



## Original Article

## Evaluation of dynamic behavior of coagulation-flocculation using hydrous ferric oxide for removal of radioactive nuclides in wastewater

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## ABSTRACT

Coprecipitation using hydrous ferric oxide (HFO) has been effectively used for the removal of radionuclides from radioactive wastewater. This work studied the dynamic behavior of HFO floc formation during the neutralization of acidic ferric iron in the presence of several radionuclides by using a photometric dispersion analyzer (PDA). Then the coagulation-flocculation system using HFO-anionic poly acrylamide (PAM) composite floc system was evaluated and compared in seawater and distilled water to find the effective condition to remove the target nuclides (Co-60, Mn-54, Sb-125, and Ru-106) present in wastewater generated in the severe accident of nuclear power plant like Fukushima Daiichi case. A ferric iron dosage of 10 ppm for the formation of HFO was suitable in terms of fast formation of HFO flocs without induction time, and maximum total removal yield of radioactivity from the wastewater. The settling time of HFO flocs was reduced by changing them to HFO-PAM composite floc. The optimal dosage of anionic PAM for HFO-anionic PAM floc system was approximately 1–10 ppm. The total removal yield of Mn-54, Co-60, Sb-125, Ru-106 radionuclides by the HFO-anionic PAM coagulation-flocculation system was higher in distilled water than in seawater and was more than 99%.

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## 1. Introduction

Coagulation-flocculation has been widely used for the purpose of wastewater treatment in many industry fields. The technique is usually applied for the removal of colloidal particles, soluble compounds, and fine solid suspensions in solution by colloid destabilization leading to the formation and growth of larger particles, often called flocs [1,2]. The coagulation-flocculation accompanying coprecipitation with hydrous ferric oxide (HFO) has often been used to treat radioactive waste solutions including actinide elements [3–7]. Typically HFO plays the role of carrier for removal of trace elements in solution by means of surface adsorption, inclusion and occlusion of the elements into the carrier phase [8–10]. In the Fukushima accident, TEPCO (Tokyo Electric Power Company) used a cleanup system to treat the wastewater generated in the early stage of the accident where seawater was used as cooling water. The system consisted of a few steps such as Cs adsorption using zeolite adsorbent columns, precipitation using Fe-

flocculation for removal of radionuclides such as Mn-54, Co-60, Sb-125, Ru-106 and RO (reverse osmosis) for desalination [11–14]. The Fe coprecipitation technique has also been used as a pre-treatment step even in the advanced liquid processing system (ALPS) operated by TEPCO, which has been operated since the first cleanup system [15].

Our previous work studied a coagulation-flocculation system using HFO and organic flocculant of poly acrylamide (PAM) to remove the radionuclides in waste seawater generated in the case of a severe accident of nuclear power plant like Fukushima accident case, wherein the coprecipitation mechanism of the nuclide ions by host phase of the HFO floc and its optimal condition for the operation in seawater were investigated [16].

In the coagulation-flocculation system, there are several important parameters which influence the treatability of pollutant source, such as selection of suitable coagulant, dosage rates, pH, velocity gradient of solution and mixing time, etc. Mixing conditions are known to be critical parameters for any coagulation-flocculation process as they influence floc kinetics such as flocs formation, breakage, regrowth, and even sedimentation for flocs-liquid separation. Floc formation behavior by mixing is dynamic in nature. However, up to now, there are little studies to

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systematically investigate the effects of mixing condition and coagulation–flocculation efficiency for removal of radionuclide ions from the wastewater by coprecipitation.

In this work, coagulation kinetics and the behavior of HFO floc formation during the neutralization of acidic ferric iron to induce the coprecipitation of several radionuclides were first looked into using a dynamic optical monitoring apparatus of photometric dispersion analyzer (PDA) [17–24]. They were studied in distilled water and seawater, because freshwater and seawater can be used in severe accident of nuclear power plant like Fukushima Daiichi case. Then, the optimal conditions for the coprecipitation such as dosage of ferric iron concentration, mixing speed, mixing time, etc. in both water systems were first looked into with the PDA by monitoring the ferric floc formation behavior. Finally, the coagulation–flocculation system using ferric hydroxide and organic flocculant PAM together was evaluated to find the effective condition to remove the target radionuclides such as Co-60, Mn-54, Sb-125, and Ru-106 present in wastewater generated in the severe accident of nuclear power plant like Fukushima Daiichi case. For that, radiometric analysis was used to evaluate removal efficiency from solution.

## 2. Experimental

The simulated wastewater used in this work was determined based on the Fukushima accident. The major radionuclides monitored by TEPCO (Tokyo Electric Power Company) in the cleanup facility were Cs-134, Cs-137, I-131, Mn-54, Co-60, Sb-125, Ru-106, etc. [12–16]. Radio-cesium was removed by Cs adsorption using zeolite adsorbent columns. The other nuclides were removed by Fe-flocculation. In the case of I-131, it was not detected in the wastewater after a few months because its half-life is very short, approximately 9 days. As mentioned above, seawater was directly used as cooling water in the early stage of the Fukushima accident. The cooling water circulated through the turbine and reactor buildings was demineralized by a reverse osmosis unit of the cleanup system installed after the accident. Therefore, it is necessary to evaluate the difference of removal behavior of the nuclides by the coagulation–flocculation using ferric ion in both solution matrixes of demineralized water and seawater. Accordingly, the simulated wastewater used in this work was prepared with seawater and distilled water including Co-60, Mn-54, Sb-125, and Ru-106 found in Fukushima case. The seawater used was taken from a southern coastal area of the Korean peninsula, and then filtered using a filter paper (Whatman Cat No 1002 150) without further treatment. The nuclides used were purchased from Eckert & Ziegler Analytics Co. The activities of the nuclides used in the solutions were approximately 20 Bq/ml similar to activity orders of the nuclides found in real wastewater of Fukushima accident [16,25]. The concentrations of the radioactive nuclides used in this work were analyzed by a MCA (Multi-channel  $\gamma$ -analyzer with a HP-Ge detector) (Cambera, GC2018), respectively. All the sample taken from the solution for analysis were filtered with 0.22  $\mu$ m syringe filter.

