln 2/k \quad (2)$$

The estimated $t_{1/2}$ under different filtration rates is shown in **Figure 5**. A trend of in-creases with the increases of the filtration rate was revealed. The values of $t_{1/2}$ fell in the range of 0.78-3.26, 1.56-5.55 and 1.29-14.59 hrs for sand layers of 0-6, 6-12 and 12-18 cm, respectively. For all filtration rates, $t_{1/2}$ followed the order of 0-6 cm < 6-12 cm < 12-18 cm. Similar results were also obtained for filtration runs performed with the spiked E2 concentration of 10 µg/L (data not shown).
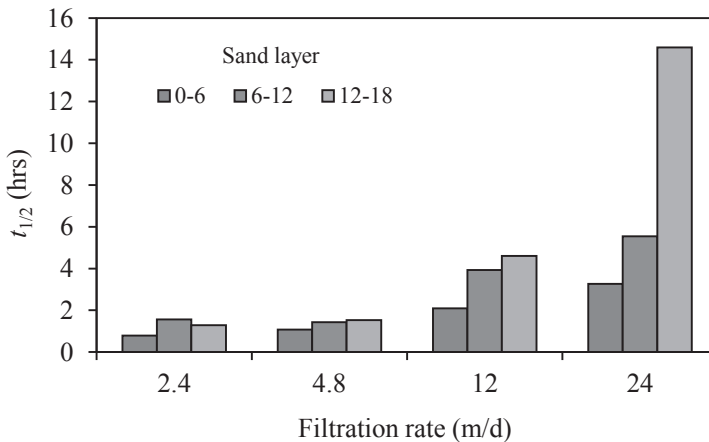

Fig 5. Effect of filtration rate on the half-life of E2 in the columns packed respectively with 0-6, 6-12 and 12-18 cm sand layers of a practi-cal SSF filter in a drinking water treatment plant with river water as the source water. The influent E2 concentration was 30 µg/L and the running temperature was 20ºC.
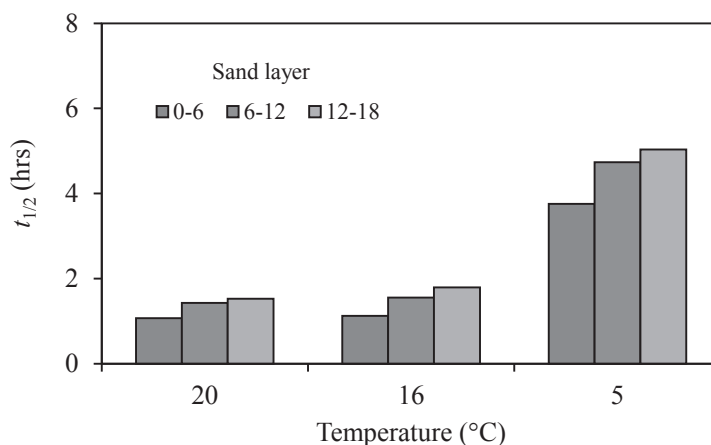
Fig 6. Effect of filtration rate on the half-life of E2 in the columns packed respectively with 0-6, 6-12 and 12-18 cm sand layers of a practi-cal SSF filter in a drinking water treatment plant with river water as the source water. The influent E2 concentration was 30 µg/L and the running temperature was 20ºC.

Figure 6 shows the estimated $t_{1/2}$ values under three different temperatures with the filtration rate of 4.8 m/d. $t_{1/2}$ fell in the range of 1.07-3.76, 1.43–4.73 and 1.52-5.03 hrs for sand layers of 0-6, 6-12 and 12-18 cm respectively, indicating an insignificant temperature effect between 16 and 20℃, and a significant effect between 16 and 5℃. The dependency of the biodegradation rate of E2 on temperatures had been confirmed in a previous study with activated sludge [4].

