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REMEDICATION OF AS - COMPARISON OF TWO DIFFERENT ELECTRODIALYTIC CELLS AND APPLICABILITY OF TREATED SOIL IN BRICK MATERIALS

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Abstract

An electro dialytic process (ED) was applied to clean-up an industrial soil from wood preservation polluted with arsenic (As). Two different cell-conditions were tested, in a 2-compartment cell set-up, using stirred soil suspensions. The experiments were carried out during 14 days, applying a constant current intensity of 5 mA. In addition, after ED a possible reuse of the soil for clay bricks was tested. The best result in the removal of As from suspended soil was obtained when suspended soil was placed in cathode compartment and the pH of the anode was maintained alkaline (pH \approx 10). This setup showed efficiency to remove 74% of As towards the anolyte. In the other setup the soil suspension was kept in anode compartment and the pH of the catholyte was maintained acid (pH \approx 2). This setup only achieved 3% of As removal towards the catholyte. These results showed that alkaline conditions favored the As desorption from soil to water and that the main transport mechanism was electromigration through the anion exchange membrane towards the anolyte. The treated soil proved to be an option to be used in bricks, which is also an advantage in the management process of soil residue.

1. Introduction

Arsenic (As) is one of the elements of major environmental concern due to its highly toxicity to all forms of the life [1]. Arsenic is a natural element with features intermediate between metals and non-metals [2]. Arsenic contamination has been reported worldwide and is cited as the most hazardous substance by the USA Agency for Toxic Substance and Disease Registry [3] and is considered one of the priority pollutants by the US EPA and the EU. The sources of As can be natural (i.e. through dissolution of As compounds adsorbed onto pyrite ores into the water by geochemical factors) and anthropogenic (i.e. through use of insecticides, herbicides, phosphate fertilizers, mining and smelting, industrial processes and coal combustion) [2]. These sources of As can damage the health of the surrounding environments and increase the risk of

soil, a serious environmental hazard. According to the U.S. Environmental Protection Agency the permissible limit of As in soil is 24 mg kg^{-1} .

Electrokinetic remediation (EKR) is a technique used to clean up waste matrices under the influence of an electric field generated between electrodes which induces different transport mechanisms (electroosmosis, electromigration and electrophoresis) and electrochemical reactions (electrolysis and electrodeposition) [4,5]. Electrodialytic remediation (EDR) adds the electrodialysis to the process, by the use of ion exchange membranes that act both as physical and chemical barriers. By the use of ion exchange membranes, the main direction for the electromigration within the polluted matrix is determined to be out of the soil. The EDR was developed at the Technical University of Denmark in 1992, was patented in 1995 (PCT/DK95/00209), and has proven to be efficient in removing a wide range of contaminants, such as heavy metals [6], polycyclic aromatic hydrocarbons [7] and polychlorinated biphenyls [8] from suspended soils. The success of EDR is reported to be dependent on the specific site conditions, including the type and amount of contaminant, soil characteristics, organic content, as well as experimental conditions such as stirring and pH [5,9].

In the present study, the ED process was applied to a soil contaminated with As in a two-compartment cell design (2C). The feasibility of inserting the soil suspension in the anode or cathode compartment together with pH adjustment (alkaline in anolyte and acid in catholyte). The potential reuse of EDR treated soil in brick was also assessed.

2. Materials and methods

2.1 Experimental soil

The soil used in the present study was sampled from Collstrop site, located in an industrial area in Denmark. Collstrop soil is highly polluted with As provided by wood preservation activities.

2.2 Soil characteristics

The soil was analyzed for the following parameters: As concentration, pH, conductivity, carbonate and organic matter content. Laser and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis was also carried out.

Arsenic concentration was determined according to the Danish Standard 259 [10]. Briefly, 1 g of dry soil was extracted with 20 mL HNO_3 and heated at 200 kPa (120 °C) for 30 minutes. The liquid phase was separated from the solid particles by vacuum filtration (0.45 μm filter) and diluted till 100 mL. Arsenic concentration was determined by inductively coupled plasma - atomic emission spectrometer (ICP-AES).