The coagulation–flocculation experiments using HFO and the organic flocculant of poly acrylamide (PAM), were carried out using a variable speed Jar tester (D-6JT Daehung science Co. Ltd. Korea) equipped with six flat paddle impellers. Each jar was filled with the simulated wastewater of 500 mL. To form HFO flocs,  $\text{FeCl}_3$  was added to the solution such that the ferric iron concentration was between 1 ppm and 100 ppm. The solution pH was adjusted to  $8 \pm 0.05$  with NaOH or  $\text{HNO}_3$  solutions using a pH meter (HI8424, HANNA) while the solution was stirred at 200 rpm. To the suspend HFO floc solution, the organic flocculant of anionic PAM (A-430P, OCI-SNF) was added followed by stirring to grow the HFO floc size in the coagulation–flocculation experiments. The PAM flocculant

stock solution of 1 g/L was prepared by dissolving the PAM powder in distilled water with mixing for one hour at room temperature. The prepared PAM solution was dispensed into the HFO solution according to necessary dosage. The kind of organic flocculant of anionic PAM and its dosage were chosen based on our previous study [16].

To monitor the floc behavior such as floc formation and its size change, etc. during the coagulation–flocculation experiments, some of the solution in the jar was taken through a clear plastic tube of 5 mm in inner diameter at a flow rate of 50 mL/min with a peristaltic pump and passed into the fiber optic probe of a photometric dispersion analyzer (PDA) (PDA-2000, Rank Brothers, UK). The solution was then re-circulated back to the jar tester. Such a method has been previously used by a number of other researchers and is largely accepted as standard practice [20–22]. The PDA measured the transmission of a narrow beam of a high intensity light (850 nm wavelength) for continuous monitoring of flowing suspensions of various concentrations and particle sizes. The transmitted light intensity consists of two components: a direct current (DC) corresponding to the average transmitted light and the root mean square (RMS) of the fluctuating transmitted intensity. The ratio (RMS/DC), defined according to equation (1), provides a sensitive measure of particle aggregation, which is strongly correlated with floc size and always increases as flocs grow larger. The ratio value is called the Flocculation Index (FI) and is used as an indicator of aggregate formation, increasing with aggregation and decreasing with disaggregation [20–24].

$$\text{Flocculation Index (FI)} = \frac{\text{RMS}}{\text{DC}} = \left(\frac{L}{A}\right)^{1/2} \left[\sum N_i C_i^2\right]^{1/2} \quad (1)$$

where L and A are the optical path length of the PDA, and the effective cross-sectional area of the light beam.  $N_i$  and  $C_i$  are the number concentration and scattering cross section of a particle of size class, respectively.

## 3. Results and discussion

### 3.1. Evaluation of dynamic behavior of HFO floc formation by using PDA

The coprecipitation method is used when direct precipitation of the target contaminant to level permissible for release is difficult to perform typically due to its low initial concentration in solution. The coprecipitation of metallic ion species occurs by their adsorption on to or incorporation in to a freshly precipitated solid phase of different metal ions as a carrier phase. The carrier phase is usually hydrous metal oxide (HMO: M = Fe, Al, etc) with an amorphous structure, which are prepared through the hydrolysis of those metal ions using their low solubilities. They show high coprecipitation efficiency and is not detrimental to environment [8–10,25–27]. Ferric iron exhibits a lower solubility across a wider pH range than aluminum ion, and ferric hydroxide flocs are reported to settle faster than aluminum hydroxide flocs so that it is widely used in treatment of radioactive wastewater in many cases [1,4–7]. Therefore the coprecipitation using HFO (hydrous ferric oxide) was chosen for the removal of radioactive ions in this work.

The hydrolysis mechanism of ferric iron in solution is very complicated, but it is known to be generally as follows [27]. When sufficient base is added into ferric iron solution, amorphous precipitate forms immediately through formation of low molecular weight hydrolysis products, called ferrihydrite, i.e.  $\text{FeOH}^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$ , and  $\text{Fe}(\text{OH})_3^{0+}$ , and their clusters [28,29]. The polymerization of the species produces a red-brown colloidal system of  $\text{Fe}_p(\text{OH})_q^{3p-q}$  and  $\text{Fe}_p\text{O}_r(\text{OH})_s^{3p-(2r+s)}$ , which gradually transforms to

amorphous precipitate or to crystalline  $\text{FeO}(\text{OH})$  or  $\alpha\text{-Fe}_2\text{O}_3$  [29]. When the contaminant metallic ions are removed by the HFO coprecipitation, its maximum removal is known to usually occur during complete formation of hydrous ferric oxide around pH 8 [9,28–31]. The metallic ions in the solution are adsorbed on or incorporated in to the hydrous ferric oxide phase. Adsorption on to the HFO surface is generally understood with the surface complexation model [26–31]. The HFO formation is crucial to the coprecipitation of target nuclide ions to be removed from the solution. Accordingly, it is very important to exactly understand the formation behavior of HFO floc in solution during its pH adjustment. This work first investigated and compared the behavior comparison of HFO floc formation in distilled water and seawater to enable variable optimization before carrying out the evaluation of removal efficiency of target nuclides from wastewater.