2.2 Behavior of hexamethylene-tetramine in biological sand filtration

Hexamethylene-tetramine (HMT) is one of the major precusors of the regulated formaldehyde in drinking water quality standard. Due to an incident release of HMT to the major drinking water source (Tonegawa River) in Tokyo in May 2015, water suppy from many treatment plants was affected due to higher concentrations of formaldehyde detected in the water after chlorination treatment. To confirm if HMT could be degraded in biological filtration, slow sand filtration experiments were conducted using columns packed with virgin silica sand from a SSF plant to a bed depth of 30 cm. The source river water of this plant was consistently supplied to the columns under 4 m/d and inside the water, HMP was added to make its concentration in the influent at about 100 µg/L. During the experiments, the influent water was intermittently shifted to a DOC-free river water added with the biodegadable glucose for three times (each time for only five hrs) to check the ripening of biofilm.
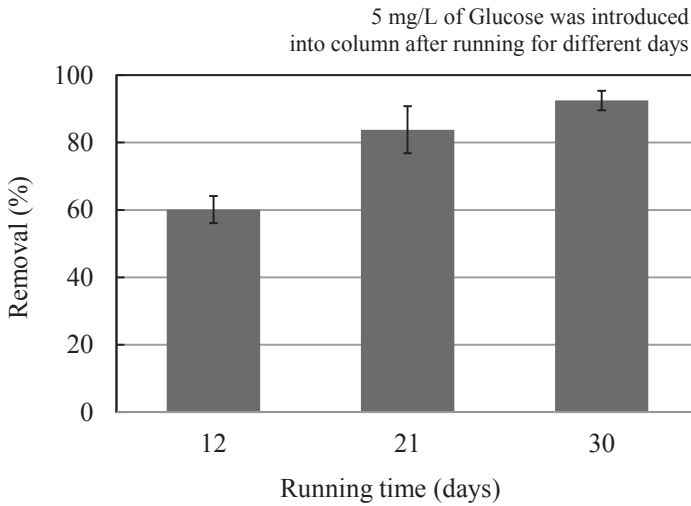
5 mg/L of Glucose was introduced
into column after running for different days

Fig 7. Removal of glucose introduced intermittently to slow sand filtra-tion column running after different time periods for treatment of the source river water of a SSF plant (DOC=0.76-0.84 mg/L). The fil-tration rate was 4.0 m/d and the running temperature was 20ºC.

As shown in **Figure 7**, with the running time increased from 12 days to 30 days, the removal for the intermittently introduced glucose increased from 60 % to nearly 92%, indicating biofilm inside the sand column was gradually approaching to its maturity.

The behavior of HMT consistently supplied to the column is displayed in **Figure 8.** Significant differences between the influent and effluent HMT concentrations were not observed, suggesting HMT could not be degraded by biofilm developed on the filter media of slow sand filtration. Other treatment technologies such as preozonation followed by biodegaradation are necessary.
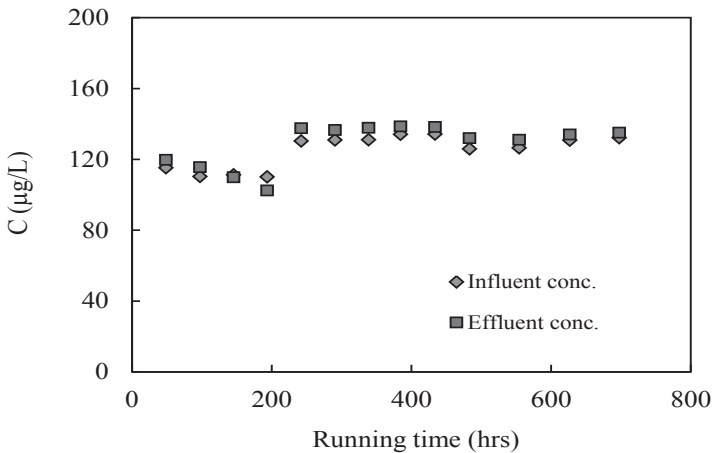

Fig 8. Behavior of HMT added consistently into the source river water of a SSF plant (DOC=0.76-0.84 mg/L) during filtration by slow sand filtration column. The filtration rate was 4.0 m/d and the running temperature was 20ºC.

2.3 Behavior of 17ß estradiol in biological activated carbon adsorption

Figure 9 displays the vertical profiles of E2 and its biodegradation byproduct E1 in a biological activated carbon (BAC) column when E2 was spiked into a source river water containing relatively lower content of NOM, namely Nagara River water (NRW), together with and without a peaty groundwater (GW) containing higher content of NOM for about 5 hours after consistent running of the adsorber with the NRW for about 2350 hours. The column was packed with F400 in the size range of 1.0-1.19 mm to a depth of 10 cm. The empty bed contact time (EBCT) was 19.5 mins.

As water flowed towards the column outlet, the concentration of E2 decreased, indicating the removal of E2 in the adsorber. The emerge of E1, the biotransformation byproduct of E2, indicated bacterial species that could degrade E2 existed within the biofilm formed. In GAC columns run in parallel with BAC columns, the removal of E2 by adsorption alone was also confirmed (data not shown). The adversary effect of higher influent NOM concentration was also revealed as a result of NOM's competition with E2 for adsorption sites. For BAC, where both adsorption and biodegradation are expected, the adversary impact caused by the increased NOM concentration may get alleviated a little bit more than that of GAC due probably to the fact that biodegradation is less affected by the enhanced NOM presence, taking into account that most NOM constitu-ents comprising mainly of humic molecules are generally considered biologically persi-stent. In this column, as the biotransformation byproduct of E2, E1 also dissipated as water flowed downwards.

