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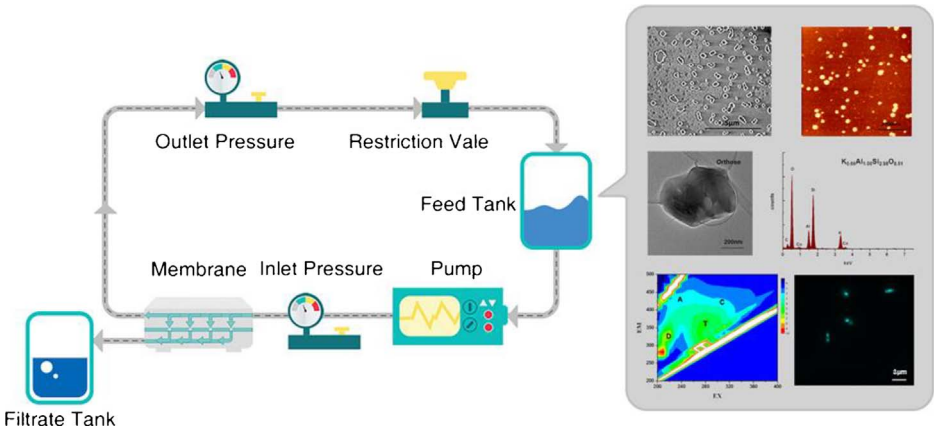
Research Paper

Concentration and characterization of groundwater colloids from the northwest edge of Sichuan basin, China

Kaifeng Wang[a], Yifan Zhao[b], Zhuanwei Yang[a], Zhimao Lin[a], Zhaoyi Tan[c], Liang Du[c], Chunli Liu[a,*]

[a] Beijing National Laboratory for Molecular Sciences, Fundamental Science Laboratory on Radiochemistry & Radiation Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China
[b] Biodynamic Optical Imaging Center (BIOPIC), School of Life Science, Peking University, Beijing, 100871, China
[c] Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, 621900, China

GRAPHICAL ABSTRACT



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ABSTRACT

Natural groundwater colloids are significantly important since they are closely related with toxic substances migration in subsurface systems. In this paper, a cross-flow ultrafiltration (CFUF) system equipped with 100 kDa cartridges was developed to enrich groundwater colloids and multiple analytical techniques were used to characterize colloid properties. Analytical techniques included scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), transmission electron microscopy (TEM) with energy dispersive X-ray spectra (EDS), excitation-emission matrix (EEM) fluorescence spectra, inverted fluorescence microscopy (IFM), and 16S rDNA sequencing. SEM and AFM results indicated that the mean diameter and height of colloids were 322 ± 90 nm and 10.4 ± 2.1 nm respectively and two different morphologies of colloids existed which seem to be hollow and platy structure. XRD analysis showed that the mineralogical composition of inorganic colloids consisted of albite ($NaAlSi_3O_8$), orthoclase ($KAlSi_3O_8$), clinochlore ($(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$, lepidocrocite ($Fe^{III}O(OH)$), muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$), calcite ($CaCO_3$) and quartz ($SiO_2$), most of which was confirmed by TEM-EDS information. Different types of dissolved organic matter (DOM) were characterized by EEM fluorescence spectra, while a larger fraction of 'protein-like' fluorescent DOM was found. Bacteria was

* Corresponding author.
E-mail address: liucl@pku.edu.cn (C. Liu).

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observed under 488 nm laser excitation by IFM and 16S rDNA sequencing revealed that Thermomonas was the most likely genus the bacteria may belong to.

1. Introduction

Groundwater colloids, namely, suspended particulate matter, include inorganic colloids (particles of rock and clay minerals), organic colloids (humic and non-humic substances), inorganic colloids coated with organic material, and microorganisms (bacteria and fungi) [1–3]. They exist naturally in groundwater and interact with non-soluble contaminants through sorption in saturated porous media [4,5]. Therefore, understanding the physicochemical and microbiological properties of groundwater colloids is of great importance for exploring the fate, transport and toxicity of non-soluble contaminants [6,7].

In consideration of the complexity and diversity of natural groundwater, multi-method approach has been used to characterize groundwater colloid properties. In general, particle size distributions and trace elements associated with colloids in natural water are analyzed by flow field flow fractionation (FlFFF) combined with inductively coupled plasma mass spectrometry (ICP-MS) [8–10]. Chemical compositions, morphologies and agglomeration of natural colloids are explored by AFM, TEM and SEM [11–15]. Detailed information of DOM is studied by the UV–vis spectrometer, fourier transform infrared spectroscopy (FTIR), the pyrolysis gas chromatography coupled with mass spectrometry (Py-GS/MS) and EEM fluorescence spectra [16–19].