Soil pH was measured by suspending 5 g of dry soil in either 20 mL 1 M KCl or in distilled water and measured using a Radiometer pH electrode. Conductivity was measured using a CMD2010 conductivity meter after suspending 10 g of dry soil with 25 mL of distilled water followed by 30 min of agitation on a shaking table.

Carbonate content was determined volumetrically by the Scheibler method (2.5 g of soil reacting with 20 mL of 10% HCl). The amount was calculated and all the present carbonate

was assumed as calcium carbonate. Organic matter was determined by loss on ignition after 1 h at 550 °C.

SEM analysis was performed on the untreated and treated soil.

2.3 Desorption of heavy metals as a function of pH

The effect of pH in As desorption was assessed by suspending 2.5 g dry soil in 25 mL of HNO₃ or 25 mL NaOH with concentrations ranged between 0.01 M to 1.0 M followed by shaking during one week. The samples were made in duplicate. Extractions in distilled water were made as reference. After desorption tests, samples were filtered (0.45 µm), pH measured and As determined by ICP-AES.

2.4 Experimental setup

A two compartment cell set-up (2C) was tested varying the position of contaminated soil (Figure 1A and 1B). The cells were made from polymethyl methacrylate. The compartment where the suspended soil was placed had a L=10 cm and the electrolyte compartment a L=5 cm. Each cell had an internal diameter of 8 cm. Ion exchange membranes separating the central compartment from the electrode compartments were from Ionics, anion exchange membrane (AEM, AR204 SZRA B02249C) and cation exchange membrane (CEM, CR67 HUY N12116B). The electrodes were platinized titanium bars, with a 3 mm diameter (Bergsøe Anti Corrosion A/S, Herfølge, Denmark). A power supply (Agilent E3612A) was used to maintain a constant current. The fresh electrolyte (500 mL of 10⁻² M NaNO₃) was circulated in a closed system ("Pan World" magnetic pumps from Plastomec Magnet pump model P05). The electrolyte was conditioned at the beginning of the experiment, and whenever necessary, to achieve an acidic (pH=2) or alkaline pH (pH=10), depending on the applied treatment.

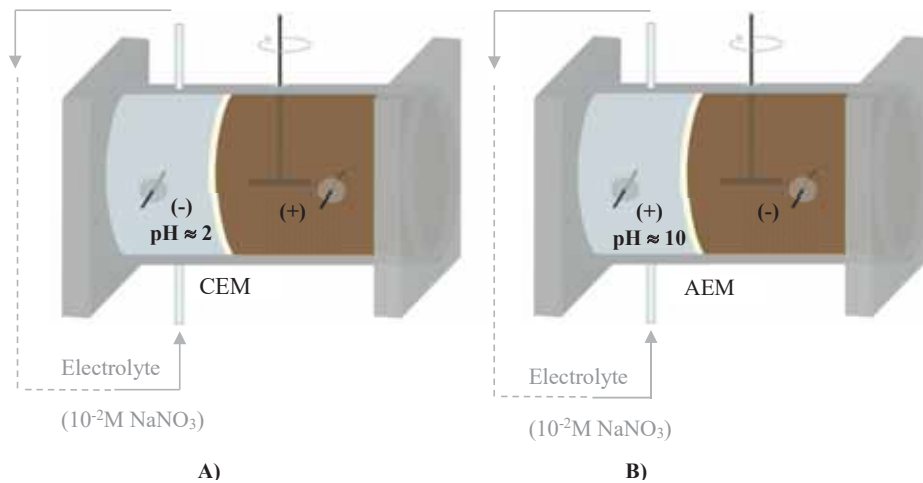


Figure 1 - Schematic presentation of the laboratory 2C cell used in experiments: A) soil suspension in the anode compartment, CEM, and catholyte pH adjusted to 2; B) soil suspension in the cathode compartment, AEM, and anolyte pH adjusted to 10.

2.5 Electrolytic experimental conditions

Two electrolytic experiments were performed (Table 1). One cell compartment was filled with 50 g of soil and 350 mL of distilled water corresponding a liquid/solid ratio of 7. In treatment 1 (T1) the suspended soil was kept in the anode compartment, a CEM was used to separate compartments, catholyte pH was adjusted to 2 throughout the treatment (Figure 1A). In treatment 2 (T2) the suspended soil was kept at the cathode compartment, an AEM was used to separate compartments, and anolyte pH was adjusted to 10 (Figure 1B).