Fig. 1 shows the FI (floculation index) as a function of time at different dosages of ferric iron in distilled water (A) and seawater (B). In the experiment for Fig. 1, addition of  $\text{FeCl}_3$  according to necessary dosage and its pH-adjustment to 8 were carried out during 250 seconds at a fast mixing of 200 rpm, then the mixing speed was changed to a slow mixing speed of 50 rpm. A target pH of

8 was selected because the solubility of ferric iron is the lowest at this pH so that most of the iron in solution precipitates as HFO in solution [16]. In the case of distilled water, the FI reading was not observed before pH 8. However, in the cases except of 1 ppm ferric dosage, when the pH reached 8, the value rapidly increased with apparently showing formation of HFO floc particles in solution. It is generally known that nano-size ferrihydrite particles occurs even below less than pH 2 and they aggregate in colloidal-size [28,32,33]. As the solution pH increased over pH 3 during the pH-adjustment, ferric iron is rapidly hydrolyzed from the solution forming brown ferric hydroxide particles. This leads to the sudden nucleation of a large number of particles, which is typical of ferric hydrolysis precipitation process. However, such particles were not obviously detected by the PDA before pH 8 in the distilled water, because the mean size of any particles present in the solution were still below the detection limits of the PDA equipment ( $\sim 0.5 \mu\text{m}$ ), which is considered to be in colloidal size. As the pH reached 8 at high levels of supersaturation of ferric hydroxide in solution, the mean size rapidly increased as the HFO particle size was developed enough to be detected by PDA, corresponding to the growth and aggregation of colloidal-size flocs [33]. In seawater, the FI values were observed earlier than pH 8 during pH-adjustment. It is considered to be because Ca ion present in seawater and high ionic strength of seawater affect formation of hydrous ferric oxide floc so that the flocs are aggregated to bigger-size flocs in the solution [34,35]. (This will be discussed more in detail later) In both cases of distilled water and seawater, when the dosage of ferric iron was 1 ppm, the FI value was not clearly observed to increase until approximately 100 seconds after pH 8 had been reached. Such an induction time of floc formation is because the nano- or colloidal-size particles of HFO have low chance of collision or coalescence to grow to the bigger-size aggregates and flocs. The slow coagulation-flocculation process is unfavorable with respects to fast treatment of wastewater generated in the emergency case like Fukushima accident. In the dosage range between 5 and 10 ppm, floc formation occurred rapidly leading to a steady state at the end of the pH-adjustment. This means that the ferric iron dosage range showed quicker response of complete formation of HFO. On the other hand, in the case of 100 ppm dosage, the FI values peaked at the end of pH-adjustment before a considerable drop in FI values was observed followed by a steady state. This is considered to be because the high concentration of ferric iron allows for the rapid generation of large HFO flocs. However, these larger flocs are unstable and undergo floc breakage leading to a larger number of smaller-sized flocs recorded as a drop in the measured FI value. The FI values at steady state were similar without much difference in the range of ferric iron dosage between 1 ppm and 10 ppm in both cases of distilled water and seawater, but the steady state values at dosage of 100 ppm were much bigger, because high population of small flocs made more chances of the flocs growth. In both distilled water and seawater in the dosage range between 1 and 10 ppm, when the FI values reached steady states during fast mixing of 200 rpm, the FI values did not change considerably after changing to slow mixing of 50 rpm, with only a marginal increase being seen ( $\Delta\text{FI} < 0.01$ ). This result means that once HFO flocs are formed, their sizes are not influenced much by a subsequent change of mixing condition. Taking consideration of HFO formation time, finally formed floc volume (which will be secondary waste volume), and removal yield of target radionuclide (which will be discussed again later), ferric iron concentration of 10 ppm was chosen as an optimal dosage in the both distilled water and seawater, which was used in following experiments.

Mixing speed is known to be crucial for the growth of flocs through floc breakage and coalescence, which eventually result in effect of floc size distribution. The floc size continuously influences

