Removal of iron from aqueous solution using phytolith-aided aggregation

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A R T I C L E   I N F O

A B S T R A C T

Phytoliths are common biogenic silica materials which can be derived from heat-treatment of Si-rich plant residues. However, there have been few studies identifying its environmental applications. This work, based on the batch experiments with quantification of surface charge and determination of colloidal properties, is an attempt to evaluate the ability of phytolith-based material (PBM) for removing Fe from aqueous solution. Oxidation and aggregation of a synthetic Fe-rich solution were examined under the presence of a PBM sample (obtained from fern *Dicranopteris linearis*) as functions of pH and ionic strength. Obtained results showed that through electrostatic interaction, the PBM can affect oxidation and aggregation of newly-formed Fe oxides at different extents depending on pH change. The fastest aggregation of the newly-formed Fe oxides was found at the pH range from 4 to 6 and in the presence of phytolith. As the PBM can make the newly-formed Fe oxides less dispersive and less transportable in aqueous solution, it suggests that practices for treatment of Fe-rich drainage or remediation of Fe-contaminated groundwater by supporting aggregation need to consider this effect.

1. Introduction

In plants, silicon (Si) assimilated from soil is transported to different parts and precipitated in inter- and intracellular spaces throughout their leaf and stem to form a silicaceous structure, so-called phytolith [1]. Phytolith content in plants may differ from species to species, but it can be in excess of 5% d.w. in rice or ferns as reported by Marschner [2] and Fraysse, Pokrovsky, Schott and Meunier [3]. In some parts of the world, plant residues from rice or ferns are still a common fuel, and after uses, their burnt products containing ash phytolith might be returned to soil or directly discharged to the environment. Recently, seeking possible applications for phytolith-based materials has been increasingly encouraged. The PBMs were tested as amendments for soils and crops [4–8], biomedical products [9] or chemical catalysts [10]. Yet, little is known about their environmental applications. Having alkaline reaction and highly-variable charged surface [11], PBMs show their potential as suitable materials for water treatment.

Since phytoliths are formed by precipitation of Si, they mainly contain SiO_2 and H_2O [1]. Other entrapped substances e.g. nutrients, organic matter can also be found within phytolith structure [4,12–14]. Polymerization of SiO_2 molecules is an initial step to form phytolith and results in surface bondings i.e. $Si-O-Si$ and $Si-OH$ [15,16]. Heat treatment or burning is a common method to separate phytolith [17],

and it can affect phytolith surface by transforming $Si-OH$ bonds to $Si-O-Si$ bonds via a dehydroxylation process [18]. It is likely that transformation of the phytolith surface functional groups results in changes in solubility and surface charge [11]. Charges on the surface of phytolith, established by protonation or deprotonation of the $Si-OH$ groups, are pH-dependent. The point of zero charge (*pzc*) of phytoliths (derived from rice straw) was found at relatively low pH values i.e. pH ~ 3 [11]. Below the *pzc*, phytoliths expose a positively-charged surface because it is protonated. On the other hand, beyond the *pzc*, phytoliths are negatively charged as a result of deprotonation of the $Si-OH$ groups. By bearing surface charge (positive or negative), phytoliths might serve as a "platform" for electrostatic adsorption, and their applicability for removal of soluble ions or colloid particles from aqueous solution can be expected.

Removal of soluble Fe in aqueous solution via enhancing oxidation and aggregation reactions can be obtained by manipulating solution chemistry or electrophoretic properties [19,20]. It is hypothesized that phytoliths can act to remove soluble Fe from aqueous solution in different manners: *i)* favoring adsorption of Fe^{2+} ion onto their negative surface (at pH > pH_{pzc}), *ii)* facilitating oxidation and chemical precipitation by raising pH since phytoliths have alkalinity [4], *iii)* facilitating aggregation of Fe oxides by serving as opposite charged surface (possible for a given pH range in between the *pzc* of Fe oxide and the *pzc*

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of phytolith) to associate with Fe oxide and form 'pseudo-coarser particulates'. A major premise of our study is that, by altering the colloidal properties of Fe oxides, phytolith can affect aggregation rate of Fe oxides in aqueous solution. We prepared phytolith-based phytoliths (PBMs) from *Dicranopteris linearis* (*D. linearis*), a common fern in humid regions of the world [21,22]. Samples obtained from dry ashing were used to identify capability of the PBM as an enhancer for oxidation and aggregation of Fe oxides. Aggregation experiments were examined using test tube method [23], while surface charge was quantified using a particle charge detector. Since fern *D. linearis* is a common fuel in many rural regions all over the world, fern-obtained ashes can be available for other uses. The findings from this study regarding the impact of the PBM on aggregation stability of Fe oxides can help to develop suitable practices for a variety of water processing needs, including treatment of Fe-rich acidic mine drainages or remediation of Fe-contaminated groundwater.

2. Materials and methods

2.1. Sample production

Fern *D. linearis* sample was collected from a mountainous region (21°30′ N lat, 104°47′ E long) in the northwest Vietnam by harvesting all biomass above ground from three separate plots (1 x 1 m), and following mixing of the harvested materials. The sample was air-dried, milled and passed through a 1.0-mm sieve. Phytolith of the fern *D. linearis* sample was identified using X-ray tomography (performed by the TOMCAT at the Synchrotron Light Source of the Paul-Scherrer-Institute in Villigen, Switzerland). The Si-rich phase (phytolith) is represented by gray levels in the range of ca. 210–255, whereas intermediate gray levels (50–200) are characteristic for the organic matter and are represented in green colors. Fig. 1a and 1b correspondingly are tomographic images of phytolith phase embedded in organic matter and phytolith phase alone.

