Chemosphere 125 (2015) 130–138

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Removal of colloidal biogenic selenium from wastewater

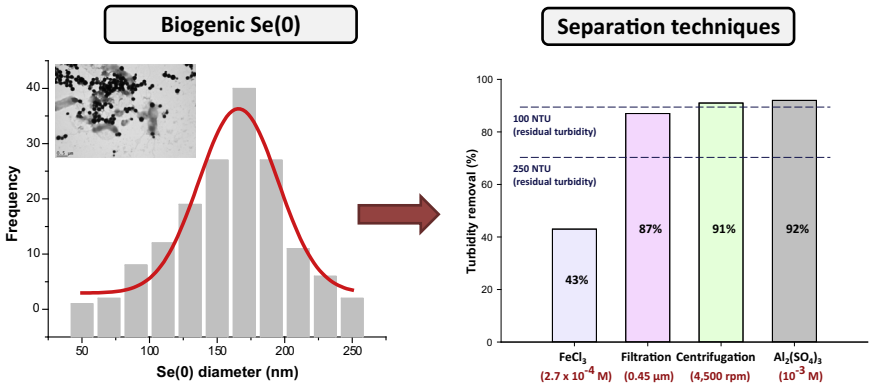
Lucian C. Staicu [a,b], Eric D. van Hullebusch [b,*], Mehmet A. Oturan [b], Christopher J. Ackerson [c], Piet N.L. Lens [a]

[a] UNESCO-IHE Institute for Water Education, PO Box 3015, 2601 DA Delft, The Netherlands
[b] Université Paris-Est, Laboratoire Géomatériaux et Environnement, EA 4508, UPEM, 5 bd Descartes, 77454 Marne-la-Vallée Cedex 2, France
[c] Department of Chemistry, Colorado State University, Fort Collins, CO 80521, United States

HIGHLIGHTS

- Colloidal stability of Se(0) is linked to its nanosize and ζ-potential (−20 ± 5 mV).
- High speed (4500 rpm) centrifugation achieved 91% Se(0) removal.
- Filtration through 0.45 μm filters yields a Se(0) removal efficiency of 87%.
- Aluminum sulfate (10^{-3} M) can sediment up to 92% of colloidal elemental selenium.
- Al–Se sediment shows better dewaterability than Fe–Se sediment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 August 2014
Received in revised form 5 November 2014
Accepted 1 December 2014
Available online 3 January 2015

Handling Editor: Min Jang

Keywords:
Elemental selenium
Colloids
Coagulation–flocculation
Aluminum sulfate
Filtration
Centrifugation

ABSTRACT

Biogenic selenium, Se(0), has colloidal properties and thus poses solid–liquid separation problems, such as poor settling and membrane fouling. The separation of Se(0) from the bulk liquid was assessed by centrifugation, filtration, and coagulation–flocculation. Se(0) particles produced by an anaerobic granular sludge are normally distributed, ranging from 50 nm to 250 nm, with an average size of 166 ± 29 nm and a polydispersity index of 0.18. Due to its nanosize range and protein coating-associated negative zeta potential (−15 mV to −23 mV) between pH 2 and 12, biogenic Se(0) exhibits colloidal properties, hampering its removal from suspension. Centrifugation at different centrifugal speeds achieved 22 ± 3% (1500 rpm), 73 ± 2% (3000 rpm) and 91 ± 2% (4500 rpm) removal. Separation by filtration through 0.45 μm filters resulted in 87 ± 1% Se(0) removal. Ferric chloride and aluminum sulfate were used as coagulants in coagulation–flocculation experiments. Aluminum sulfate achieved the highest turbidity removal (92 ± 2%) at a dose of 10^{-3} M, whereas ferric chloride achieved a maximum turbidity removal efficiency of only 43 ± 4% at 2.7×10^{-4} M. Charge repression plays a minor role in particle neutralization. The sediment volume resulting from $Al_2(SO_3)_4$ treatment is three times larger than that produced by $FeCl_3$.