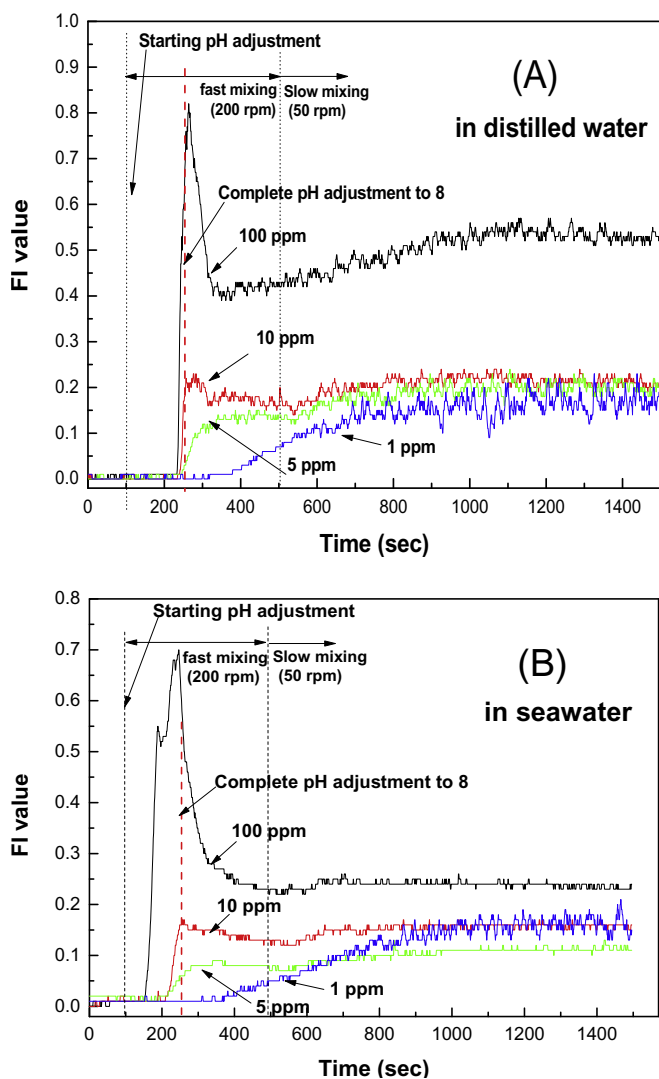


Fig. 1. FI graphs measured by PDA to monitor dynamic coagulation-flocculation behavior of HFO with as function of time at different dosages of  $\text{Fe}(+3)$  in distilled water (A) and seawater (B), respectively.

the total surface area of flocs in solution for metal nuclide ion to be adsorbed on, which leading to higher coprecipitation yield of target radionuclide ions. Further, floc size plays an important role in determining floc settling rates and filterability of floc suspensions. The results of Fig. 1 mean that the size of flocs already formed is not significantly affected by change in stirring speed. Therefore, it was evaluated how the change of mixing speed during the ferric iron dosing and pH-adjustment for the formation of HFO flocs affect the FI value. Fig. 2 shows the FI graphs measured by PDA to monitor dynamic coagulation-flocculation behavior of HFO as a function of time at different mixing rates between 50 rpm and 200 rpm at a ferric iron dosages of 10 ppm in distilled water (A) and seawater (B). Each chosen mixing rate was kept constant for 1500 seconds including ferric salt dosing and accompanied pH-adjustment. Then the mixing stopped while monitoring the change of FI values in the HFO sludge solution. When the solution in the jar without mixing was taken at a fixed position of the bottom of jar (in the middle of jar) through the tube to measure the FI value by PDA, the change of FI value indirectly represents the settlement speed of HFO particles suspended in solution. In distilled water, the steady state FI values during mixing generally decreased with a little irregularity with an increase of mixing speed, but their difference were small. However,

in the case of seawater, the steady state FI values greatly decreased with increasing mixing speed. They were almost the same at mixing rate beyond 100 rpm and were very similar to those in distilled water. In Fig. 2, a rapid increase of FI value before complete pH-adjustment to 8 was observed in seawater at mixing rates below 100 rpm. This is similar to the case of seawater in Fig. 1 for iron dose rate of more than 10 ppm. Such a big change in recorded FI values in seawater with a change of mixing speed, compared to that those in distilled water, is considered to be attributed to the effect of Ca ion and high ionic strength in seawater on the formation of hydrous ferric oxide during the pH-adjustment. Ca is known to enhance the precipitation of hydrous ferric oxide [34]. The metal chloride in solution affecting ionic strength is known to improve the floc settlement speed [35], which means that the floc size increases in solution. However, it is considered that such Ca-combined hydrous ferric oxide flocs in seawater were not strong enough to be broken into smaller size particle at the strong mixing condition over 100 rpm with showing lower FI values similar to those in distilled water. After stopping the mixing in Fig. 2, the FI values started to decrease. But they hardly dropped below a FI value of approximate 0.1 regardless of used mixing rates in both cases of distilled water and seawater. These results mean that the formed HFO flocs are hardly developed to stable and bigger flocs and that some fine HFO flocs must be suspended in solution even after bigger floc particles settle down. This phenomena is disadvantageous in views of fast wastewater treatment by coprecipitation using coagulation-flocculation in the emergency case. In that case, additional separation equipment such as centrifuge, media-filtration system, etc. are necessary for separation of particles-suspension sludge.

The fine floc particles suspended in solution can be grown in size by using an organic flocculant, which results in increased settling times of the final flocs for separation of flocs from the solution. This was confirmed in our previous work by dosing an organic flocculant of anionic poly acrylamide (PAM) in the HFO coprecipitation system [16]. All the HFO particles formed in distilled water and seawater at pH of lower than 8 is known to have positive zeta potentials, and the anionic PAM has negative zeta potential in the whole pH range [16]. So they can combine to form bigger HFO-anionic PAM flocs through electrostatic attraction. The anionic PAM plays role of not only making bigger flocs, but also enhancing the removal yield of the target radionuclide ions due to its sweep flocculation action to other species present in solution [16]. Fig. 3 shows the FI graphs measured by PDA to monitor dynamic coagulation-flocculation behavior of flocs as a function of time at different mixing rates for preparation of HFO-anionic PAM composite floc system in distilled water (A) and seawater (B) with dosages of 10 ppm ferric iron and 6 ppm anionic PAM, respectively. The ferric salt was first added to give the ferric iron dosage and the solution pH was adjusted to 8. Then anionic PAM, which was chosen based on our previous work [16], was dosed 250 seconds later after the pH-adjustment. Each chosen mixing rate was kept constant during all the steps for the preparation for HFO-PAM composite floc system. Finally the mixing stopped while monitoring the change of FI values to evaluate the settling speed of final HFO-PAM flocs. The FI behaviors before adding the PAM were similar to those in Fig. 2 in distilled water and seawater. However, when the PAM was added, the FI values generally increased and started to greatly fluctuate in both cases of distilled water and seawater, being different from those of only HFO system without using the PAM in Fig. 2. These results mean that the HFO-PAM flocs are bigger, more diverse in size, and more irregular than only the HFO flocs. The FI value of HFO-PAM flocs did not change much with the mixing rate. The FI values of HFO-PAM flocs in the seawater were higher than those in distilled water. The reason also is considered to be related