The voltage between working electrodes, conductivity and pH of both cell compartments were measured twice a day. The pH of the electrolytes was adjusted whenever needed by addition of HNO_3 (1:1) and NaOH (6M).

At the end of the ED experiments, the suspended soil was drained using filter paper aiming to separate the solid from the liquid phase. The water content was measured. The soil solution was then filtered ($0.45 \mu\text{m}$) and the solid phase dried until constant weight (105°C), crushed by hand and extracted (analysis description in section 2.2). Membranes and electrolytes were soaked in 1 M and 5 M HNO_3 , respectively, for 24 h to release metals and the liquid phase filtered ($0.45 \mu\text{m}$). The As concentration in the different parts of the cell (soil, soil solution, electrolyte, membrane, electrodes) was then determined by ICP-AES.

Table 1: Experimental conditions of the treatments.

| Treatment (T#) | Cell Type (see Figure 1) | Soil compartment | Liquid/Solid (mL/g) | pH of electrolyte | Time (days) | Current (mA) |
|----------------|--------------------------|------------------|---------------------|-------------------|-------------|--------------|
| T1 | A) | Anode | 7 | 2 | 14 | 5 |
| T2 | B) | cathode | | 10 | | |

2.6 Brick pellets

Pellets were made with EDR treated soil (T2) in order to study the suitability for further reuse in ceramics. Different amounts of soil were joined with pure clay (yellow wienerberger from soft-molded bricks) to test the stability of the pellets. The samples had a total weight of 2 g and 10 % of distilled water was added. Brick pellets (2 cm in diameter) were made in a form and pressed to pellets in an Instron 6022 tester at 3.14 kN. The wet pellets were weighted before being heated at a furnace with a gradual temperature increase (until 1025 °C) where they were kept by 1 h. After cooling to room temperature, the fired pellets were weighted and characterized by porosity, density and leaching (Section 2.6.1.).

2.6.1 Parameters of brick pellets

Aiming to determine porosity and density, the brick pellets were placed in a desiccator under vacuum for 3 h (100 N m^{-2}). After this time, the desiccator was filled with deionized water and pellets left for 1 h. The desiccator was then opened to the air during 1 day. The pellets were weighed over and under the water [11]. The leaching of As was also tested according to DS/EN 12457-3 [12]. The fired pellets were crushed and distilled water was added, liquid/solid ratio of 2. The suspension was agitated for 16 h and the liquid phase separated from the solid particles by vacuum filtration ($0.45 \mu\text{m}$). As concentration was determined by ICP-AES.

3. Results and discussion

3.1 Soil characteristics

The characteristics of the soil are listed in Table 2. The soil has a sandy loam texture. The initial concentration of As was 594 mg/kg. Like was expected according with literature [13], the pH of the soil in distilled water was of 6.3 whereas pH in KCl was of 5.4. The conductivity of the soil was of 0.2 mS/cm.

Table 2: Initial characteristics of Collstrop soil.

| Type of soil | As (mg/kg) | pH _{KCl} | pH _{H2O} | Conductivity (mS/cm) | Carbonate content (%) | Organic matter (%) | Grain size distribution (%) | | |
|--------------|------------|-------------------|-------------------|----------------------|-----------------------|--------------------|-----------------------------|------|------|
| | | | | | | | Clay | Silt | Sand |
| Sandy Loam | 594 ± 100 | 5.4 ± 0.05 | 6.3 ± 0.3 | 0.2 ± 10 | 2.2 ± 0.04 | 19 ± 1 | 6 | 43 | 51 |

3.2 Desorption of As as a function of pH

The concentrations of As extracted from soil at different pH values is shown in Figure 3. In distilled water 61 mg/kg of As was extracted.

The results showed that As is desorbed from soil under highly acid ($0.1 < \text{pH} < 0.4$) and alkaline ($8 < \text{pH} < 13$) pH values. The lower pH values ($0.1-0.4$) released ≈ 514 mg/kg of As whereas the higher pH (≈ 13) released 533 mg/kg.

