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Soil Arsenic Removal by a Permeable Reactive Barrier of Iron Coupled to an Electrochemical Process

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This paper presents a study in which it is tested the effectiveness of zero-valent iron for arsenic remediation of a soil treatment leachate, experimental approach considers to investigate Fe° permeable reactive barrier performance for the treatment of arsenic polluted soil obtained from a mining area in central Mexico. By applying electro-remotion using a series of continuous-flow columns, allowed to obtain experimental data for critical parameters optimization to electro remediate the polluted soil, as electroosmotic flow occurs across the columns. A flow-through electrochemical reactor with major capacity was used to scale up the treatment. This experimental disposition was used with a soil sample in which porosity was enhanced by the presence of glass-fiber (relation of 1:1). Application of a 45 mA current during 7 h in an electrochemical treatment allowed obtaining arsenic removal efficiencies around 94 % at pH 7 and close to 41 % at pH 11. Polarography results indicates there is a strong interaction of $Fe(OH)_{3(s)}$ - AsO_4^{3-} in specific conditions, which results the highest electroremotion of As(III) at neutral pH.

Keywords: Electroremotion, barrier, iron, arsenic, soil.

1. INTRODUCTION

Pollution of soils with heavy metals constitutes a serious threat not only to biota but also to human lives, because those metals are characterized by high toxicity and non-biodegradability properties. Regarding soil trace metals, environmental issues often have been centered on ionic mobility; although, in a two phase system made of soil and liquid, solute movement through soil is a complex process that depends on the physical and chemical properties of both phases. Presence of arsenic (As) in polluted soils can be attributed to natural or anthropogenic sources, examples of the last are industrial activities like mining, smelting, combustion of arsenical coals, petroleum recovery involving extraction, refining, chemical production; as well as use of products like wood preservatives and biocides, fertilizers, animal food additives, and groundwater extraction with high-arsenic contents which is used for human consumption and irrigation [1].

Arsenic is a highly toxic metal and can lead to a wide range of human health problems, such as carcinogenic, mutagenic, and teratogenic effects. Arsenicosis symptoms include skin lesions (melanosis, keratosis) and skin cancer. Internal cancers, such as bladder and lung cancer, have also been associated with arsenic poisoning. Other examples of health problems are cardiovascular disease, respiratory problems, and diabetes mellitus [2 - 4].

The liothropic serie for soil ions retention in the cationic interchange process follows the order: $Fe^{2+} > Al^{3+} > Pb^{2+} > Cr^{3+} > Hg^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$ [5]. In the specific case of As, several methods have been applied for its recovery either from water or soil, examples are coagulation / filtration, active alumina, inverse osmosis, ionic interchange, nanofiltration, lime softening and permeable reactive barrier (PRB) for *in situ* treatment of liquid phase pollution [4, 6].

As polluted groundwater moves passively through the treatment wall, pollutants are removed by physical, chemical and / or biological processes, examples of these are precipitation, sorption, oxidation / reduction, fixation, and/or degradation. Barriers may contain agents that react with the pollutant of interest, and they can be placed either: a) in the path of contaminant plumes to prevent further migration; or b) immediately down gradient of the contaminant source to prevent plume formation [4].

The PRB technology can be employed to provide a long-term sink for metals and, at the same time, maintaining permeability and hydraulic connectivity between the contaminant plume and the reactive treatment zone [4]. The last condition is created by using different reactive materials like granular iron, active carbon, zeolites and amorphous iron oxides; contaminants passing through the permeable barrier can be degraded, adsorbed or precipitated, depending on the reactive material used; an example is the zero-valence granular iron which has shown being an efficient reagent for degradation of organic compounds and inorganic ions [7], other reactive metals are aluminum (Al) and lanthanum (La). If chemical reaction between As ions and reactive metals (Fe, Al, La) takes place in alkaline conditions then, a massive precipitation of arsenic hydroxides is developed inside the PRB [8].

It is assumed that arsenic removal reaction mechanism by metallic hydroxides, it depends on how molecular interactions between arsenic / water / hydroxide – clay occur, since the last one has an active surface, which allows to form complexes with soluble arsenic mainly by intermolecular chemical reactions of surface sites with arsenic, as well as the coordination of arsenic with water molecules [5].