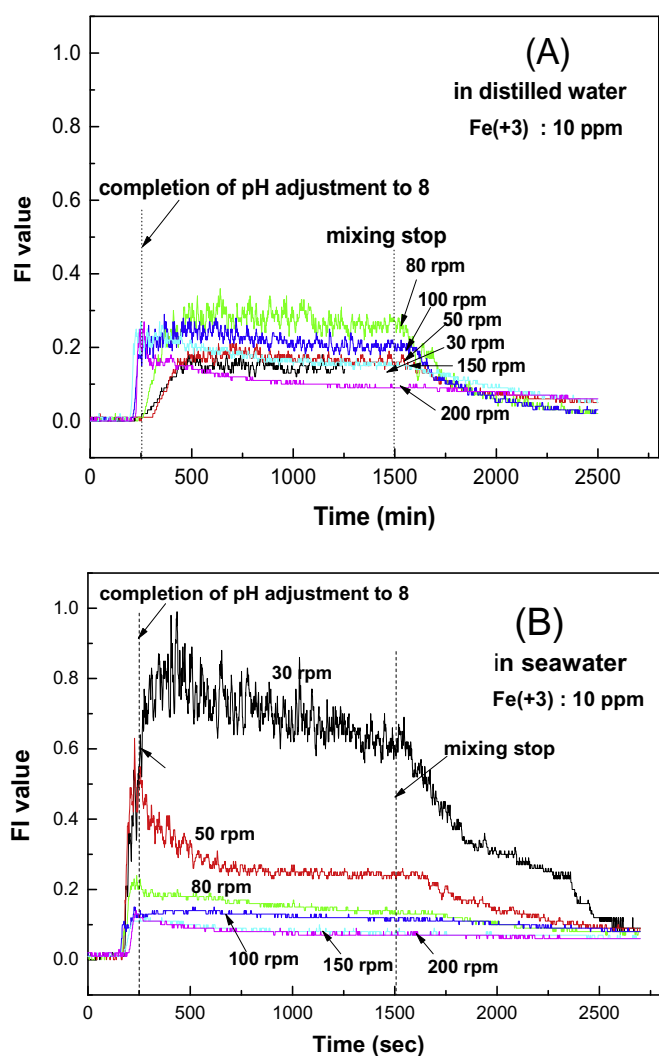


Fig. 2. FI graphs measured by PDA to monitor dynamic coagulation-flocculation behavior of HFO as a function of time at different mixing rates in distilled water (A) and seawater (B) with Fe(+3) dosage of 10 ppm.



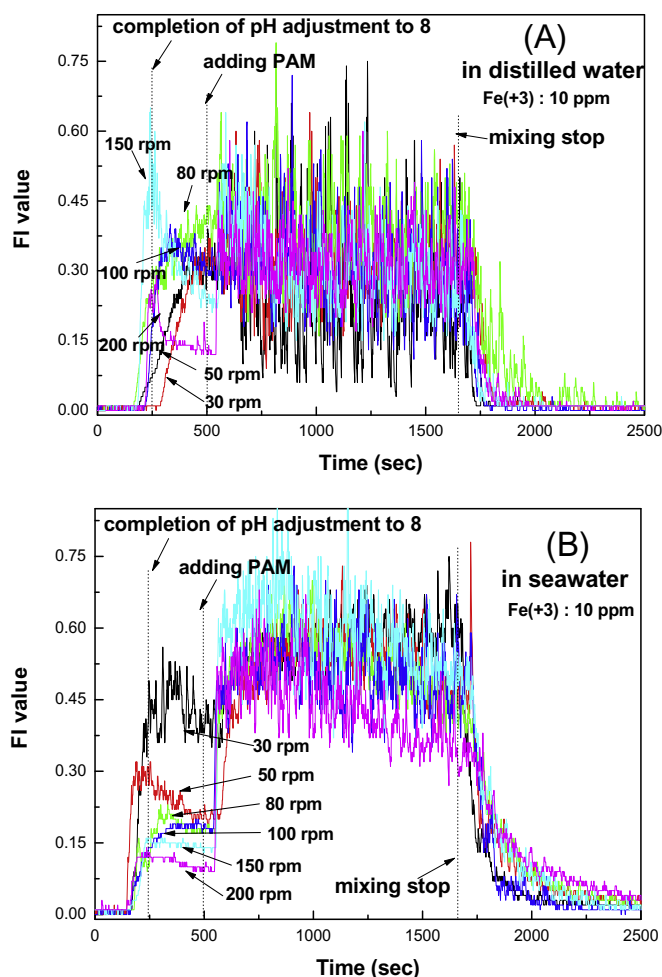


Fig. 3. FI graphs measured by PDA to monitor dynamic coagulation-flocculation behavior of HFO-anionic PAM composite flocs as a function of time at different mixing rates in distilled water (A) and seawater (B) with dosages of 10 ppm Fe(+3) and 6 ppm anionic PAM, respectively.

