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Preferential adsorption of Cu in a multi-metal mixture onto biogenic elemental selenium nanoparticles

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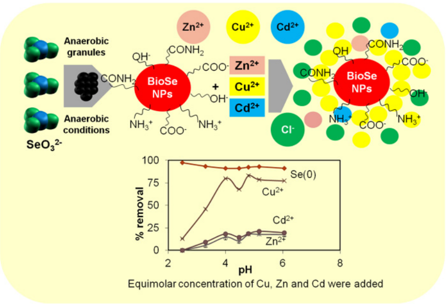
HIGHLIGHTS

- BioSeNPs adsorb 2.3–6.6 times more Cu than combined Zn and Cd.
- Initial pH and metal to BioSeNPs ratio can be varied to preferentially adsorb Cu.
- Cu, Cd and Zn interact with COO^- groups present on the BioSeNPs' surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Preferential adsorption of Cu contained in wastewaters is desirable as the Cu can then be reprocessed and reused more easily. In this study, biogenic elemental selenium nanoparticles (BioSeNPs) were assessed for their ability to preferentially adsorb Cu from an equimolar mixture containing Cu, Cd and Zn. Variations in metal to BioSeNPs ratios and initial metal solution pH improved the preferential adsorption capacity of BioSeNPs toward Cu, with the ratio of Cu adsorbed to combined Cd and Zn adsorbed varying from 2.3 to 6.6. More than 78% of the added Cu was adsorbed at an initial metal solution pH of 5.2 and metal to BioSeNPs ratio of 0.21 $mg\ mg^{-1}$ when the ratio of Cu adsorbed to the sum of Cd and Zn adsorbed was 2.3. Infrared spectroscopy revealed that the Cu, Cd and Zn were interacting with the hydroxyl and carboxyl surface functional groups of the BioSeNPs. The modeling of BioSeNPs' acid–base titration revealed the presence of high concentrations of carboxylic groups ($C = 60.3\ mol\ kg^{-1}$) with a pK_a of 3.9, providing further evidence of their interaction with Cu. The adsorption of Cu resulted in a lower colloidal stability of the BioSeNPs as indicated by more than 99% retention of added BioSeNPs after adsorption of heavy metals and filtration. BioSeNPs showed a good preferential adsorption capacity toward Cu as compared to other adsorbent. This study provides a proof-of-concept for the preferential adsorption of Cu onto BioSeNPs which are present in the effluent of a bioreactor treating selenium oxyanions containing wastewater.

Abbreviations: AAS, atomic absorption spectroscopy; BioSeNPs, biologically produced elemental selenium nanoparticles; DSM, Donnan shell model; EPS, extracellular polymeric substances; FT-IR, Fourier transform infrared spectroscopy; HDD, hydrodynamic diameter; Qe–Me, mg of metal adsorbed per g of biogenic elemental selenium nanoparticles; UASB, upflow anaerobic sludge blanket reactor.

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1. Introduction

Copper (Cu) is one of the most extensively utilized heavy metals in industries such as electrical and electronic, manufacturing, building and construction as well as industrial machinery and equipment production [1]. The future availability of Cu may not be guaranteed due to its increasing demand and shrinking reserves [1,2]. Thus, it is imperative to recover Cu from non-conventional sources such as acid mine drainage or electroplating industry wastewaters [3,4]. However, Cu present in these waste streams is often mixed with other heavy metals such as zinc (Zn) and cadmium (Cd) [4,5]. Thus, to separate, reprocess and reuse Cu, its preferential recovery from multi-metal wastewaters is required [6].

Preferential recovery of heavy metals from multi-metal wastewaters can be achieved through ion-exchange, flotation, membrane filtration, electrochemical treatment and adsorption [7]. Recovery of desired heavy metals by adsorption can be attractive due to faster kinetics, higher capacity and process simplicity [7]. Preferential recovery of heavy metals from a multi-metal mixture follows a two step process: preferential adsorption followed by preferential desorption, the latter can be induced by a change of pH to acidic conditions. On the other hand, preferential adsorption of heavy metals onto the adsorbent depends on the metals' properties, such as ionic radius, electronegativity, ratio of ionic radius and ionization potential, as well as the metal speciation in the wastewater [8]. The presence of functional groups such as carboxyl and hydroxyl on the surface of adsorbents further contributes to the preferential adsorption of heavy metals [9,10]. Also, the wastewater pH plays a significant role in optimizing the preferential adsorption of heavy metals onto the adsorbent. Indeed, the change in pH affects the metal speciation in the wastewater and protonation/deprotonation of the functional groups present on the adsorbent [9,11]. Most adsorbents have to be pretreated to improve their preferential capacity, which increases their cost of application [10]. Thus, there is a constant search for adsorbents with lower cost and better preferential capacity.