For the adsorption mechanism to take place, arsenic must exert the highest possible contact across both phases, that is why the As – surface reaction is very important, since coordinated links should be constructed by hydrolysis, surface complexation, ligand exchange, hydrogen links and redox reactions in which are pH and electric potential dependence of the media [2].

In an clay-aqueous system, there are surface hydroxyl groups (S – OH), which can either win protons from water producing a positive charge to the surface; or lost protons, creating surfaces with a negative charge in which metallic ion coordination with water can be established. The adsorption of arsenates in clay – hydroxide system depends on the OH^- groups density, and their selectivity with respect of other anions in water.

In the specific case of the PBR, arsenic removal in alkaline water conditions occurs by the adsorption of arsenates onto previously adsorbed metal ions proceeding from other dissolved elements. This process produce ternary surface complexes which can be represented by the following reaction: $S - OH + M^{z+} + L + As^{+5} + 4HO^- \rightarrow S - O - ML_1^{(z-1)} + AsO_4^{-2} + 5H^+$, where the adsorbed metallic cation (M^{z+}) does not coordinate completely with surface ligands, and it reachs neutrality as it coordinates with other water dissolved ligands (L). In this case the cation (M^{z+}) makes the function of bridge between the negative surface site and the ligand (S - OM – L), which produces arsenate adsorption onto ligand L.

Another mechanism of PBR occurs if the ligand L, is adsorbed directly onto the coordination center S, and the cation accomplish the superficial coordination as follows: $S - OH + L + M^{z+} \rightarrow S - L - M^{(z+1)} + OH^-$, these kind of complexes are formed when ligand L forms a bridge between the surface and the cation (S – L – M), and over this the arsenate can be absorbed by electrostatic action in basic conditions: $S - L - M^{(z+1)} + 4OH^- + As^{+5} \rightarrow S - L - ML_1^{(z+1)} + AsO_4^{-2} + 4H^+$.

Important factors to be accounted in the adsorption process are: the surface charge, pH and interactions clay – hydroxide / arsenate, respectively. A consequence of the sorbent surface chemical transformations is that the sorbent can change their properties and their capacity to remove arsenic in the selected media.

Application of electro kinetics to polluted soil involves first installing trenches or wells that encompass the polluted soil zone. Electrodes are then inserted into these trenches or wells, and a low DC voltage gradient or current is applied across the electrodes. Electrodes should be strategically located, and they can work as cathodes (negatively charged) or anodes (positively charged). Under the induced electric potential, electro kinetic ion transport occurs by mechanisms such as electromigration, electro-osmosis, and electrophoresis; this type of transport makes the pollutant species to migrate through the soil towards either the cathodes or the anodes. During the electro kinetic process, or after the process has been completed, the contaminant – laden solution is collected from the electrode compartments / reservoirs, from these solutions pollutants can then be extracted using conventional wastewater treatment techniques [9].

Based on the electro-chemical background, and approach for As removal in a polluted soil of Mineral de Pozos, Guanajuato, was intended by electro-remotion coupled with the traditional chemical reaction of PRB using neutral and alkaline experimental conditions, which are enhanced by the presence of water electrolysis reactions: (1) oxidation in the anode, $2H_2O - 4e^- \rightarrow 4H^+ + O_{2(g)}$ and (2) reduction in the cathode, $2H_2O + 2e^- \rightarrow 2OH^- + H_{2(g)}$. Iron reaction can take place in acid condition (anodic region), as $Fe^{2+} + As^{3+} \leftrightarrow Fe^{3+} + As^{5+} + 3e^-$, and in basic condition (cathodic region), the redox reaction could be: $Fe(OH)_{2(s)} + H_3AsO_3 + 4OH^- + 1/2O_2 \leftrightarrow Fe(OH)_{3(s)} + AsO_4^{3-} + 3H_2O + e^-$.

2. MATERIAL AND METHODS.

A sample of sandy loam soil was collected near the outcrop of weathered igneous acid rock (rhyolite) at the town of La Merced, Mineral de Pozos, Guanajuato (21º12’17.9”N and 100º29´40.1”W). The sample was collected from the A-horizon (0 – 10 cm) using stainless steel shovels, and having weather conditions of 293 K with 30 Km / h wind speed.