Comparison of the removals of E2 and NOM inside the BAC column is displayed in Figure 10. It is clear that the removal values of E2 were markedly higher than those of NOM assessed using either DOC or UV260. The role of biodegradation may become eminent and could be easily distinguished from adsorption once the adsorption capabili-ty of activated carbon is nearly exhausted.
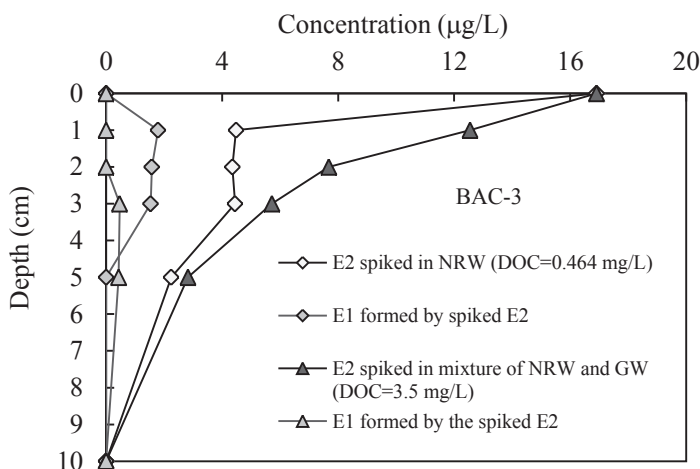

Fig 9. Vertical profiles of E2 and its biodegradation byproduct E1 in fixed bed carbon column when E2 was spiked into Nagara River water (NRW) together with and without the peaty groundwater (GW) for about 5 hours after consistent running of the column under the EBCT of 19.5 minutes with the NRW for about 2350 hours.
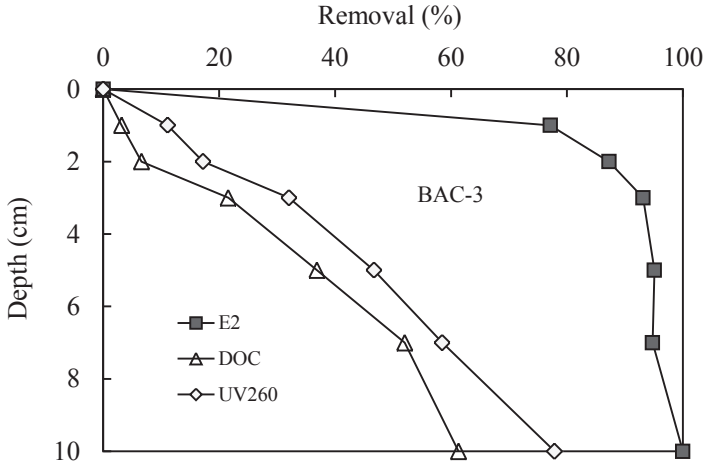
Fig 10. Comparison of the vertical distribution of removals for E2 and NOM in fixed bed carbon column when E2 was spiked into the Nagara River water (NRW) together with the peaty groundwater (GW) for about 5 hours after consistent running of the column for 10,000 hours. The spiked E2 concentration was 30 μg/L, and the NOM concentration was 3.07 mg/L as DOC and 9.981 m⁻¹ as UV260. EBCT was 19.5 minutes.