1. Introduction

Selenium (Se) is a chalcogen element sharing common properties with sulfur (S) and tellurium (Te). Se has a complex

* Corresponding author. Tel.: +33 1 49 32 90 42; fax: +33 1 49 32 91 37.
E-mail address: Eric.vanHullebusch@u-pem.fr (E.D. van Hullebusch).

http://dx.doi.org/10.1016/j.chemosphere.2014.12.018
0045-6535/

biogeochemistry and is circulated through environmental compartments via both natural and anthropogenic processes (Chapman et al., 2010). Natural sources of selenium are crustal weathering and leaching, volcanism, sea salt spraying, and biological activities (Wen and Carignan, 2007). The anthropogenic release of selenium in the environment is mainly related to fossil fuel combustion, mining, non-metal smelting, and agriculture practiced on seleniferous soils (Lemly, 2004).

Of special interest is the very narrow window between selenium essentiality and toxicity (Levander and Burk, 2006). Based on blood plasma glutathione peroxidase activity as the selenium biomarker, a dietary reference intake (DRI) of 55 $\mu g\, d^{-1}$ is proposed (IOM, 2000). In excess, selenium poisoning (i.e. selenosis) can result in hair loss, brittle nails and neurological pathologies (e.g. decreased cognitive function, convulsions, and weakness) (Tinggi, 2003). Estimated maximal intake levels of 910 $\mu g\, Se\, d^{-1}$ caused by agriculture practiced on seleniferous soils were linked to endemic selenosis in China (Yang et al., 1989). The toxicity elicited by Se on biota is mainly related to the chemical speciation that selenium undergoes under changing redox conditions. Amongst its oxidation states, Se oxyanions, namely selenite (Se[IV], SeO_3^{2-}) and selenate (Se[VI], SeO_4^{2-}), are water-soluble, bioavailable and toxic (Simmons and Wallschlaeger, 2005). In contrast, elemental selenium, Se(0), is solid and less toxic (Dungan and Frankenberger, 1999). Nevertheless selenium nanoparticles (SeNPs) exhibited significant toxicity to mice (Zhang et al., 2005). In addition, particulate Se(0) has been reported to be bioavailable to bivalves (Luoma et al., 1992; Schlekat et al., 2000) and fish (Li et al., 2008). Furthermore, Se(0) is prone to re-oxidation to toxic SeO_3^{2-} and SeO_4^{2-} when discharged into aquatic ecosystems (Zhang et al., 2004).

A number of treatment technologies, including biological methods, aim to remove selenium oxyanions present in industrial wastewaters by reducing them to solid-phase elemental selenium (Lenz and Lens, 2009; Sobolewski, 2013). When biological treatment of selenium-laden wastewaters is performed, biogenic Se(0) is the solid end product that can be removed from the aqueous phase (Staicu et al., 2014). Due to its surface charge and nanometer size, biogenic Se(0) exhibits colloidal stability making its removal from the water phase difficult (Buchs et al., 2013). Coagulation–flocculation is one of the main processes employed both in drinking and wastewater treatment for the removal of colloidal and suspended particles (Duan and Gregory, 2003). The principle relies on the destabilization and settling of the colloids and suspended particles that cannot settle by gravity within practical time frames. Because of their proven efficiency and low cost, aluminum sulfate and ferric chloride are currently employed as coagulants on a large scale (Gregory and Duan, 2001). When coagulants are added to water, the metal ions (e.g. Al^{3+}, Fe^{3+}) hydrolyze spontaneously and form a series of metastable metal hydrolysis products (Richens, 1997). These metal hydrolysis products act upon the negatively charged particles held in suspension by hydrostatic repulsion forces (Russel et al., 1992). They alter the physical state of the suspended particles by repressing their charge (i.e. charge repression) and by forming large aggregates of $Al(OH)_3$/$Fe(OH)_3$ (i.e. sweep flocculation) which lead to particle sedimentation (Gregory and Duan, 2001). The use of filtration has been reported for removing colloidal particles other than Se(0). In a recent study, Johnson et al. (2014) has investigated the removal of particulate and colloidal silver in the sewage effluent discharged from several British wastewater treatment plants. On the other hand, centrifugation is rarely used for removing colloidal particles because it is an energy intensive process, but this approach can become feasible when treating highly turbid wastewaters (Thuvander et al., 2014).

