

Comparison of selenite removal from water using alginate Fe(III) beads and dried sludge as adsorbents

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Resumen

Selenito (Se(IV)) es la forma más tóxica de selenio debido a su biodisponibilidad. Las perlas de alginato y Fe(III), un adsorbente biodegradable y el lodo seco, un residuo de las plantas de filtración de agua, se utilizaron para la remoción de oxianiones de selenio a niveles traza del agua. La adición de hierro en el alginato y como cloruro férrico en el lodo, mejora la eficiencia de adsorción hacia los iones de selenito. El comportamiento de adsorción se ajustó mejor utilizando modelos de isotermas de Freundlich debido a la rugosidad de ambas superficies. El *parámetro k* de Freundlich para Se(IV) fue 0.407 (alginato) y 0.100 (lodo) (mg/g)(L/mg)ⁿ indicando una mejor capacidad de absorción relativa cuando se utilizaron las perlas de alginato y Fe(III). Nuestros resultados sugieren que el principal mecanismo de remoción de los oxianiones de selenio se debió a la formación de complejos de esfera externa, lo que implica una atracción electrostática. Nuestros resultados demuestran que las perlas de alginato de Fe(III) son mejores adsorbentes, mientras que el lodo podría estar ampliamente disponible. Nuestro trabajo presenta las perlas de alginato de Fe (III) y el lodo seco como adsorbentes verdes, que podrían usarse para remediar los niveles de trazas de oxianiones de selenito de aguas potables y subterráneas contaminadas.

Palabras clave: selenito, perlas de alginato y Fe(III), adsorción, lodo seco

Abstract

Selenite (Se(IV)) is the more toxic form of selenium due to its bioavailability. The alginate Fe(III) beads, a biodegradable adsorbent and dried sludge, a waste from water filtration plants, were used for the removal of selenium oxyanions at trace levels from water. The addition of iron into the alginate and as ferric chloride in the sludge, enhance the adsorption efficiency towards selenite ions. The adsorption behavior was better fitted using Freundlich isotherms models due to the roughness of both surfaces. The Freundlich parameter *k* for Se(IV) were 0.407 (alginate) and 0.100 (sludge) (mg/g)(L/mg)ⁿ indicating a better relative uptake capacity when the alginate Fe(III) beads were used. Our results suggest that the main mechanism of removal of selenite oxyanions was due to the formation of outer-sphere complexes, which involves electrostatic attraction. Our results demonstrate that alginate Fe(III) beads are better adsorbent, whereas the sludge could be widely available. Our work presents the alginate Fe(III) beads and the dried sludge as green adsorbents, which both could be used to remediate trace levels of selenite oxyanions from contaminated drinking and groundwaters.

Keywords: selenite, alginate Fe(III) beads, adsorption, dried sludge

1. Introduction

Selenium is a micronutrient essential for humans but is potentially harmful if taken in excess (Zoroufchi-Benis *et al.* 2022). Selenium has four natural oxidation states (-II, 0, IV, VI), instead the most stable forms in natural waters are selenite (Se(IV)) and selenate (Se(VI)) oxyanions, being selenite the more toxic species because it is more bioavailable (Barceloux *et al.* 1999). Selenium sources come from anthropogenic and natural activities. Human sources are mainly from activities related to coal and petroleum industries and natural occurrence from marine biosphere and volcanoes (Feinberg *et al.* 2020, Gebreyessus *et al.* 2019). Although it is a micronutrient, in the United States the Environmental Protection Agency (EPA) regulates the amount of selenium in drinking water at 0.05 ppm concentration due to health problems in hair, nails and circulatory system (EPA website). Current technologies to remove oxyanions, heavy metals and anions are reported in literature by physical methods (filtration and adsorption), chemical methods (precipitation and coagulation), and biological methods (bioremediation) (Alvarado *et al.* 2008, Boukhalfa *et al.* 2010, Cakmakci *et al.* 2009, Hu *et al.* 2009, Lichtfouse *et al.* 2019, Maheswari *et al.* 2009, Mohan *et al.* 2007, Song *et al.* 2006, Saitiua *et al.* 2005 and Qian Yu *et al.* 2018). Adsorption has gained a lot of attention in comparison to other methods due to a low-cost, easily to scale up, functionality, and reusability (Benis *et al.* 2022, Guan *et al.* 2009 and Lenoble *et al.* 2002). Although selenium is a micronutrient important for human beings, its excess could be harmful and cause toxicity. It is important then, to monitor and remove selenium ions in an effective and ecofriendly technology such as adsorption. This study explores the use of alginate Fe(III) beads and dried sludge as environmentally friendly adsorbents. Also, it incorporates the competitive adsorption to confirm the coulombic attraction between the adsorbent-oxyanions interface and predict the Freundlich isotherm model due to the roughness of both surfaces.

2. Procedures

2.1 Alginate Fe (III) beads synthesis

The alginate Fe(III) beads were synthesized using the procedure previously reported in Sánchez-Rivera *et al.* 2013. A 2% w/v alginate solution was dropwise added to 0.1 M of CaCl₂ and 0.5 M FeCl₃ solution at pH 8.0 ± 0.1 at slow magnetic agitation. The beads were vacuum filtered after 24 hours of contact and let air dried for 2-3 days.

