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Concentration and characterization of organic colloids in deep granitic groundwater using nanofiltration membranes for evaluating radionuclide transport

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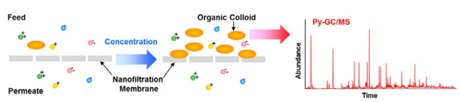
HIGHLIGHTS

- Nanofiltration membranes were applied to concentration of organic colloids.
- Organic colloids in groundwater were successfully concentrated.
- Structures of organic colloids in deep granitic groundwater were revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

Understanding the properties of organic colloids is important for geological disposal of high-level radioactive waste in terms of radionuclide transport. To analyze organic colloids in deep groundwater, concentration techniques using adsorption resins and reverse osmosis (RO) membranes have been widely applied, because their concentrations in deep groundwater are very low and detection of the organic colloids in raw groundwater is difficult. However, these techniques have respective disadvantages such as chemical disturbance and membrane fouling caused by cations. To overcome their disadvantages, we propose a new concentration method using nanofiltration (NF) membranes to concentrate organic colloids rapidly without chemical disturbance and to selectively remove monovalent and divalent ions, which may cause inorganic and/or organic fouling. Concentration performance of the NF and RO membranes for aqueous solutions for humic acids was evaluated using a laboratory-scale membrane test unit. The time course of permeate flux and concentration of humic acids were measured. These membranes were applied to the concentration of actual groundwater obtained at a depth of 300 m at the Mizunami Underground Research Laboratory in Japan. The permeate flux and concentration of major ions and organic colloids were measured. The organic colloids concentrated by the NF membrane were successfully analyzed using pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS) owing to their high concentrations and low concentrations of salts. The NF membrane was useful for the concentration of organic colloids and rare earth elements (REEs) in deep groundwater, and the findings of the organic colloid structures revealed by Py-GC/MS provided valuable information for evaluating the effect of organic colloids on radionuclide transport.

1. Introduction

Colloids, such as particles and macromolecules ranging from 1 to 1000 nm in size, are widespread in various natural water sources [1]. Groundwater contains inorganic colloids, such as fragments of rock and clay minerals from dissolution and precipitation of the

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Table 1
Hydrochemistry of groundwater sampled from 09MI20 borehole section 1 at a depth of 300 m on December 25, 2014.

pH	EC [mS/m]	Na^+ [mg/L]	K^+ [mg/L]	Ca^{2+} [mg/L]	Cl^- [mg/L]	F^- [mg/L]	$SO_4{}^{2-}$ [mg/L]	Mg [mg/L]	Al [mg/L]	Fe [mg/L]	Mn [mg/L]	Dissolved inorganic carbon [mg/L]	Dissolved organic carbon [mg/L]	M-alkalinity [meq/L]
8.5	43	76	0.4	9.0	64	9.8	13	0.11	<0.01	<0.005	<0.003	13	<0.5	1.19

rock, and organic colloids such as humic substances [2–5]. Additionally, it has been clearly shown that the migration velocity of radionuclides can either increase or decrease in the presence of colloids [6–11]. Therefore, investigation of the physicochemical properties (e.g., concentration, size, shape, and chemical composition) of colloids is of great importance for geological disposal of high-level radioactive waste (HLW). In particular, the detailed structures of organic colloids, which have more complex structures than inorganic colloids, are not yet well understood.

Organic colloids, most of which are humic substances, are metabolized through natural or biological degradation, and involve mainly aromatic carbon and carboxyl groups [12–15]. Organic colloids have negative charges in their internal structures and adsorb radionuclides in groundwater. Although field investigations have been conducted to understand the effect of organic colloids on radionuclide transport [16,17], precise analysis of organic colloids in groundwater is difficult owing to their low concentrations [18,19]. To solve this issue, groundwater concentration techniques using adsorption resins [20,21] and reverse osmosis (RO) membranes [22,23] have been attempted. Although the method using adsorption resins concentrates samples into disproportionately enriched organic colloids, the samples are exposed to severe chemical conditions, resulting in chemical or physicochemical changes of the organic colloids. The method using RO membranes can concentrate organic colloids highly efficiently and rapidly without strong chemical exposure. However, this method requires sample pretreatment using a cation exchange resin to remove cations that cause precipitation onto the membrane surface [22,23]. This pretreatment using a cation exchange resin affects the composition of rare earth elements (REEs) in the sample, which are regarded as analogues of trivalent actinides [24] and are important for HLW analysis.