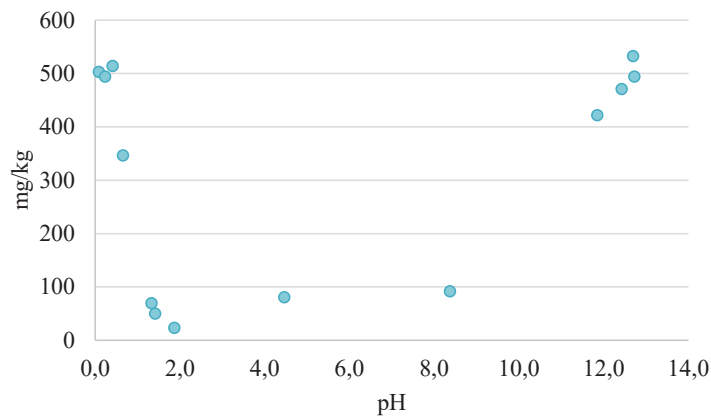
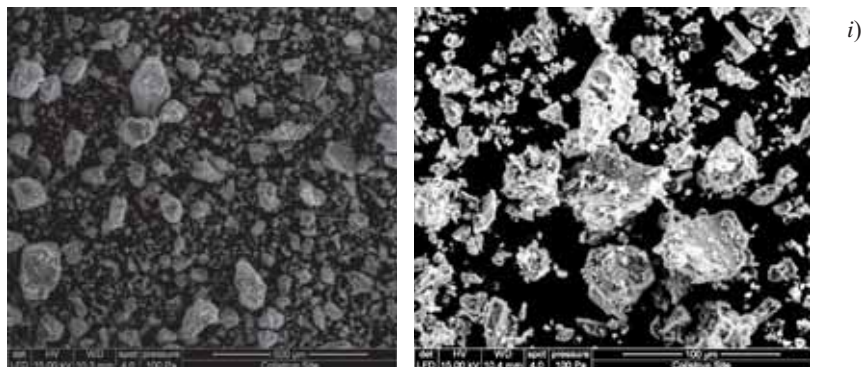


Figure 3 - Arsenic desorption as a function of pH.

3.3 SEM analysis

Figure 2 shows the differences in soil particles before and after EDR treatments. The largest changes in shape/morphology occurred in T2 where the suspended soil remained in cathode. This means that higher pH values may have influenced particles distribution. In T2, the small particles are adsorbed onto the surface of the largest ones forming aggregates (Figure 2 *iii*) whereas before EDR treatment (Figure 2 *i*) or in T1 (Figure 2. *ii*) the small particles are separated from the other particles.