Regardless of the utilization of coagulation–flocculation on a large scale for the removal of colloidal particles (Duan and Gregory, 2003), no systematic study has been done to investigate the separation of biologically-produced colloidal Se(0) from the bulk solution. The objectives of this study were, therefore, to characterize surface charge, stability and particle size distribution of biogenic Se(0) particles and to assess the solid–liquid separation potential of colloidal elemental selenium by filtration, centrifugation and coagulation–flocculation.

2. Materials and methods

2.1. Chemicals and media

Sodium selenate, Na_2SeO_4, ⩾98.0%, was purchased from Sigma Aldrich and fresh solutions were prepared before each experiment. All other reagents were of analytical grade. Ferric chloride hexahydrate, $FeCl_3{\cdot}6H_2O$ (ACS reagent, >98%) and aluminum sulfate octadecahydrate, $Al_2(SO_4)_3{\cdot}18H_2O$ (ACS grade, >98%) were purchased from Sigma Aldrich and Fischer Scientific, respectively. All solutions were prepared using deionized water.

Incubations were done using Basal Mineral Medium (BMM) containing ($g\, L^{-1}$): NH_4Cl (0.3), NaCl (0.3), $CaCl_2.2H_2O$ (0.11), $MgCl_2.6H_2O$ (0.1), 1 $mL\, L^{-1}$ acid trace element solution, 1 $mL\, L^{-1}$ basic element solution, and 0.2 $mg\, L^{-1}$ of vitamin solution (Stams et al., 1993). 10 mM sodium selenate and 20 mM lactate (as sodium L-lactate) were amended to the BMM.

2.2. Production of biogenic red Se(0)

BMM containing sodium selenite and 15 $g\, L^{-1}$ (wet weight) inoculum was transferred to serum bottles. Anaerobic granular sludge sampled from an Upflow Anaerobic Sludge Blanket (UASB) reactor treating brewery wastewater was used as inoculum. The sludge was kindly provided by Biothane Systems International (Delft, the Netherlands) and the same sludge was used throughout all experiments. The inoculum had a Total Suspended Solids (TSS) and a Volatile Suspended Solids (VSS) content of, respectively, 54.6 $g\, L^{-1}$ and 39.8 $g\, L^{-1}$, corresponding to a VSS/TSS ratio of 0.73 (Kijjanapanich et al., 2013).

The bottles were closed with butyl rubber septa and aluminum caps, the headspace was flushed with nitrogen gas for 15 min and the final headspace pressure adjusted to 1.7 bar (Astratinei et al., 2006). Incubation was performed at 30 °C, in the dark and under constant shaking at 100 rpm for 14 d.

At the end of the incubation period, the colorless Na_2SeO_4 solution had developed a red color (Fig. 1a), indicative of biogenic Se(0) formation (Oremland et al., 2004). The Se(0) particles produced through microbial reduction of selenium oxyanions are designated 'biogenic' and represent the red allotrope of elemental selenium (Fellowes et al., 2011). After 14 d of incubation, bottles containing red Se(0) were left in a vertical position for 6 h allowing for the separation of the granular sludge inoculum from the bulk Se(0) solution. Se(0)-containing supernatant was carefully transferred to new recipients and used for coagulation experiments.

2.3. Se(0) protein-coating characterization

After sampling biogenic Se(0), the red suspension was centrifuged at 10 000*g* for 5 min and the pellet was washed three times in sterile Phosphate Buffer Saline (PBS). The proteins that were attached onto the biogenic Se(0) particles were denatured by the addition of 160 mM dithiothreitol (DTT) and 1% SDS (Sodium Dodecyl Sulfate) followed by boiling the samples at 95 °C in a water bath for 5 min. The denatured samples (60 µL) were loaded into 15% denaturing gels and run at constant current (30 mA) for 2 h in TBE (1×) buffer using Polyacrylamide Gel Electrophoresis