Arsenic Retention on Technosols Prepared with Nanoparticles and Ferric Soil from Mine Drainage Water

1. Introduction

Arsenic is a trace element of high toxicity and carcinogenicity, whose natural environmental distribution presents an enormous variability and ubiquity due to a combination of climate and geology but without a significant correlation [1, 2]. Arsenic concentrations in the environment may increase due to anthropogenic activities, being agriculture, mining, and petroleum refining, the main activities contributing to the contamination of soil and water resources [3].

Specifically, mine drainage water may present enormously high concentrations of heavy metals, with the consequent risks for the ecosystems and human health. This contaminated water may leach and migrate (according to soil and geological properties and environmental conditions) to ground and spring water, becoming a potential contaminant of drinking water sources [4]. Therefore, the elimination of As from water bodies is considered one of the most important environmental challenges at a global level. All over the world, many studies have been carried out by the World Health Organization (WHO), the European Union (EU), and the United States Environmental Protection Agency (US EPA), among other international organizations, in order to establish the best water decontamination techniques according to toxicity and economical studies [5].

There are many available technologies to clean up As-contaminated water, whose efficiency and applicability will
mainly depend on the chemical form of As in water [3]. The techniques most commonly applied include oxidation to solid As(V) and filtration [3]; phytoextraction (mainly by phytoremediation and phytotransfer) [6]; coagulation-flocculation using ferric and aluminium salts [7]; adsorption on solid sorbents [8]; ion exchange using resins [9]; and membrane technologies (by micro- and nanofiltration or osmosis) [10].

Particularly, the immobilization (adsorption) of As in specific sorbents has been widely used due to its high versatility, easy operation and handling, and low costs. Furthermore, due to the development and application of novel materials with extremely high sorbent capacities, this technique can be applied with a significant efficiency. In this context, the use of nanosorbents has emerged as a promising alternative for the cleanup of As-contaminated water (particularly, zero valent and iron oxide nanoparticles), due to their distinctive and advantageous properties, such as the small size, high surface area, and high reactivity due to the large number of sorption active sites [11, 12].

On the contrary, the application of specifically “tailored” technosols (in this case, composed of soil components and nonharmful residues with sorption capacities for specific contaminants) has shown successful results on the restoration of degraded mining areas contaminated with a wide variety of trace metals and metalloids [13]. One of the main advantages of the use of “tailored” technosols is managing the increasing production of (nonharmful) residues, taking advantage of their properties to adsorb contaminants [14].

Adsorption is a very complex water remediation process that depends on a wide variety of parameters, including (a) water properties, such as pH, redox potential, and ionic composition of water (other ions present in water can compete with As for sorption sites); (b) As properties (particularly, the speciation or oxidation state); and (c) sorbent properties, such as the surface area, the size, the reactivity, and the number of sorption active sites [3]. Thus, modelling can be a very useful tool to help the researchers to design dynamic water remediation processes based on sorption, and models may be used to determine the amount and lifetime of the sorbent needed according to the volume and As concentration of the contaminated water to treat.

Within this context, the objective of the present work was to characterize the arsenic sorption capacity of a tailored technosol composed of a ferralsol with 25531 mg/kg of Fe (2% w/w, associated with Fe and Mn oxides) and multi-component nanoparticles synthesized from orange peel residues. An adsorption model was also developed to simulate the real application of those sorbents to the remediation of mine drainage water rich in As. The model proposed will allow scaling-up the remediation procedure from the laboratory to field application in a gold mining area in Portovelo (South Ecuador).

2. Materials and Methods

2.1. Soil and Water Sampling and On-Site Characterization.
Water samples (acid discharges) were collected at three discharges of artesian gold-processing plants located in the border of the Amarillo River (Figure 1), Portovelo town, Ecuador, the main collector of liquid wastes from the gold-processing artesian plants. pH, Eh, and electric conductivity were measured on-site using portable equipment (Mettler Toledo). Three zones were chosen for soil sampling taking into consideration their beneficial properties and the vicinity of the study area. All soil samples had a high content of iron oxides.

2.2. Soil Characterization.
Chemical characterization of Cu, Cd, Zn, Cr, Pb, As, and Fe in soil was carried out by sequential digestion using methods 3111-B and 3114-C of the Standard Methods, with atomic absorption spectroscopy, AAnalyst 800 Atomic Absorption Spectrometer (Pelkin Elmer), using the air-acetylene flame method. Determination of arsenic was made with the FIAS injection system coupled to the atomic absorption spectrophotometer AAnalyst 800 Atomic Absorption Spectrometer (Pelkin Elmer).

Values of pH of soil were determined using the potentiometric method. For texture of soil, percentages of clay, silt, and soil sand were quantified, and to determine the granulometry of the soil, the method ASTM D422-6 was applied.