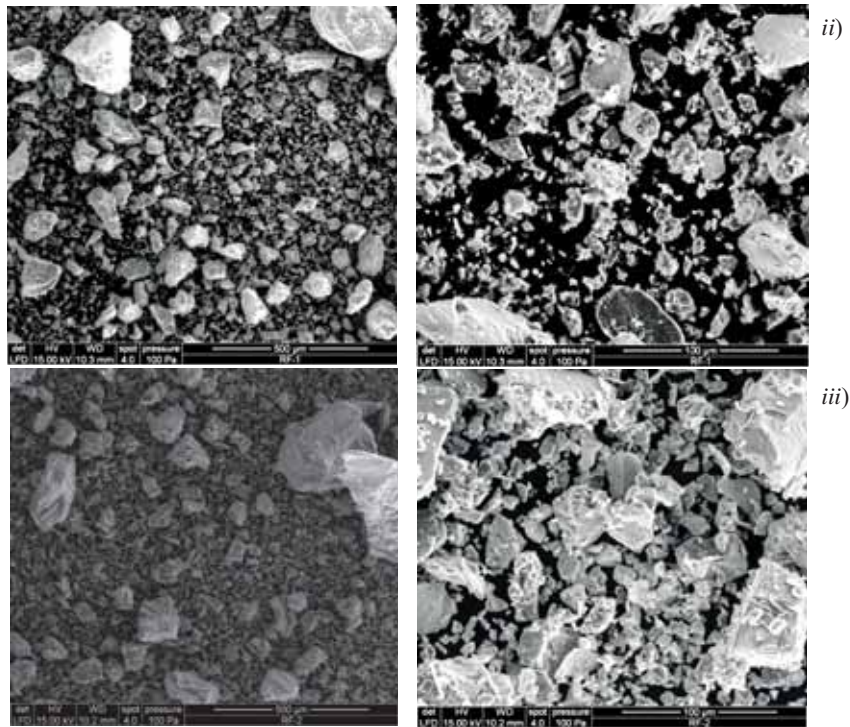


Figure 2 - SEM picture of Collstrup soil before EDR (i) and after EDR treatments under acid, T1 (ii) and alkaline, T2 (iii) conditions.

3.4 Electrolytic experiments

3.4.1 General results

The voltage, conductivity and pH of the soil suspension during the EDR experiments are shown in Figures 3, 4 and 5, respectively.

Both treatments presented a similar behavior in voltage. From the beginning of the treatment until day 8, the voltage gradually dropped followed by a stabilization tendency. This pattern is probably because ions from electrolysis at the electrodes (H^+ or OH^-) decreased the conductivity in the suspension in the first phase.

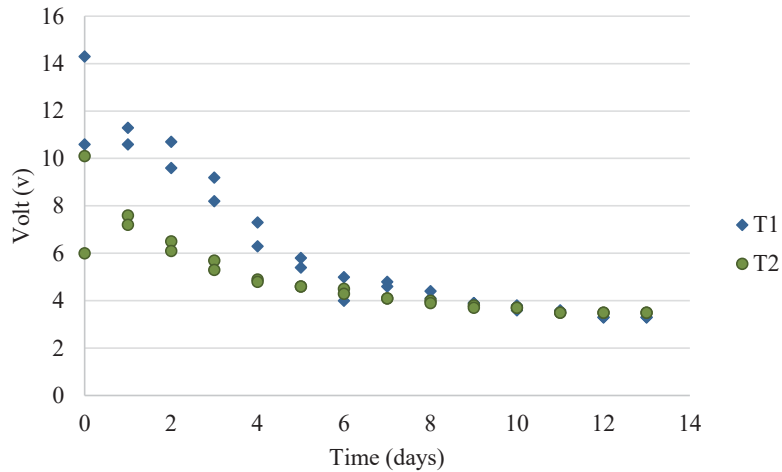


Figure 3 - Voltage over the cells during the EDR treatment

The electrical conductivity (Figure 4) increased in both treatments, corroborating voltage decrease due to a decreased electrical resistance (e.g. due to H^+ and OH^- produced from water electrolysis).

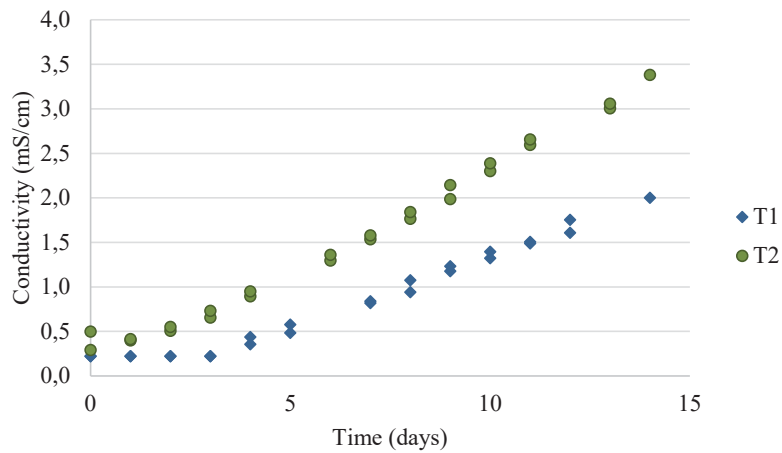


Figure 4 - Conductivity variation in the soil suspension during the EDR treatment.

The pH in the soil suspension is shown in Figure 5. When the soil suspension was placed in the anode (T1) the pH decreased until ≈ 2 whereas when placed in the cathode (T2) it increased to ≈ 11 . The pH changes are due to water electrolysis, resulting in the formation of H^+ in the anode and OH^- in the cathode compartment.