3.   Activated carbon adsorption

Activated carbon adsorption is the best available technology for advanced water treatment. In addition to targeted trace organic compounds of special concern, such as pesticides, hormones and odors, the major fractions of organic matter presented in most source water can be also eliminated [5-8].
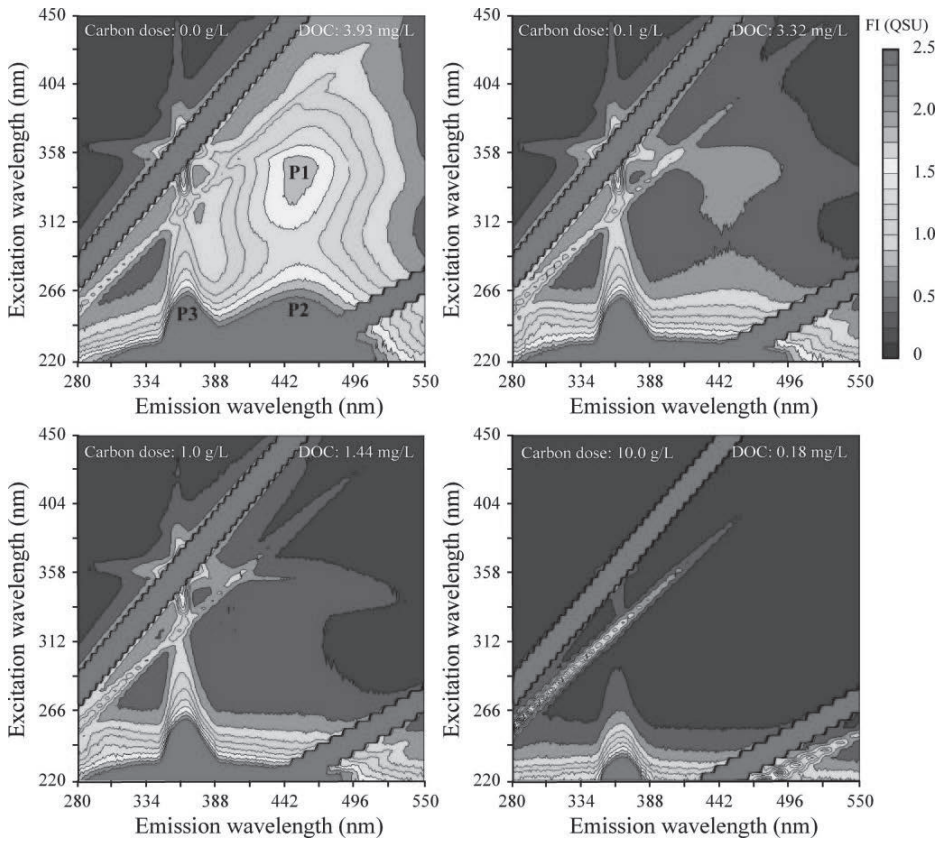
Fig 11. Changes of the fluorescence EEM of organic matter released from the soil sample of a representative broadleaf forest in Kiso River catchment after adsorption by F400 under different dosages.
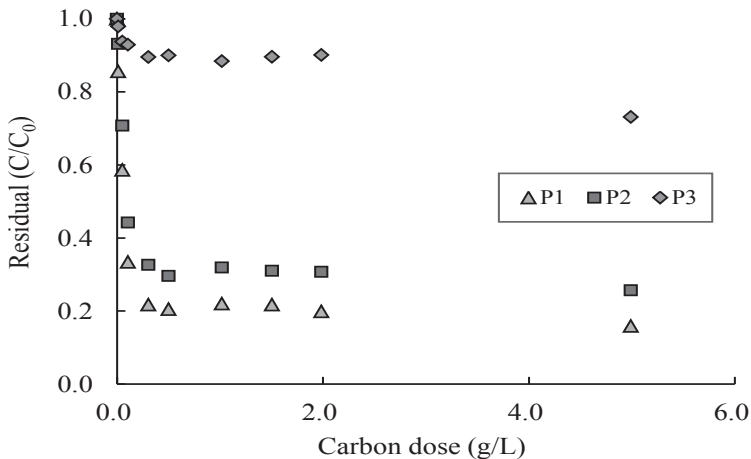

Fig 12. Decreasing trends of the fluorescence intensity of the fluorescence EEM peaks of organic matter released from the soil sample of a representative broadleaf forest in Kiso River catchment by adsorption with F400 under different dosages.

Most importantly, no matter if targeted for removal or not, and if the features and presence levels are known or not, in dependency with their affinity with the type of activated carbon used, organic compounds that can access to the pores of activated carbon may get adsorbed. Many factors affect the adsorption performance by activated carbon. In addition to the operation conditions, the physicochemcial features of activated carbon, organic compounds to be adsorbed, and the chemistry of the water for treatment are important influential factors, requiring detailed investigation when a granular activated carbon adsorbtion facility is to be introduced.

3.1 Adsorbability changes among the constituents of natural organic matter

Figure 11 displays the fluorescence EEM [9-11] of natural organic matter (NOM) released from a soil sample of a representative broadleaf forest in Kiso River catchment to a DOC-removed tap water before and after equilibrium adsorption with F400 under different dosages. Three peaks, namely P1, P2 and P3, appeared in water containing the released organic matter before adsorption. P1 and P2 were in the positions reported reflecting humic acid- and fulvic acid-like substances, respectively; while, P3 in the position of aromatic protein-like substances. It is clear from this figure that compared to the substances reflected by P1 and P2, the substances reflected by P3 were much less adsorbable. This could be more easily seen from **Figure 12**, in which the decreasing trends of the fluorescence intensity of all these three peaks with increasing the carbon dosages are depicted.