2.3. Synthesis of Nanoparticles. Fabrication of multicomponent nanoparticles (MCNPs) was achieved by mixing 5.0 mL of 1.0 M FeCl3·6H2O and 3.5 mL of 1.0 M Na2SO4 and purging the content with nitrogen for 15 min in a 1000 mL flask. Then, 20 mL of 0.8 M NaBH4 and 20 mL of orange peel extract were added as reductants. The mixture was homogenized with slow shaking at 30 rpm during 15 min at room temperature. During the evolution of the reaction, a color change from yellow to black was observed indicating the formation of MCNPs.

2.4. Preparation of Technosol. The technosol was prepared mixing 99.95% of a clay-silty soil (iron-rich soil) and 0.05% of dried MCNPs.

2.5. Sorption Isotherm Tests. Arsenic sorption was performed in batch tests using 5 g of technosol (4.9875 g of soil and 12.5 mg of nanoparticles). The sorbent material was mixed with 100 mL of artificially contaminated water, containing 10.9, 16.5, 80.6, 346.4, 2732.5, and 5286 μg/L of arsenic at pH 7. After 24 hours of agitation at 40 rpm, the treated samples were centrifuged and filtered, and the supernantant was analyzed for free arsenic using the same method as for water samples. The amount of arsenic sorbed on the technosol was determined by mass balance using the following equation [15]:

\[ q = \frac{V}{m}(C_i - C_f), \]

where \( q \) is the concentration of As in the soil, \( V \) is the volume of water contaminated with As, \( m \) is the mass of soil, and \( C_i \) and \( C_f \) are the initial and final As concentrations, respectively.
2.6. **Kinetic Test.** The kinetics was performed with 5 g of technosol and 100 mL of artificially contaminated water at pH 7 and 20°C. During the test, two milliliters of the treated aqueous phase were centrifuged and filtered with 0.2 μm PVDF filters for arsenic analysis.

2.7. **Chemical Analysis.** Heavy metals were analyzed using an atomic absorption spectrometer AAnalyst 800 (Perkin Elmer) (AA800) following standardized methods (i.e., Cu, Cd, Zn, Cr, Pb, Fe, and As). For arsenic analysis, AA800 was coupled with a FIAS 110 (Flow Injection for Atomic Spectroscopy System) and the method 3114-C was used.

2.8. **Model Formulation Based on System Dynamics Methodology.** The system under study can be considered as a suspended-bed mixed reactor where the contaminated mine water enters and stays in contact with the sorbent until the complete water cleanup. Figure 2 shows the stock-and-flow diagram constructed using Vensim software (Ventana Systems, Inc.).
Based on system dynamics methodology, two stocks (or variables where positive or negative accumulation takes place; represented by squares) were considered within the reactor system: “As free” (i.e., mass of As remaining in the residual water which enters the reactor) and “As sorbed” (i.e., mass of As retained by technosol = soil + nanoparticles). The flows that modified those stocks (represented as double-lined arrows) are as follows: “water discharge” (discharge of As-contaminated water; inflow to “As-free” stock), “soil sorption,” and “nanosorption” (As sorption on soil and on nanoparticles, resp.; outflows from “As-free” stock and inflows to “As sorbed”). Note that there is no outflow from the system, since during the simulation time the reactor was not emptied. The rest of variables, namely, auxiliary variables, were connected to the variables that help to calculate using single arrows. “INITIAL TIME,” “FINAL TIME,” and “Time,” intrinsically included in the modelling were considered shadow variables and were introduced in the model for the calculation of specific flows. The auxiliary parameters to simulate the system were estimated from field observations and calculations (As concentration in drainage water and the discharge inflow) and those calculated from the laboratory experiments described before (soil and nanoparticle mass and \( Q_{\text{max}} \) and \( K \) of soil and nanoparticles) (Table 1).