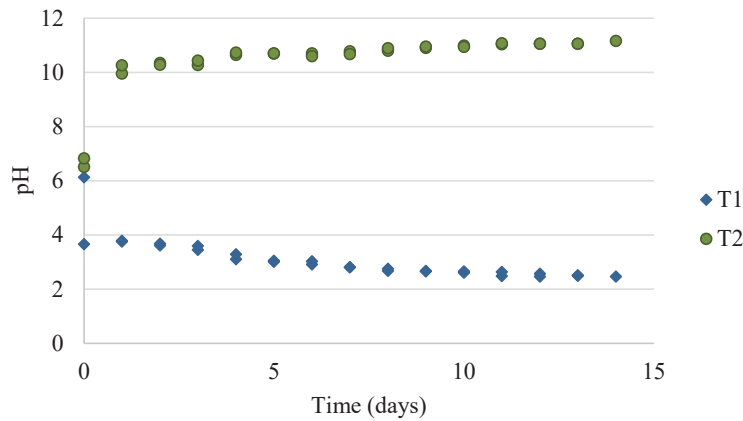


Figure 5 - pH variation in the soil suspension during EDR treatment.

3.4.2 Electrodialytic arsenic removal

An overview of As removal after EDR treatment is given in Table 3. The removed As is defined as the element found in the electrolyte compartment and in the ion exchange membrane. The removal percentage is calculated dividing the mass of element removed (electrolyte + membrane) by the final mass found in it (soil + soil solution + electrolyte + membrane). The mass balance ranged between 77% and 99%. The As distribution in the different parts of cell after the ED process is shown in Figure 6. Also, the distribution pattern of As differed significantly when compared with acid and alkaline pH cell-conditions.

Table 3: Overall results of EDR of soil.

| Treatments (T#) | Removal efficiency (%) | Amount removed (mg/kg) | Mass balance (%) |
|-----------------|------------------------|------------------------|------------------|
| T1 | 3 | 31 | 99 |
| T2 | 74 | 502 | 77 |

The EDR with acid cell-conditions (T1) resulted in 3% of As removal, corresponding to 31 mg/kg whereas the in the presence of alkaline cell-condition (T2) 74 % of As were removed towards the anode compartment corresponding to 502 mg/kg of As.

The soil suspension in the anode compartment (T1) was subject to oxidizing conditions and due to the CEM, only the movement of cations towards the catholyte was allowed which, in turn, was acidic due to pH adjustment (neutralization of OH⁻ by H⁺ addition). At the final pH achieved in anode compartment of T1 (pH 2), As presented a weak soil desorption (see Figure 6) but also the typical negative charge at this pH ($H_3AsO_4 + H_2O \rightleftharpoons H_2AsO_4^- + H_3O^+$, pka=2.20) limits its migration through CEM towards catholyte, as the prevailing As species is uncharged. Arsenic desorption is highly dependent on pH and redox potential conditions which influences

its chemistry and composition [14]. Arsenic is a metalloid, which the primary forms in soils are arsenate-As(V) (H_2AsO_4) in oxidizing environment and arsenite-As(III) (H_3AsO_3) in reducing environments [15]. The experiments made so far were conducted in open laboratory cells with stirring and As(V) is expected to be the primary form and the main stable specie in an oxidizing environment. At neutral to acidic pH, the uncharged specie (H_3AsO_3) is expected to be present and therefore it will not be able to electromigrate [14]. From the 10% of As desorbed from soil to water (at pH 2), only 3% was able to pass through the CEM towards the catholyte. Ottosen et al. (2000) [14] reported that the efficiency of EDR treatment increased for As removal at low pH by adding an enhancement solution in order to desorb As from the soil.

The T2 treatment showed high (74%) As removal which is explained by the high As desorption at the pH achieved in the cathode compartment (pH 11). The presence of the AEM allowed the migration of As towards the anolyte, due to its negative charge under this chemical conditions. During the ED process, NaOH was added to the anolyte to keep the pH alkaline (≈ 10) at both sides of the membrane.