The modified Freundlich isotherms of all three peaks based on the following modified isotherm model are shown in **Figure 13**:
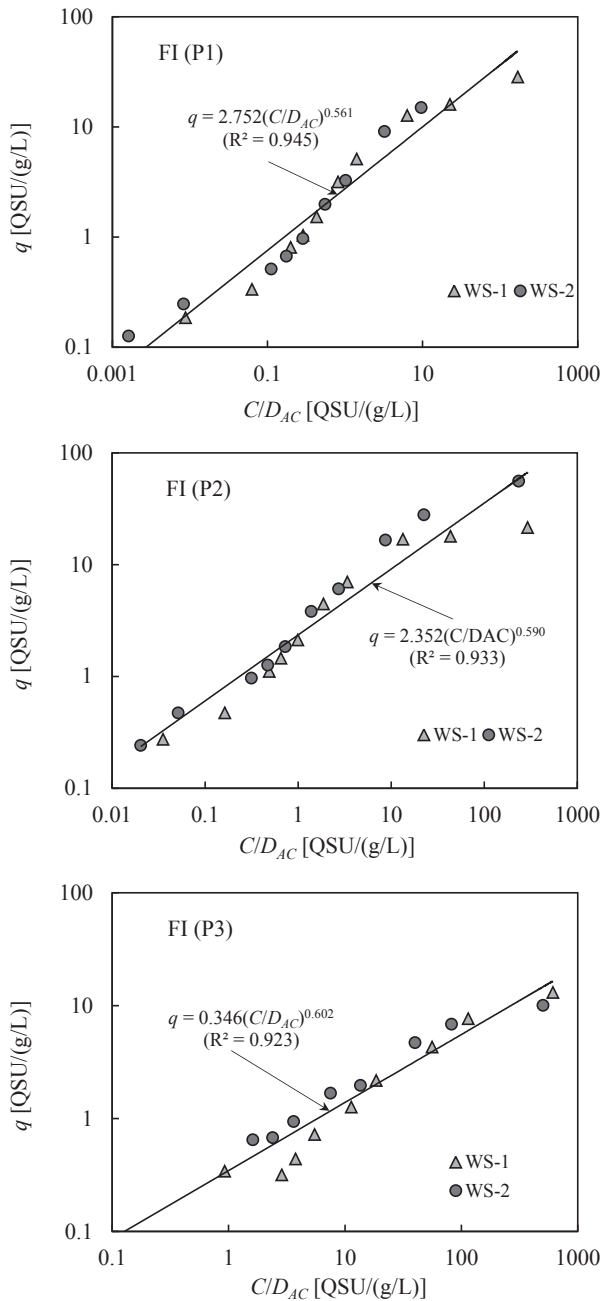
Fig 13. Modified Freundlich isotherms of the fluorescence EEM peaks of organic matter released from the soil sample of a representative broadleaf forest in Kiso River catchment by adsorption with F400.

$$q = K(C/D_{AC})^{1/n} \qquad (3)$$

where, q and C are the equilibrium solid phase and liquid phase concentrations evaluated by relative fluorescence intensity, respectively, and C_{AC} is the dosage of the activated carbon.

For each fluorescence EEM peak, two set of isotherms data obtained with two diluted working solutions of the NOM to different initial concentrations were fairly well converged to a line better described the modified Freundlich isotherm model. It is clear from the determined K values given in the figure that the adsorbability of P1 and P2 was much stronger than P3, suggesting that aromatic protein-like substances that may release to surface source water during rainfall are difficult for removal through adsorption by activated carbon.
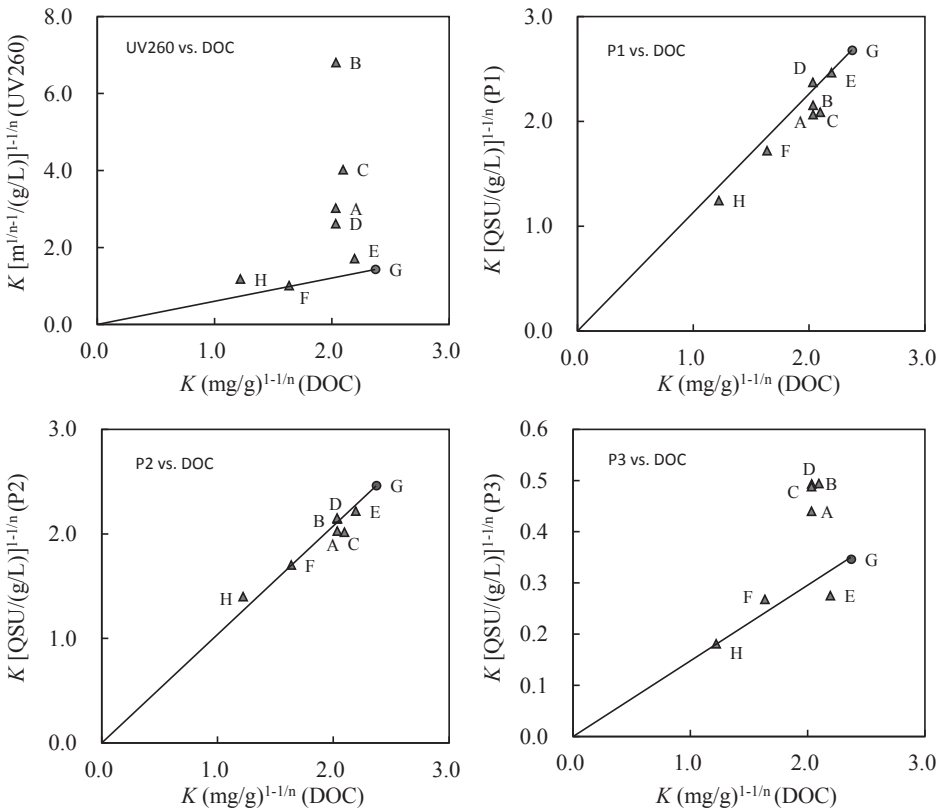