with the effect of Ca in seawater on the hydrous ferric oxide formation before the pH-adjustment to 8. As mentioned above, the formed hydrolysis particles is unstable, but they are considered to become more stable and rigid even at stronger mixing condition when they are combined with anionic PAM. Accordingly, the FI value due to hydrolysis products of other metal ions in seawater combined with PAM as well as HFO-PAM is higher than that only due to HFO-PAM flocs in distilled water. However, after the mixing stopped, the FI values decreased to almost zero with time, different from the cases using only HFO in Fig. 2 where the FI values hardly decreased even at the end of experiments. As mentioned above, the change rate of FI value after stopping mixing represents the settling speed of flocs in solution. The settlement rate of floc is complicatedly influenced by many floc properties such as floc density, flow size, floc shape, floc distribution, viscosity of solution, floc zeta potential, interfacial tension between floc and solution etc. The FI value in the distilled water containing HFO-PAM systems rapidly dropped to almost zero, but that in seawater decreased relatively slow. The results means that the HFO-PAM flocs are denser and more compact than only HFO flocs. This result means that using the organic flocculant PAM is beneficial from the view point of rapid treatment of radioactive wastewater by coprecipitation due to decreased settling times. Fig. 4 shows the photos of HFO (A) and HFO-PAM (B) flocs formed in distilled water, and HFO (C) and

HFO-PAM (D) flocs formed in seawater, which were taken approximately 1 hour later after the mixing stopped. The HFO flocs looked loose and gelatinous. On the other hand, the HFO-PAM flocs looked bigger and more compact.

Fig. 5 shows the FI graphs of HFO-PAM floc system prepared in the same way in used in Fig. 3. However, the mixing rate was changed between 200 rpm and 30 rpm every 1000 seconds to evaluate the change of floc size. Then finally the mixing stopped. The FI graphs of only HFO floc behavior, which were carried out in the same way, were displayed together for comparison. The FI value of seawater were a little bigger than that of distilled water because the bigger inorganic flocs made by the ferric iron and other metals ions included in the seawater were combined with the PAM to form the bigger HFO-PAM flocs. The FI values in distilled water and seawater were observed to slowly increase or decrease with decrease or increase in mixing rate, but the change were less than 0.1. The bigger flocs or the smaller flocs are known to be formed at slow mixing or fast mixing, respectively [17–21]. In the case of seawater, the FI value showed a peak on adding the PAM, but that was not observed in distilled water. The peak is considered to be because the more inorganic flocs of HFO and other metal ion hydrolysis product instantly caused formation of big HFO-PAM flocs and they were broken into smaller size by the mixing. After the mixing stopped, the FI values got down to almost zero with time, different from the cases using only HFO, which are similar to results in Fig. 3. The decrease rates of FI values at the beginning after mixing stop in Fig. 5 were  $-0.064 \text{ hr}^{-1}$  in distilled water and  $-0.028 \text{ hr}^{-1}$  in seawater. Those of HFO-PAM flocs were  $-29.5 \text{ hr}^{-1}$  and  $-1.21 \text{ hr}^{-1}$  in distilled water and seawater, respectively. Accordingly, the settling speeds of HFO-PAM flocs in distilled water and seawater were approximately 460 times and 43 times faster than those of HFO flocs.

### 3.2. Evaluation of removal yield of radionuclide ion by coprecipitation using HFO-PAM coagulation-flocculation system

From Figs. 1–5 showing the HFO or HFO-PAM composite floc behaviors monitored by the PDA, following results could be obtained, which were used to determine the effective condition for removal of the radionuclide ions by coprecipitation using HFO material. A dosage of at least 10 ppm ferric ion is necessary for fast formation of HFO without induction time. Fast mixing speed over 100 rpm is preferable for production of fine HFO flocs, which resulting in bigger adsorption area for coprecipitation of target nuclide ions at a constant amount of HFO. Using organic flocculant of anionic PAM after formation of HFO flocs is necessary for fast settlement of HFO particles. To ensure that the conditions found from the standpoint of HFO floc formation behavior by using PDA are appropriate for actual removal of radionuclide ions in solution, a set of experiments to evaluate removal yield of real radionuclides ions of Co-60, Mn-54, Sb-125, and Ru-106 in distilled water and seawater were carried out. The total removal yield of the nuclides, which were defined according to equation (2), were measured in each experiments.

Total removal yield of radioactivity (%)

$$= \frac{\sum a_{i, \text{initial}} - \sum a_{i, \text{residual}}}{\sum a_{i, \text{initial}}} \times 100 \quad (2)$$

where  $a_{i, \text{initial}}$  and  $a_{i, \text{residual}}$  are initial and remaining radioactivities of each nuclide before and after treatment by the coprecipitation, respectively.