2.2 Dried Sludge preparation

The sludge was recollected as a waste from the water filtration and treatment plant located in Mayaguez, Puerto Rico. The sludge was oven dried and ready for further analysis and use (Sánchez-Rivera *et al.* 2013).

2.3 Adsorption isotherms

Se(IV) duplicate solutions within a concentration of 100-2000 ppb were placed in plastic bottles with 5g/L of alginate Fe(III) beads or 5g/L dried sludge with 10 ppm of ferric chloride at the desired pH, generally 6.0. All analyses were made under room temperature (25 °C) in a water shaker bath at 200 rpm. Samples (1.00 mL aliquots) were withdrawn at certain time intervals until the equilibrium time was reached. All samples were acidified with nitric acid to pH 2.0 and then measured by inductively coupled plasma mass spectrometry technique (Agilent ICP-MS 7500 ce).

2.3.1 Competitive analysis

Se(IV) duplicate solutions of 100 ppb were placed in plastic bottles in presence with competitor oxyanion (sulfate, carbonate or phosphate) at diverse ratios (1:1, 1:3 and 1:5). The solutions were processed as a regular adsorption experiment as described in Section 2.3.

2.3.2 Adsorption isotherms

The presented study models the Freundlich and Langmuir adsorption isotherms that describe common adsorption scenarios.

Langmuir isotherm model suggests that the coverage available sites are homogeneous and denotes a dynamic equilibrium between the adsorbate and adsorbed species. The Langmuir model is expressed using the Equation 1:

$$q_e = q_{max} \frac{b C_e}{1 + b C_e} \quad (1)$$

The Langmuir equation above can be expressed

in a linear model as follows:

$$C_e/q_e = (1/q_{max}) C_e + 1/q_{max} b \quad (2)$$

where the q_{max} is a Langmuir constant, that express the adsorption capacity of the adsorbent (mg/g) and the b represents the affinity of the solute in the adsorbent surface (L/mg). The parameters C_e correspond to the concentration of the solute ions (mg/L) and q_e the adsorption capacity of the sorbent (mg/g) at equilibrium (Allen *et al.* 2004, Ayawei *et al.* 2017, Guo *et al.* 2009 Zheng *et al.* 2009).

Freundlich isotherms is better fitted to adsorbates with heterogeneous surfaces active sites. Freundlich model assumes that the adsorption sites are distributed exponentially with respect to their energies as described by Equation 3:

$$q_e = k C_e^{1/n} \quad (3)$$

The Freundlich equation could be expressed in a linear model as follows:

$$\ln q_e = \ln k + 1/n \ln C_e \quad (4)$$

where k ((mg/g)(L/mg)ⁿ) is a Freundlich constant, that measure the relative adsorption capacity of the adsorbent and n related to the intensity of adsorption. The n value is related to the energy and the heterogeneous of the surface-active sites. The intensity of adsorption increase

as the value of $1/n$ is greater. (Ayawei *et al.* 2017 and Lim *et al.* 2007).

The Langmuir and Freundlich isotherms models were employed for selenite adsorption using alginate Fe(III) beads and dried sludge to determine the best suitable model to describe the systems.

2.3.3 Desorption studies

Selenite species adsorbed on the alginate Fe(III) beads or dried sludge surfaces were treated using 0.1M of strong acids (nitric, hydrochloric, and sulfuric acids). The solutions with the adsorbent were agitated in a rotamix at 30 rpm for a period of 24 hours. At the end of the 24 hours, samples were taken, diluted and analyzed by ICP-MS.

3. Results and discussions

3.1 Competitive analysis

The results show (Table 1) that the removal efficiency for selenite species decreased from 100% (in absence of phosphate, carbonate or sulfate as competing ions) to 87.6- 92.7% range in presence of them. Statistical analysis of the t Student at a 95% confidence level revealed a significant difference between the removal efficiency of selenite ions in presence/absence of competitive oxyanions.

These results suggest that the adsorption process depends on the ionic strength of the solution. That dependence could be associated to the formation of outer sphere complexes. Those complexes are form due to electrostatic attractions. In Figure 1 shows a possible Selenite-Fe outer sphere complex. (Wang *et al.* 2018, Manohar *et al.* 2005 and Liu *et al.* 2008). However, selenite adsorption process remained above 85% of removal in presence of all the competitive anions studied. These results suggest the potential application of both adsorbents in real water scenarios where the presence of other species is common.