Fig 14. Relationships of the K values of the modified Freundlich isotherm for the organic matter released from the same soil sample mentioned in Figs. 11-13 assessed using the quality indices of UV260 and the fluorescence intensity of all three EEM peaks (P1, P2 and P3) against the K values assessed using DOC for 8 types of activated carbon compared (A-H).

3.2 Dependency of the adsorption efficiency of natural organic matter on the types of activated carbon

Figure 14 shows the relationships among the *K* values estimated from the modified Freundlich isotherm model on the basis of the isotherm data obtained from equilibrium adsorption experiments for the same organic matter mentioned in Figs. 11-13 and 8 types of activated carbon (A-H) compared. The indices used for quantification of the organic matter included the well-used ultraviolet absorbance at the wavelength of 260nm (UV260), dissolved organic carbon (DOC), and the relative fluorescence intensity of three fractions reflected by the peaks appeared in the fluorescence EEM (P1, P2 and P3) shown earlier in Fig. 11. Carbon A, B, C and D are four wood-based powered activa-ted carbon, and carbon E, F, G and H are four coal-based activated carbon after pulverization and sieving to particles with sizes below 45 μm. The differences of these 8 types of carbon in physico-chemical features were evaluated according to their pore size distribution (pore volumes and surface areas) and zeta potentials.

Obvious differences in the magnitude of K could be seen among the 8 types of activated carbon, indicating different adsorption capacity with the adsorbents compared. And, it is also obvious that the differences in K differed with the quality indices and the peaks-based fractions. For all activated carbon types, the aromatic protein-like substances reflected by P3 were found less adsorbable.

4. Membrane filtration

Membrane filtration is a newer treatment technology for drinking water production. Its application is revealing a trend of expansion from the quality stream water to ordinary source water treated generally by rapid sand filtration system. In Japan, since many water treatment facilities built in 1960s and 1970s are facing the need for renovation or reconstruction, the application of membrane filtration is estimated to increase in a pace much faster than that in the past. The major concerns with membrane filtration include two aspects: one is membrane fouling and the other one is its low capability in dealing with dissolved contaminants including taste and odors. Optimum combinations with other treatment processes are key to solve the problems [12]. Depending on the source water qualities, the processes to be combined may include coagulation, sedimentation, sand filtration, biological filtration, activated carbon adsorption, chlorination and ozonation, and even ion exchange if some ionic contaminants of great health concern, such as radioactive cecium, are involved.

Figure 15 shows the configuration of a membrane filtration system proposed by the authors for treatment a drinking surface water source with comparatively serious algal pollution and higher organic matter content.

During the pilot scale experiment perfor-med during February 2013 to November 2014, the raw water quality was as follows; turbidity: 8.4-35.9 (ave. 19.1) NTU, color: 3.0-10.6 (ave. 6.9) degree, TOC: 3.1-4.8 (ave. 4.0) mg/L, DOC: 2.7-3.8 (ave. 3.3) mg/L, UV260: 0.063-0.098 (ave. 0.079) cm^{-1}, THMFPs: 0.068-0.154 (ave. 0.098) mg/L, chlorine demand: 0.9-6.7, 2-MIB: <1.0-835 (ave. 88) ng/L, geosmin: <1.0-222 (ave. 29) ng/L, general bacteria: 45-110,000 (ave. 10,700) CFU/mL, chlorophyll a: 0.0424-0.108 mg/L, and total algae count: 5,770-58,810 (ave. 32,400) cell/mL.