Fig. 6 shows the change of total removal yield of the radionuclides by using HFO-PAM coagulation-flocculation system as a

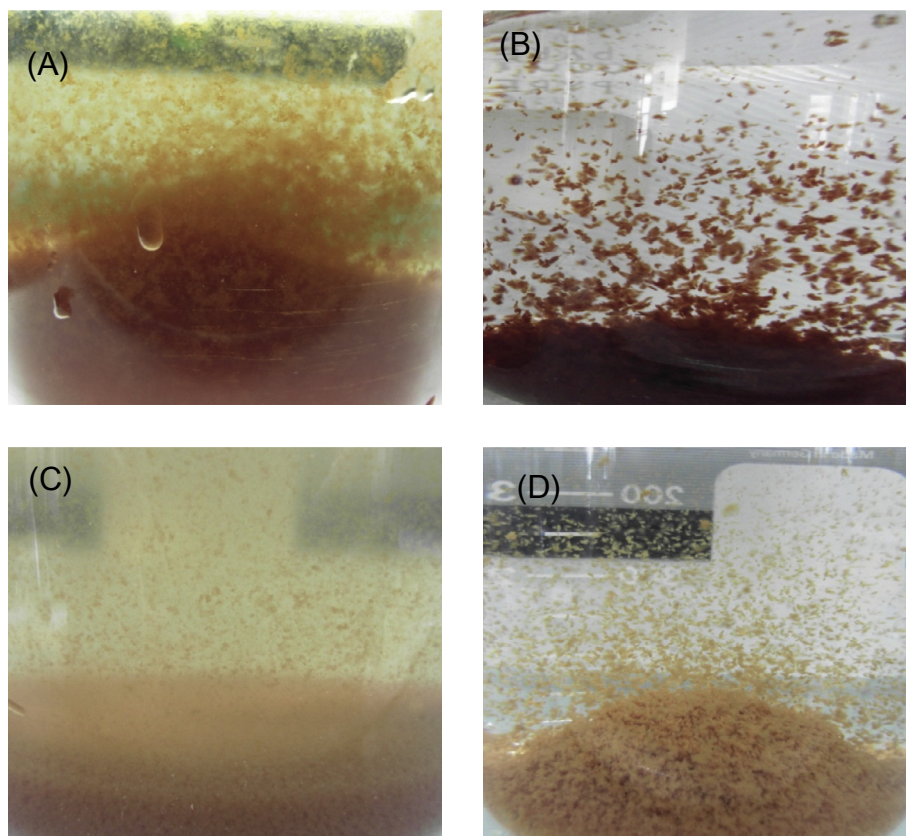


Fig. 4. Photos of flocs of HFO (A) and HFO-anionic PAM (B) in distilled water, and HFO (C) and HFO-anionic PAM (D) in seawater.

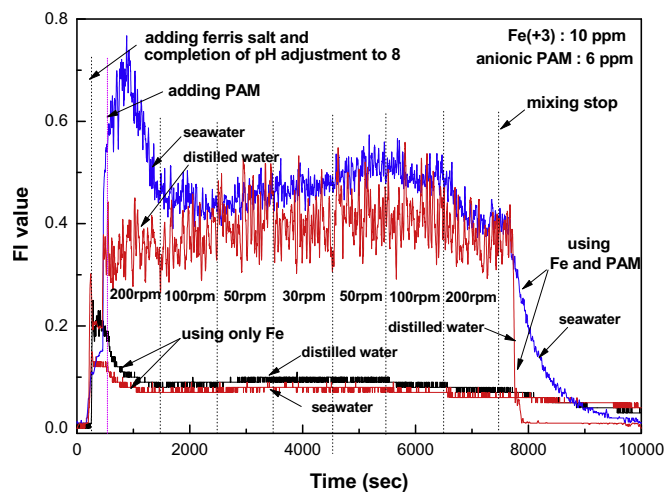


Fig. 5. FI graphs measured by PDA to monitor dynamic coagulation-flocculation behavior of HFO-anionic PAM composite flocs as a function of time with different mixing rates in distilled water and seawater with dosages of 10 ppm Fe(+3) and 6 ppm anionic PAM, respectively.

function of ferric iron dosage at a fixed anionic PAM dosage of 6 ppm in distilled water and seawater, respectively. The mixing speed was fixed at 200 rpm during dosing ferric salt and PAM and the pH-adjustment, then changed to 100 rpm for 10 minutes. The total removal yields of radionuclide ion in distilled water and seawater increased with ferric iron dosage in the range between 0.01 ppm and 10 ppm. Further dosage appears to have no additional benefit. The total removal yields of radioactivity in distilled water

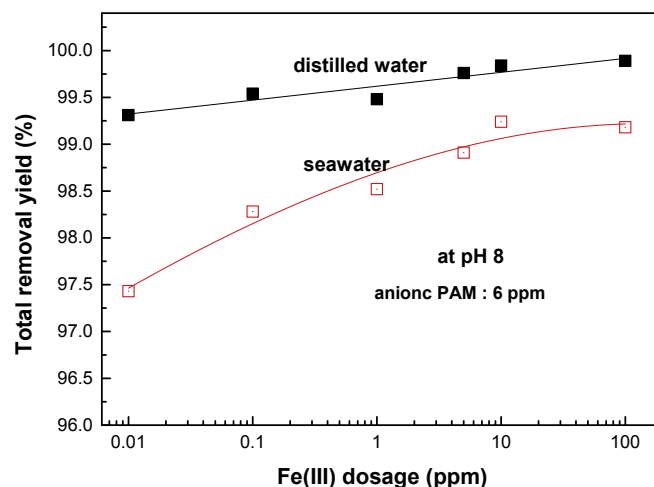


Fig. 6. Change of total removal yield of radioactivity as a function of Fe(+3) dosage at anionic PAM dosage of 6 ppm and at pH 8 in distilled water and seawater, respectively.

were higher than those in seawater. The maximum yields in distilled water and seawater were 99.85% and 99.3% at 10 ppm ferric iron dosage. The reason of higher total removal yield in distilled water is considered to be because other metal ions in seawater compete with target radionuclide ions to adsorption site of HFO for coprecipitation and because some of ferric ions in seawater is consumed to combine several anions in seawater to hydrolysis precipitation.