During sampling, a variety of methods have been employed for the isolation of aquatic colloids. Conventional ultracentrifugation method combining with membrane can enrich aquatic colloids on membrane, but it may alter the colloid structure through membrane interaction and normally lead to damage microorganisms by high centrifugation speed [20]. The availability of FlFFF coupled with a series of detectors (e.g. UV spectrometer, laser light scattering and ICP-MS) has presented as a powerful analytical technique for separation and characterization of aquatic colloids. Unfortunately, the analyst must be aware of certain limitations and optimize the experimental conditions due to relatively low concentration of aquatic colloids [21]. CFUF system equipped with different molecular weight cut-offs is to develop as a promising technique for separation and concentration of groundwater colloids with relatively low processing shear force and without chemical disturbance, which can feed large volumes of water sample in a relatively short time [22,23].

The aim of this study is to develop CFUF system with 100 kDa cartridges for concentrating groundwater colloids and couple multiple analytical techniques to characterize the properties of colloids. We intend (1) to measure particle size distributions and microscopic morphologies of colloids by SEM and AFM. (2) to determine mineralogy of inorganic colloids by XRD and TEM-EDS. (3) to investigate DOM for optical characterization by EEM fluorescence spectra. (4) to identify which specie the bacteria strain belongs to by blasting the sequencing result in the NCBI data base.

2. Experimental section

2.1. Study sites and sampling

A 1000 L of groundwater sample was obtained from a borehole at a depth of 30 m on May 1, 2016 from an area in the northwest edge of Sichuan basin, China. Hydrochemistry of the groundwater sample was summarized in Table S1. The groundwater sample was filtered through a 1 μm polyethersulfone membrane (Jinlong, China) as soon as it was obtained to remove large particulate materials. The filtrate was further concentrated and desalted using deionized water (18.2 MΩ cm) by CFUF system equipped with 100 kDa cartridges (Centramate™, Pall) until the electrical conductivity of percolate was less than 5 us/cm. The retentate (500 mL) was stored in a polypropylene bottle rinsed with dilute nitric acid (Aladdin) and deionized water (18.2 MΩ cm), and then sealed at 4 °C prior to be used. Fig. 1 showed the procedure used for concentration and characterization of groundwater colloids.

In strain culture experiment, 1 mL sample was inoculated into 1 mL fresh LB (Sangon Biotech) and incubated at 37 °C with shaking for 12 h. The obtained bacteria was collected by centrifugation (10,000*g*, 10 min, room temperature). Pellet was resuspended with 2 mL of 0.85% NaCl and incubated for 15 min. About 3 μL SYTO 9 (ThermoFisher) was added into 1 mL sample and the suspension was mixed thoroughly and incubated for another 15 min. 0.02% poly-L-lysine (0.1%) (Sigma P8920) was added into channel on the coverslip and incubated for 3 – 5 min and then 20 uL sample was injected into the channel and bacteria were attached onto the coverslip.

2.2. Cross-flow ultrafiltration (CFUF) system

CFUF system equipped with different molecular weight cut-offs is often applied for purification, concentration or separation of nucleic acids, proteins, bacteria, viruses or dissolved organic matter

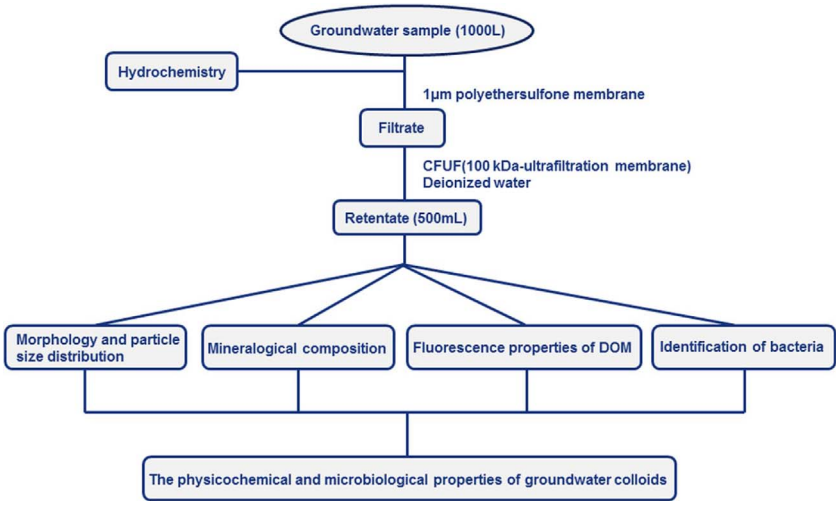

Fig. 1. Procedure used for concentration and characterization of groundwater colloids.