Biogenic elemental selenium nanoparticles (BioSeNPs) can be a good adsorbent for preferential removal of divalent heavy metals due to the presence of carboxyl and hydroxyl functional groups on their surface as shown previously [12,13]. These carboxyl and hydroxyl groups can be attributed to the presence of extracellular polymeric substances (EPS) on the surface of the BioSeNPs [13]. Moreover, the median diameter of BioSeNPs is 180 nm, thus providing a high surface to volume ratio as compared to bulk materials, resulting in elevated adsorption of metals per g of adsorbent [12]. Also, BioSeNPs are a low cost adsorbent, as they can be produced from selenium oxyanions containing wastewaters by microbial reduction [14,15]. Moreover, the solid–liquid separation upon adsorption of heavy meals onto BioSeNPs can be easily carried out using gravity settling, thus enhancing the attractiveness of the process [12,16]. Jain et al. [12] already evidenced the adsorption capacity of BioSeNPs toward Zn. However, there is so far no study carried out with adsorption of multi-metal mixtures onto BioSeNPs.

The preferential recovery of Cu from wastewater involves two steps: preferential adsorption followed by preferential desorption. The objective of this study was to optimize the preferential adsorption step of Cu from an equimolar mixture of Cu, Cd and Zn onto BioSeNPs using variable initial metal solution pH and metal to BioSeNPs ratios (mg mg^{-1}). Though the equilibrium pH determines the adsorption, the initial metal solution pH is characteristic of the wastewaters generated from the metal finishing industry and was thus used as a control parameter in this study. The interaction of BioSeNPs with different metals was also studied by Scanning Electron Microscopy–Energy Disperse X-ray Spectroscopy (SEM–EDXS), Fourier Transform Infrared Spectroscopy (FT-IR) and ζ-potential measurements.

2. Materials and methods

2.1. Production and purification of BioSeNPs

BioSeNPs were produced and purified as described in a previous study [12]. Briefly, BioSeNPs were produced by selenite reduction using anaerobic granular sludge under anaerobic conditions. The produced BioSeNPs were purified by NaOH treatment followed by a hexane separation step and washing with Milli-Q water (18 MΩ cm). The production of BioSeNPs was evidenced from the appearance of the red color in the supernatant as reported in the previous studies [12,13]. The pH of the BioSeNPs containing solution was 7.3 as it is the pH of the effluent of the upflow anaerobic sludge blanket (UASB) reactor treating selenium rich wastewater in a pH controlled environment [13,17].

2.2. Modeling of acid–base titration data to determine charge density on BioSeNPs

The BioSeNPs have a coating of EPS, thus making a core–shell structure with a core of selenium and a shell of EPS [13]. The Donnan shell model (DSM) has been demonstrated to reasonably fit the acid–base titration of the core–shell system of latex dispersion and bacterial surface [18,19]. As the pK_a of the functional groups present on the surface of BioSeNPs were known, the DSM model was optimized using the pK_a as constrained parameters [13]. The simulation of acid–base titration was carried out using PROTOFIT 2.1 software [20]. Four discrete acidic surface sites and extended Debye–Hückel activity coefficient were used. The experimental acid–base titration data for determining the charge density of BioSeNPs has been reproduced with permission from Jain et al. [13].

The Donnan shell volume was calculated by subtracting the volume of BioSeNPs from the combined volume of the BioSeNPs and their shell. The combined volume of BioSeNPs and their shell was calculated by assuming the hydrodynamic diameter (HDD) as diameter of the BioSeNPs and their shell (Fig. S1 in Supporting Information (SI)). The volume of BioSeNPs without its shell was calculated using 180 nm as diameter obtained by the SEM images observed in an earlier study by Jain et al. [12]. As the HDD was varying with the pH, the Donnan shell volume varied between 2.27×10^{-6} and 3.7×10^{-4} m^3 g^{-1} when the HDD varied from 402.1 (±8.3) nm to 2130.3 (±184) nm, respectively. To obtain the experimentally determined pK_a of the functional groups present on the surface of the BioSeNPs, the Donnan shell volume was optimized at 6.9×10^{-5} m^3 g^{-1}. The specific surface area used for this calculation was 7.5 m^2 g^{-1} calculated using 180 nm as diameter. The specific gravity of selenium used was 4.5 g mL^{-1} [21]. BioSeNPs were considered to be perfect spherical particles. It is important to note here that the HDD values of more than 1000 nm are only indicative as the HDD measurements are prone to high errors due to coagulation of BioSeNPs at acidic pH [13]. However, in this study, the HDD values were only used as an initial guess for calculating the optimized Donnan shell volume and the model was constrained by the experimentally determined pK_a values of the functional groups.