Furthermore, several assumptions were considered to formulate the model. (i) The system is perfectly mixed, and therefore, the concentration of As in water is homogenous in each water discharge, and all sorbent particles are in intimate contact with water. (ii) The discharge of residual and drainage water (“water discharge”) in the mine was supposed to be discontinuous and should be modelled as a “binary” discharge (presence or absence of inflow to the reactor). When a discharge of water occurs, the inflow to the reactor was supposed to be constant. According to field observations of the mine activity, the discharge of residual water occurs each week (each 168 h), and the water enters the reactor continuously for only 72 h (corresponding also to the “discharge time”) at a constant flow of 3 L/h (i.e., 216 L of contaminated water entered the tank at each discharge), after which it stops for 4 days, completing a discharge cycle of one-week duration. (iii) The maximum capacity of the reactor tank was assumed to be 1000 L. Therefore, it can hold a volume of water corresponding to maximum four consecutive discharge cycles (i.e., 864 L), then, during 4 weeks (672 h, which corresponds to the final time of the simulation). After a month, the reactor should be emptied and the system was supposed to be discontinuous and should be modelled as a “binary” discharge (presence or absence of inflow to the reactor). When a discharge of water occurs, the inflow to the reactor was supposed to be constant. According to field observations of the mine activity, the discharge of residual water occurs each week (each 168 h), and the water enters the reactor continuously for only 72 h (corresponding also to the “discharge time”) at a constant flow of 3 L/h (i.e., 216 L of contaminated water entered the tank at each discharge), after which it stops for 4 days, completing a discharge cycle of one-week duration. (iii) The maximum capacity of the reactor tank was assumed to be 1000 L. Therefore, it can hold a volume of water corresponding to maximum four consecutive discharge cycles (i.e., 864 L), then, during 4 weeks (672 h, which corresponds to the final time of the simulation). After a month, the reactor should be emptied and the water inside should be completely cleaned up. (iv) Sorption on technosol particles (including soil and nanoparticles) followed the Langmuir sorption model, and the partial derivative of that equation with respect to time was used to simulate sorption flows (Table 1). (v) A first order exponential delay was supposed to occur at the first moments of the contact between the contaminated water and the sorbent; that is, sorption is not immediate and is delayed while the complete contact between the contaminants and the sorbent...
3. Results and Discussion

Mine drainage samples collected near to the Amarillo River presented a pH of 8.56 and an Eh of −107.50 mV. Under those conditions, arsenic is probably precipitating into the river basin. However, the variation of these parameters can easily lead to the release and mobilization of As to water, what is evidenced by the variation of As concentrations from 4.80, 8.60, and 27.46 µg/L. Aqueous samples had a very high EC (964 µS/cm). A clay-silty soil with pH of 5.34 and 20.25 meq/100 g soil of cation exchange capacity was chosen for preparing the technosol. Concentrations of metals in soil are shown in Table 2. Important to note that iron content was 25531.24 mg/kg with 432.88 mg/kg of Fe associated with oxides (i.e., 2% w/w). Sorption isotherm of the technosol is shown in Figure 3. It is observed that experimental data fit very well with the Langmuir model. The calculated Langmuir isotherm parameters are $Q_{\text{max}} = 7184.66$ mg/kg and $K = 7.5$ L/mg. Results of the kinetic tests of arsenic are shown in Figures 4(a) and 4(b). The experimental values fit a pseudo-second-order reaction shown below:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (2)

where $k_2$ (g/mg/min) is the pseudo-second-order rate constant, $q_e$ is the amount of arsenic sorbed (mg/g) at the equilibrium, and $q_t$ is the amount of the sorption at any time $t$ (min). Good removal efficiency for arsenic was achieved with technosol (124 mg-As/kg) even though these tests were performed with heavy metals as competitor elements.

The fitting curve exhibits a good linearity with a correlation coefficient around the unity as shown in Figure 4. This trend suggests that chemical sorption is the main mechanism for the removal of arsenic from the mine drainage [16, 17].

3.1. Model Simulations. The sorption model was simulated using the equations and parameters described in Table 1. The model was simulated from 0 (“INTIAL TIME”) to 672 h (4 weeks) (“FINAL TIME”), and the variation of As mass in water (“As free”) and As mass sorbed on the technosol (“As sorbed”) was recorded. Note that these data are presented in Figure 5 as the concentration of As on the accumulated water in the reactor (mg/L) and the concentration of As sorbed on the technosol (mg/kg).

It can be observed that the concentration of As in water (“As free”) was decreased very fast and was maintained at approximately 0.17 mg/L at the first moments of the simulation (until 168 h, one week, during the first step of water discharge) (Figure 5), from when the concentration of As in water started to increase (up to 1.61 mg/L during the second discharge of water), following the discontinuity of the cycles of water discharge considered in the model (Table 1). On the contrary, a rapid increase of As concentration on the sorbent could be observed, but it started to slow down after the first week of treatment, mainly due to the saturation of the sorbent. Thus, near 96% of As of the first discharge of contaminated water was eliminated by sorption on technosol. The level of As in water after the treatment of two water discharges (up to 336h) was observed to be very high (1.61 mg/L), indicating that the second discharge of water cannot be treated completely with the same sorbent under the same conditions to reach our final quality objectives.

Since both soil and nanoparticle sorption followed the Langmuir sorption model, “soil sorption” and “nanosorption” flows presented very similar patterns (Figure 6). It can be observed that As sorption increased until a maximum reached around the first 25 h, from when sorption slows down, indicating the beginning of the saturation of the sorbent sorption sites.