Fig. 7 shows the change of total removal yield of radioactivity as a function of anionic PAM dosage in the HFO-anionic PAM system at

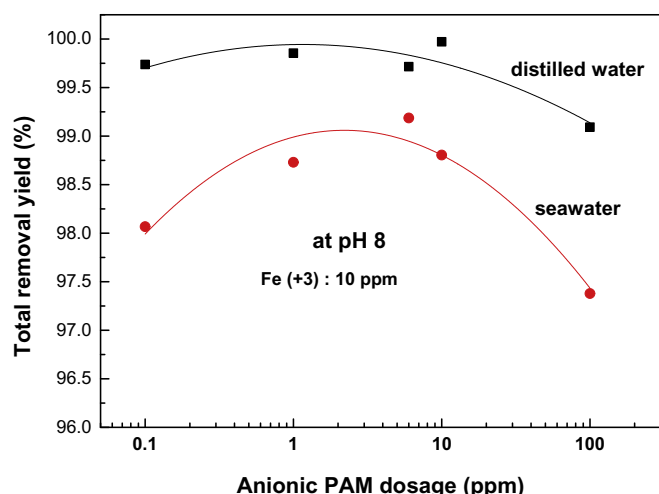


Fig. 7. Change of total removal yield of radioactivity as a function of anionic PAM dosage at Fe(+3) dosage of 10 ppm and at pH 8 in distilled water and seawater, respectively.

a fixed ferric iron dosage of 10 ppm and at pH 8 in distilled water and seawater, respectively. The total removal yield of radioactivity showed maxima in the PAM dosage range between 1 ppm and 10 ppm in both distilled water and seawater, as found in our previous work [16]. The reason can be explained as follows. The anionic PAM can bind with the cation of radionuclide with opposite charge [16]. The metal ion-bound PAM also combines with the HFO flocs to make HFO-PAM flocs. Such a combination of PAM and nuclide ion leads to increase in total removal yield of radioactivity from the solution, compared with the system using only HFO. However, the anionic PAM can combine with cation ferric iron species so that amount of HFO causing the coprecipitation decreases, which results in the decrease of total removal yield of radioactivity. Accordingly, optimal dosage of anionic PAM must exist in the HFO-PAM coagulation-flocculation system.

Fig. 8 shows the change of total removal yield of radioactivity as function of mixing rate at dosages of 10 ppm Fe(+3) and 6 ppm anionic PAM in distilled water and seawater, respectively. There were no significant change of total removal yield of radioactivity in

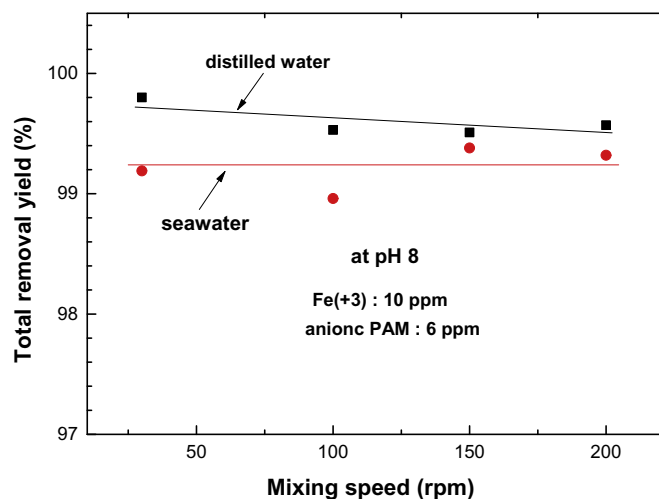


Fig. 8. Change of total removal yield of radioactivity as a function of mixing rate at dosages of 10 ppm Fe(+3) and 6 ppm anionic PAM in distilled water and seawater, respectively.

both cases of distilled water and seawater. As shown in Figs. 3 and 5, the HFO-PAM floc size was not affected much by its preparation mixing rate. Accordingly, the change of mixing rate did not give any apparent effect on the total removal yield of radionuclides from the distilled water and seawater.

#### 4. Conclusions

The dynamic behavior of flocs in the HFO-anionic PAM coagulation-flocculation system for removal of radionuclide ion from wastewater was effectively evaluated by using a photometric dispersion analyzer (PDA). A ferric iron dosage of 10 ppm for the formation of HFO causing coprecipitation of the radionuclides was suitable in terms of fast formation of HFO flocs without induction time, and maximum total removal yield of radioactivity from the wastewater. The HFO flocs were suspended in solution for long time, but they could be quickly and effectively settled down by changing them to HFO-PAM composite floc form. The HFO floc size was affected by mixing rate during its formation, but once HFO flocs bound with anionic PAM, the size of HFO-PAM composite floc was not much affected by mixing rate. The optimal dosage of anionic PAM for HFO-PAM floc system was approximately 1–10 ppm. The total removal yield of Mn-54, Co-60, Sb-125, Ru-106 radionuclides by the HFO-anionic PAM coagulation-flocculation was higher in distilled water than in seawater and reached 99.8%.

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