The major features of the ceramic membrane used were: norminal pore size 0.1 µm, length/diameter 1 m/0.03 m, channels per membrane 55, channel dimeter 2.5 mm, membrane area per membrane 0.43 m^2, pure water flux at 25ºC/100 kPa 45 m/d. During the experiment, the membrane filtration flux was set at 4 m^3/m^2/d.
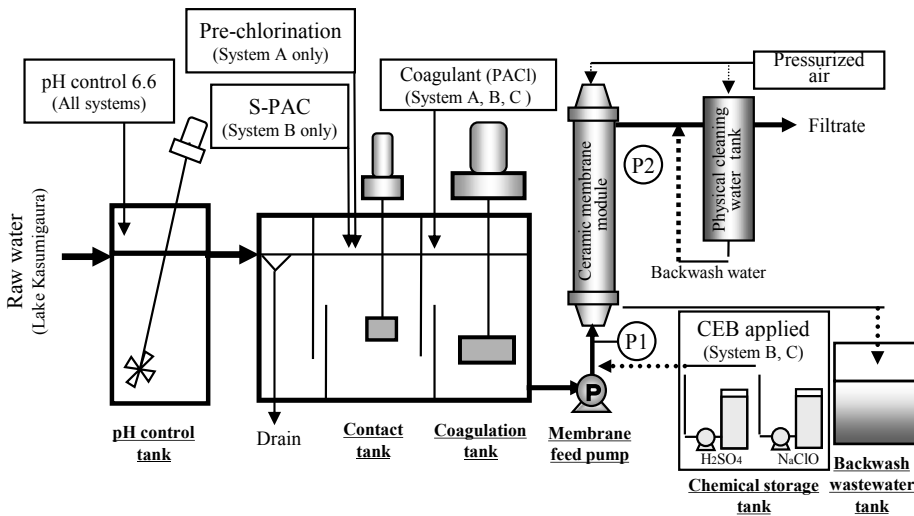

Fig 15. Pilot scale advanced water treatment system with ceramic MF membrane filtration in combination with pre-chlorination, coagulation, super-fine powdered activated carbon adsorption, and chemical enhanced backwashing (CEB).
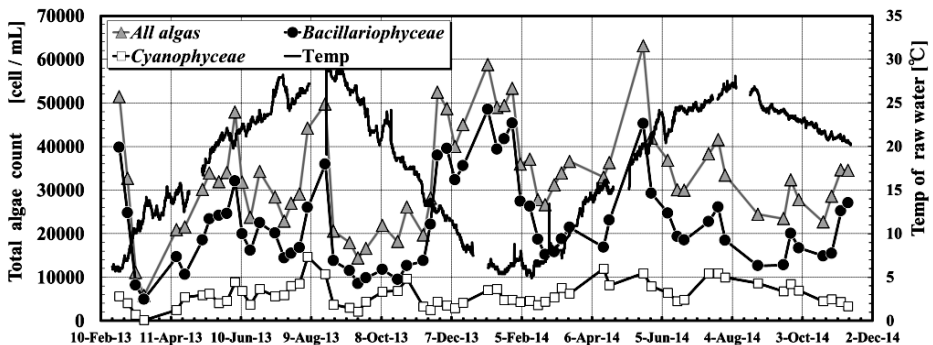

Fig 16. Variations of algal concentrations in raw water during the membarne filtration experiment.
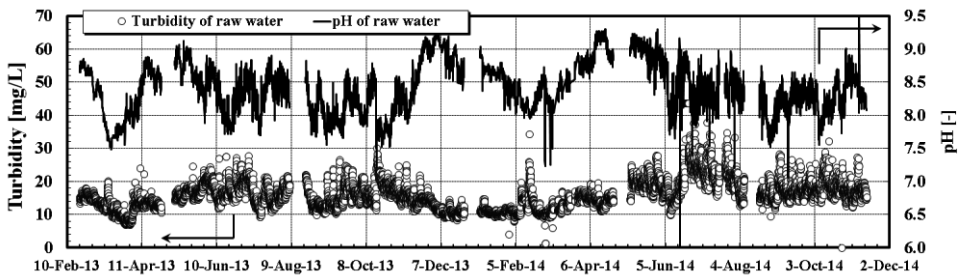
Fig 17. Variations of turbidity in raw water during the membarne filtration experiment.
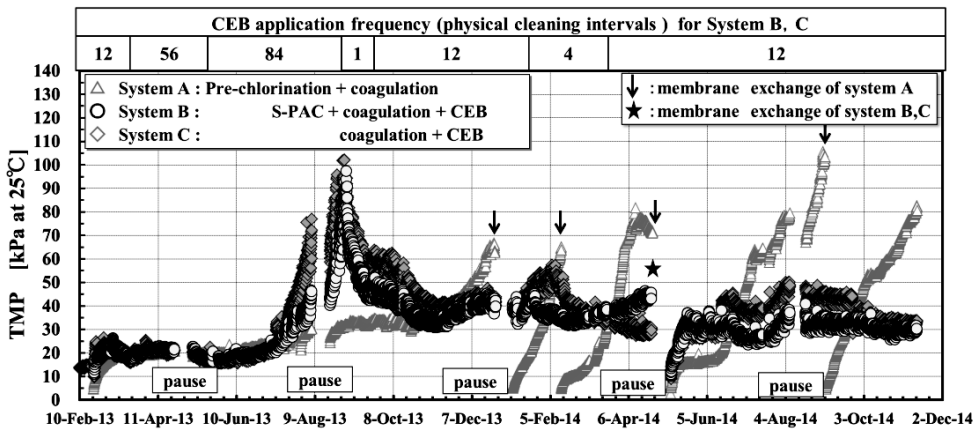