Therefore, we can assume that considering the contaminant concentration and inflow to the reactor (Table 1), the amount of sorbent included in the reactor (5 kg of soil and 0.025 kg of nanoparticles) will work for one entire contaminated water discharge (i.e., during the first cycle of 168 h) reducing the concentration of the effluent to nearly 0.17 mg/L. After that moment, the sorbent should be renovated at each discharge under the same operational
conditions; that is, the sorbent should be renovated 4 times, with each weekly water discharge, after emptying the tank after 4 weeks.

Considering those initial simulations, the model can be used to anticipate the behavior of the system if any of the initial conditions changed. Figure 7(a) shows the simulations of the behavior of the sorption process (in this case, the modification of the concentration of arsenic in water, “As free”) when modifying the concentration of As in the water discharge (initially, 4.5 mg/L) to a lower and a higher value, respectively, 2 and 6 mg/L; and Figure 7(b) shows the response of increasing the mass of sorbent to 10 and 20 kg of soil + 0.05 and 0.1 kg of nanoparticles (i.e., twice and four times the initial value 5 kg of soil and 0.025 kg of nanoparticles, always changing one parameter at a time).

The simulations presented in Figure 7(a) indicate that if the concentration of As in the inflow decreased to 2 mg/L, it will take more time for the sorbent to saturate. Indeed, the concentration of As in the treated water was under 0.10 mg/L until 338 days (approximately 2 weeks, i.e., 2 discharge cycles), from which it started to increase reaching a maximum of 0.57 mg/L at the end of the simulation. Therefore, in this case, the renovation of the sorbent could be done each 2 weeks (i.e., only 2 renovations during 4 weeks, after emptying the tank). On the contrary, at a higher As concentration (6 mg/L), the saturation was occurring very fast, and only half of the As entering can be eliminated during the first water discharge (up to 168 h). This indicated that under our specific conditions (water inflow and mass of sorbents), the reactor cannot efficiently clean up water contaminated with higher concentrations than that initially considered.

The simulations of As concentration in water, varying the mass of sorbent present in the reactor (Figure 7(b)), indicated that an increase in the mass of sorbent will decrease the amount of As present in water (i.e., that the
amount of As sorbed increased). Also, the moment from when the sorbent started to saturate (and therefore the time of sorbent renovation) was longer when a higher mass of technosol was present: technosol started to be saturated at 168 h with 5 kg of soil + 0.025 kg of nanoparticles, at 192 h with 10 kg of soil + 0.05 kg of nanoparticles, and at 338 h with 20 kg of soil + 0.1 kg of nanoparticles. These results indicated that it is preferable to maintain a low proportion of sorbent in the reactor and carry out sequential renovations than increasing the amount of sorbent present. In the case of the initial simulations (Figure 5), the results indicated the need of renovating the sorbent weekly with each water discharge (i.e., 4 times before emptying the tank), which is a total of 20 kg of soil + 0.1 kg of nanoparticles. However, if that amount of soil was introduced from the beginning of the treatment (Figure 6), the model predicted that the sorbent should be renovated after 2 weeks (two discharge cycles). This could be caused by a hindered and slower sorption process by decreasing the proportion of water/soil (the contact between As-contaminated water and all the possible sorption sites was more difficult because of a hindered accessibility).

4. Conclusions

Technosol prepared with 99.95% of soil and 0.05% of nanoparticles showed a good efficiency for removing arsenic from mine drainage (124 mg As/kg). Soil rich in iron (25531.24 mg/kg) could be the main component of the technosol for removing arsenic; however, nanoparticles may also play an important role in the formation of precipitates or inner sphere complexes with the metalloid. The process of arsenic sorption using a technosol showed a linear retention behavior approximately in first 10 min of treatment and reached steady state after 50 min. Results of isothermal sorption fitted very well with the Langmuir model, and the maximum sorption capacity of the technosol is 7184.66 mg/kg.

A model of As retention from mine waters through the application of technosol, prepared with soil and MCNPs, was developed using the software Vensim PLE. It achieves elimination of more than 96% of As in water entering the remediation tank at each water discharge (216 L), using only 5 kg of soil and 0.025 kg of nanoparticles.

Further investigation is required to include new parameters to the model such as pH, influence of As speciation, and impact of other contaminants or other ions, which could compete for sorption sites. Furthermore, field experiments should be carried out to validate the model and test the real effect of soil + nanoparticles mixtures on arsenic sorption. This will help us to determine if sorption capacities are simply additive, synergistic, or even antagonistic.

Data Availability

Researchers who require the data of this research can contact the corresponding author.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References