Despite the 74% of As removal in T2, the EDR treated soil still contained approximately 150 mg/kg of As. The application of this soil in construction material was tested aiming to optimize the re-use of industrial contaminated soil.

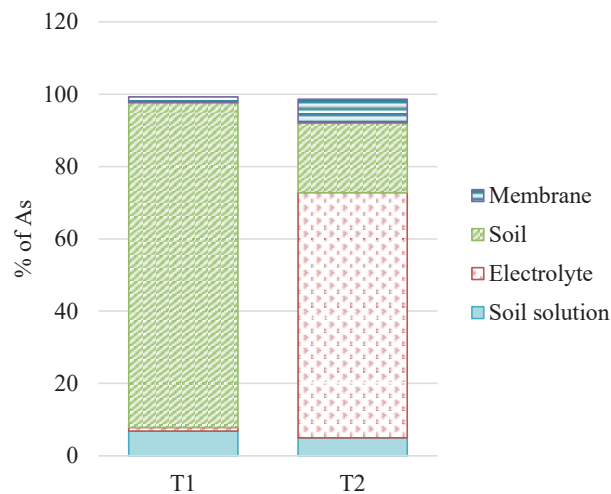


Figure 6 - Distribution of As after EDR treatments under acid, T1, and alkaline, T2, conditions.

3.5 Brick pellets

Figure 7 shows the brick pellets made with different amounts of soil. Due to the insufficient particle aggregation observed in pellets constituted by 100 % of treated soil, clay was joined at different amounts (50%, 75% and 90%). Clay minerals brought plasticity to the bricks showing consistence for all the tested percentages (50, 75 and 90%). Also, the brick pellets showed a different appearance (e.g. color) in accordance to the amount of clay.

The suitability of the brick pellets to be used as a constructed material was defined by porosity, density and As leachability (Section 3.4.1.; Table 4).

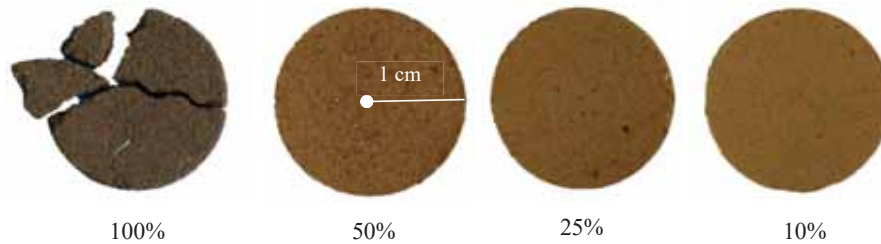


Figure 7 - Brick pellets with different amounts of soil (100 %, 50 %, 25 % and 10 %).

Porosity, which is directly related to the amount of water present, increased (between 27% to 34%) with the addition of clay to the brick pellets. This is explained by carbonates that decompose during sintering with gas releases conducting to pore formation in bricks [16]. Higher amount of pores means higher water absorption, which can reduce the brick resistance and durability. Regarding to dry matter density, the bricks showed to be very similar.

Leaching tests proved that As present in EDR treated soil was not released from the bricks. That means the use of treated soil as building material does not represent a risk to the environment, open a path to use this soil also for construction materials.

Table 4: Brick pellets parameters (mean \pm SD).

| Parameter | Amount of soil (%) | | |
|------------------------------|--------------------|-------------|---------------|
| | 50 | 25 | 10 |
| Porosity (%) | 27 \pm 1 | 32 \pm 1 | 34 \pm 1 |
| Density (mg/m ³) | 2.6 \pm 0.1 | 2.7 \pm 0 | 2.7 \pm 0.1 |
| Leaching (mg/kg) | ud | ud | ud |

ud: under value

4. Conclusions

This work showed that the electrode compartment where the contaminated soil is located, is determining the As removal due to the prevailing pH changes. The set-up with suspended soil in the cathode compartment showed 74% of As removal towards the anolyte. The high pH of the cathode compartment promotes As desorption followed by electromigration through the AEM. The EDR treated soil may be further reused in ceramic bricks (together with clay) without risk of As leachability.

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