In this study, we propose a novel concentration method using nanofiltration (NF) membranes, which can be operated rapidly without chemical disturbance, and does not require additional sample treatment such as cation exchange. NF membranes are generally looser than RO membranes [25]. Typically, monovalent ion rejection of NF membranes is not very high, while multivalent ions can be rejected at high levels. First, an aqueous solution of commercial humic acid was concentrated as a model of organic colloids using two types of NF membranes and an RO membrane. The recovery yield of humic acid was measured using a UV–vis spectrophotometer. Then, we sampled groundwater in granite at a depth of 300 m and concentrated the groundwater using the membranes. To confirm the applicability of this method for groundwater, concentrations of cations and anions in both the concentrate and permeate water were measured by ion chromatography (IC). To characterize the chemical structures of the concentrated organic colloids, the concentrate water was analyzed by pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS). Py-GC/MS is commonly used to obtain detailed structural information on the components of natural organic matter, although salt removal is required [26]. Moreover, REE concentrations in the concentrated groundwater enriched by the two types of NF membranes and the RO membrane were measured by inductively coupled plasma mass spectrometry (ICP-MS).

2. Materials and methods

2.1. Materials for performance evaluation of NF and RO membranes

Two types of commercial NF membranes (NTR7410 and NTR7450; Nitto Denko, Osaka, Japan) composed of sulfonated polyethersulfone and a commercial RO membrane (ES20; Nitto Denko, Osaka, Japan) composed of aromatic polyamide were used. All solutions used in this study were prepared using ultrapure water and analytical-grade chemicals. Humic acid derived from peat (H16752; Sigma–Aldrich, St. Louis, MO, USA) was used after the following pretreatment process. The humic acid was dissolved in a NaOH solution (pH 10) and the pH was adjusted to 1 with a HCl solution to remove fulvic acid and heavy metals. The sample was centrifuged to remove ash, and then the residue was freeze-dried. The elemental composition of this humic acid has been previously reported: 55.5% C, 38.9% O, 4.6% H, and 0.6% N [27]. This humic acid has been used extensively as a model organic colloid by many researchers [28–31] owing to its easy availability and well-characterized properties.

2.2. Groundwater sampling

Groundwater was collected from the 09MI20 borehole in the −300 m access/research gallery of Mizunami Underground Research Laboratory (MIU) on December 25, 2014. The Miocene sedimentary rocks (Mizunami Group) unconformably overlie the Cretaceous granitic rocks (Toki granite) at a depth of ~160 m at the MIU site. The groundwater in the granite was weakly alkaline Na–(Ca)–Cl-type, and the salinity increased with depth as a result of mixing of deeply lying saline water with recharged meteoric water [32]. The 09MI20 borehole is a horizontal borehole with a length of 102 m and was designed for investigations of hydrochemical changes related to facility construction. The borehole is divided into six sections by impermeable packers and the sections are numbered from 1 to 6 according to the distance from the base

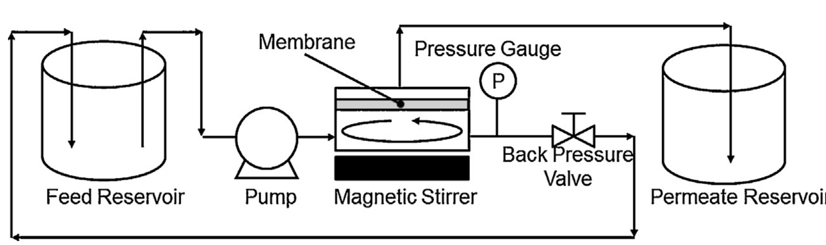

Fig. 1. Schematic diagram of the cross-flow concentration apparatus.