Fig 18. Transmembrane pressure with filtration time for three different systems

Figure 16 and **Figure 17** show the variations of algal concentration and turbidity of the raw water treated during the membrane filtration experiment. Larger number of algae and marked variations with time were confirmed. The transmembrane pressure profiles for compared three operation systems are displayed in Figure 18. The system with combined application of coagulation and chemical enhanced backwashing (CEB), and the system combining PAC adsorption, coagulation and CEB could effectively inhibit membrane fouling and, at the same time, alleviate the risk from byproducts formed when prechlorination was applied as a pretreatment process for controlling the membrane fouling.

The results also demonstrated that, with the combined application of PAC adsorption, the removal for THMFPs, 2-MIB and geosmin could be greatly enhanced, as shown in **Figure 19** and **Figure 20**.
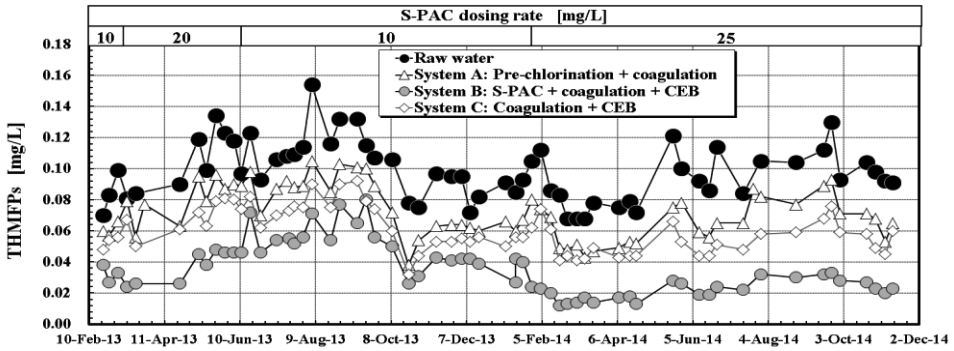
Fig 19. Concentrations of THMFPs before & after treatment with different systems.
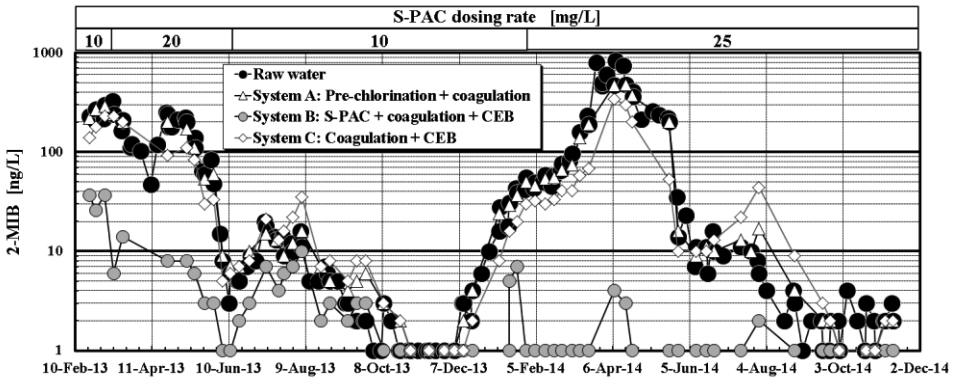

Fig 20. Concentrations of 2-MIB before & after treatment with different systems

5. Conclusions

Biofilm formed in biological filtration process (SSF and BAC) can degrade E2 but can not degrade HMT. Compared to humic- and fulvic-like substances, aromatic protein-like substances released from forest soil to water are much less removable through activated carbon adsorption, and the adsorption efficiency also depends greatly on the types of activated carbon. Ceramic MF membrane fouling and its difficulty in dealing with dissolved organic compounds can be alleviated by combined use of coagulation, activated carbon adsorption and chemical enhanced backwashing. The results support authors' consideration that optimum combination of existing treatment processes and/or newer treatment technologies in relation to the quality of source water is essential for elevation of drinking water quality.

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