3.2 Adsorption isotherms

The results show (Table 2) demonstrated a better linear correlation coefficient for the Freundlich isotherms (0.9989-0.9732) than the Langmuir model (0.9649-0.7989). Predicting that our adsorption process takes place on heterogeneous surface-active sites, which agrees with the non-specific binding of electrostatic attraction that we proposed. Another valuable constant of the Freundlich isotherms is the n value. The n values for selenite are 1.56 and 1.0 using alginate Fe (III) beads and dried sludge, respectively. Those n values between 1 to 10 are indicative of a good adsorption relation between adsorbate-surface. Meanwhile, the value of $1/n$ indicates the adsorption intensity. $1/n$ values of 0.64 and 1.0 were obtained for alginate and dried sludge, respectively, meaning that the interaction of Se-dried sludge is stronger than Se-alginate Fe(III) beads. Another useful Freundlich constant that suggests a good sorption capacity is the value of k , the greater the value represent a better sorption capacity (Patil *et al.* 2011). In this case, Se(IV) has a k value of 0.407 for the alginate Fe(III) beads and 0.100 for dried sludge. The results evidence that the alginate beads have a greater sorption capacity than the dried sludge.

3.3 Desorption studies

Selenite species could be recovered up to 96.3% using 0.1M sulfuric acid from the alginate beads and up to 18.4% when used dried sludge. Those values are consistent with the $1/n$ value from the Freundlich isotherms that suggest that the Se-dried sludge interaction was stronger, then more difficult to break down.

4. CONCLUSIONS

The results showed that alginate Fe(III) beads and the dried sludge are effective adsorbents for selenite oxyanions at trace concentrations. The results suggest that selenite species are adsorbed on the heterogeneous surface sites of the

alginate Fe(III) beads and the dried sludge as suggested from the Freundlich model. The general mechanism of removal was due to coulombic attraction by the formation of outer-sphere complexes as predicted by the competitive analysis. The maximum recovery (96.3 %) of the selenite species was for alginate Fe (III) beads in presence of 0.1 M sulfuric acid. It implies the reusability of the alginate Fe(III) beads. The k value indicates that alginate has a better adsorption capacity than the dried sludge. The use of one adsorbent or another will depend of diverse conditions such as cost, ecofriendly, availability and efficiency. Our results confirms the both adsorbents, alginate Fe(III) beads and dried sludge could be useful to remove trace amounts of selenium ions in drinking and groundwater in the presence of diverse competing ions which are expected to be present in natural water scenarios.

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Table 1. Removal efficiency of selenite ions using 5g/L alginate Fe(III) beads or 5g/L dried sludge + 10 ppm ferric chloride in the presence of other oxyanions at pH 6.0

| | Ratio | Alginate % Removal | SD | Sludge % Removal | SD |
|------------------------------------|-------|--------------------------|-----|------------------------|-----|
| No competitive anion added | 1:0 | 100 | 0 | 100 | 0 |
| CO₃²⁻ | 1:1 | 92.5 | 0.6 | 85.8 | 0.3 |
| | 1:3 | 91.8 | 0.1 | 88.7 | 0.9 |
| | 1:5 | 92.6 | 0.3 | 87.6 | 0.5 |
| SO₄²⁻ | 1:1 | 92.3 | 1.0 | 90.0 | 0.4 |
| | 1:3 | 92.8 | 0.5 | 90.0 | 2.1 |
| | 1:5 | 92.7 | 1.2 | 90.3 | 0.4 |
| PO₄³⁻ | 1:1 | 92.3 | 1.6 | 90.8 | 0.6 |
| | 1:3 | 92.6 | 0.7 | 89.8 | 0.1 |
| | 1:5 | 90.8 | 0.3 | 88.8 | 0.5 |

Figure 1. Representation of an outer sphere complex between Se(IV) and Fe containing surfaces

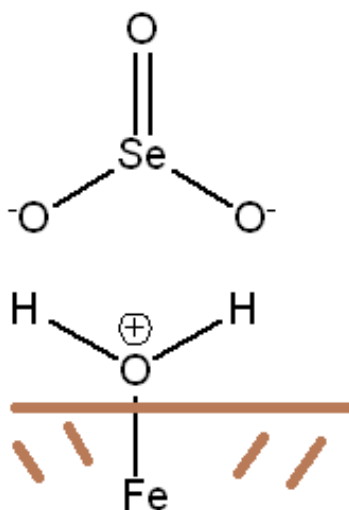


Table 2. Langmuir and Freundlich isotherms parameters for selenium ions using 5g/L alginate Fe(III) beads

| Se(IV) | Langmuir | | | Freundlich | | |
|-----------------|---------------------|---------------|--------|----------------------------------|------|--------|
| | q_{max} (mg/g) | b (L/mg) | R^2 | k (mg/g)(L/mg) ⁿ | n | R^2 |
| Alginate | 0.247 | 2.83 | 0.9649 | 0.407 | 1.56 | 0.9732 |
| Sludge | 0.263 | 3.09 | 0.7989 | 0.100 | 1.00 | 0.9989 |

Table 3. Desorption of selenium ions using 0.1M nitric, hydrochloric or sulfuric acid

| 0.1 M | alginate % desorbed | SD | sludge % desorbed | SD |
|------------------------------------|--------------------------------|-----------|------------------------------|-----------|
| HNO₃ | 48.6 | 9.2 | 2.1 | 0.1 |
| HCl | 76.4 | 7.3 | 2.6 | 0.2 |
| H₂SO₄ | 96.3 | 9.0 | 18.4 | 1.7 |