It was found from preliminary heat-treatments that a large amount of organic matter was still remained in the sample at the temperatures below 800 °C. Therefore, the plant sample was ashed at 900 °C in a furnace for 2 h. The derived PBM was ball-milled, passed through a 100-µm sieve and washed three times with DI water and then dried at 60 °C in an oven for 24 h. The PBM was used for determination of pH (measured for the suspension of 50 mg of PBM sample and 50 mL of DI water) by using a pH meter (Toledo, FE20, Switzerland). Content of organic carbon and other elements was analyzed with an Elemental Analyser (Perkin Elmer PE2400CHNS) and XRF (Rigaku, Nex CG). Chemical composition of the original plant sample and its derived PBM was shown in Table 1.

2.2. Solution preparation

Fe-rich solution was prepared from 4.9645 g of $FeSO_4.7H_2O$ dissolved in 1000 mL of 0.01 N HCl solution. The obtained solution has a concentration of $1\ mg\ mL^{-1}$ and pH ~ 2. Each 3 mL of Fe solution ($1\ mg\ mL^{-1}$) was mixed with 30, 60 and 120 mg of the PBM sample. To each of these mixtures, 27 mL of varying proportions of 0.01 N HCl, NaCl or NaOH solution was added to attain targeted pH values from ~2 to 11 at an ionic strength (IS) of 0.01 N. Obtained suspensions were then transferred into a 30 mL plastic test tube and kept standing for 15 min and used for examinations of surface charge, aggregation rate and soluble Fe remaining in the solution.

2.3. Determination of surface charge and aggregation properties

For quantification of surface charge, each 10 mL of the suspension, prepared as described above (section 2.2), was taken and transferred into the titration cell of a particle-charge detector (PCD 05, Mütek, Herrsching, Germany). The titration using the polyelectrolyte (Poly-DADMAC or PesNa), was terminated at the point of zero charge, where the electro-kinetic potential is zero. This method was described in more detail in a study on determination of electro-kinetic charge with a particle charge detector [25]. Since heterogeneous oxidation of Fe can lead to strong aggregation, dynamic light scattering (DLS) appears unsuitable. Therefore, aggregation of the newly-formed Fe oxides in the presence of the PBM as functions of pH and IS was evaluated in plastic test tubes following the procedure of Lagaly, Schulz and Ziemehl [23] with only a minor modification. Because the combined homogeneous and heterogeneous oxidation of Fe(II), which would be occurring under the experimental conditions, is non-linear over time, and furthermore is variable with pH, we conducted preliminary experiments in a time span from 5 to 120 min. The 15-minute procedure, which well interprets the colloidal properties at the entire pH range from 2 to 11, was selected. The suspensions were dispersed by sonication for 30 s and then held statically for 15 min. An amount of 3 mL of each suspension was sampled from the surface of the suspension (corresponding to 3-cm top layer), and the transmittance (T%) was determined using a UV-VIS spectrophotometer (Shimadzu, UV-2101PC) at a wavelength of 380 nm. In our preliminary tests, at this wavelength, presence of the newly-formed Fe oxides can be clearly identified, while there is only minor change in T value for the absence or presence of the PBM. To reduce possible effects of dissolved oxygen on oxidation and aggregation processes, all experiments were carefully performed following the same procedures in a closed room with temperature controlled at 20 °C. All experiments were carried out in triplicates.
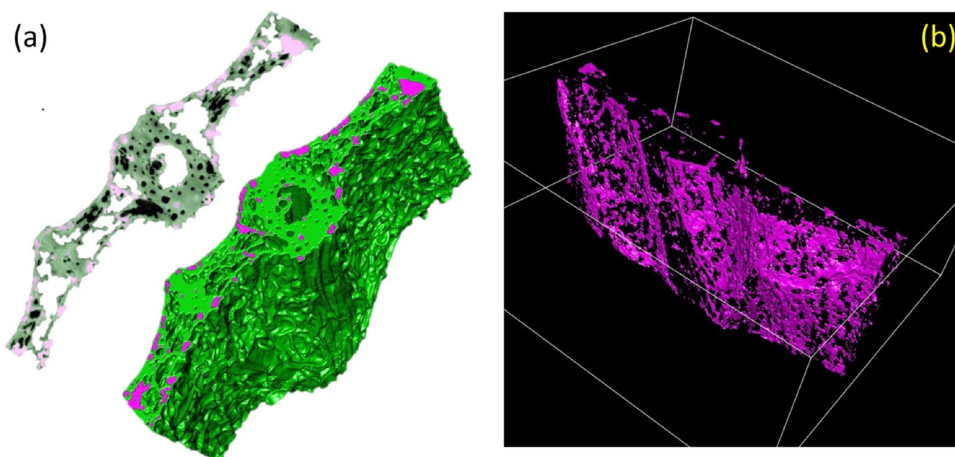
Fig. 1. Tomographic images showing phytolith phase of the leaf, colored in pink (a), and 3D view with only phytolith phase of the leaf (b). The TOMCAT (TOmographic Microscopy and Coherent rAdiology experimenTs) beamline receives photons from a 2.9 T superbending magnet with a critical energy of 11.1 keV, producing a monochromatic beam. A sample is fixed on a centering and rotation stage in front of a microscope, detecting the monochromatic X-ray beam. A 3D-view, consisted of 2160 individual 2D slice images, with 2560 × 2560 isotropic pixels each and the pixel size was 0.325 µm, was reproduced by using YaDiV software [24], in which silica and organic phases can be separately represented.