Characterization of soil was done by Scanning Electron Microscopy (SEM) and Energy - Dispersive X-Ray Analysis (EDX) using 15 kV of voltage acceleration and 1000 *x* with a Jeol JSM-5400LV Scanning Microscope. Soil samples were prepared as follows: over the surface of a stainless steel piece was placed an emulsion of toluene and soil, then the organic solvent was evaporated and detection was made with infrared light, in this way it was possible to observe it with the SEM.

For assessing the mineralogical structure of iron oxide and soil, they were characterized by X-Ray Diffraction (XRD) with a Bruker AXS Advanced X-Ray Solutions Equipment. In all cases, samples were scanned from 30 to 90 of 2θ, and the scanning rate was fixed at 0.05°, 2θ / s.

Infrared spectroscopy technique was performed in a Thermo Spectra-Tech equipment with Zentrum program, analysis conditions considered an angle of 70 grades for incident light, and 0.5 g of polluted soil samples.

Sample characterization by Inductively Coupled Plasma (ICP) probes, required sample digestion which was made using 5 mL of 2 % HNO_3 solution, and deionized water up to a final volume of 50 mL of solution. The ICP equipment employed is a Perkin Elmer, Optima 3300 model with an absorbance of 193.69 nm.

The PRB experiments were made in a 2cm inner diameter by 10cm length glass columns equipped with stainless steel sampling ports. A layer of glass-fiber was used as a membrane in the bottom and top of the column, by doing so it is prevented soil or iron losses. Over the at the bottom, was placed a 5 cm soil layer, with a particle size of 2 mm, followed by 2 cm of dust form iron; and another layer of glass-fiber.

A peristaltic pump was used for recirculation of containing As solution.

The electro kinetic test setup used for this study consists of: an electro kinetic cell with two electrode compartments, each one contains a titanium electrode working as anode and cathode respectively; a soil porosity enhancement was obtained by mixing glass-fiber with soil in a ratio of 1:1 before placing it into de cell. A power source was used to apply a constant voltage to the electrodes and a multimeter was used to register both voltage and current flow through the soil sample during testing [10].

The electrokinetic cell has a capacity for 300 g of soil, it was made of acrylic material; a peristaltic pump allowed to introduce the water into the soil with an iron PRB.

Polarography experiments were made using a Polarograph Radiometer MDE150 interface TraceMater. The lineal voltammograms were obtained with 1 M HCl and 0.5 M Pirogalol (1:1 v/v), a potential window from -0.2 to -1.2 V at pH 7 and 11, a scan speed of 0.005 V s^{-1} and the deep time was 1s. The As (III) standard reactive was 15.3 ppm by the reducing environment, As(V) was not observed in these working conditions, since it is present only in oxidizing environments [3].

3. RESULTS AND DISCUSSION.

The sampling place for this study was located at the inactive mining area of Mineral de Pozos, Guanajuato, central part of Mexico. Six sandy soil samples were collected for chemical analysis.

ICP analysis was used to determine the concentrations of different ions in every sample. Analyzed elements were As, K, Mn, Li, Cu, Al, Fe, Si, Ca, Mg and Na. Table 1 shows the results of chemical analysis of the soil samples. As it can be observed, sample 4 had the highest concentration of As (731.71 mg As / Kg of soil), plus the highest concentration of Si and Mg too (68 372.65 and 11 435.43 mg / Kg of soil, respectively). So, sample number 4 was selected as the subject of study for As removal in the polluted soil of Mineral de Pozos.

Table 1. ICP analysis of the six samples took since sampling step in Mineral de Pozos, Guanajuato, México.

Sample	Identified Metallic Ions / mg metal by Kg sample										
	K	Mn	Li	Cu	As	Al	Fe	Si	Ca	Mg	Na
1	4419.12	239.95	225.96	20.40	41.79	58188.37	21795.64	45390.92	4339.13	2179.56	142.97
2	5960.00	324.00	396.00	73.60	584.00	20600.00	38400.00	34400.00	0.000	1534.00	134.60
3	4838.07	139.94	427.83	27.59	679.73	18512.60	23790.48	28988.41	0.000	7297.08	205.92
4	14634.15	268.29	271.09	39.98	731.71	43182.73	58776.49	68372.65	0.000	11435.43	77.97
5	5078.98	305.94	255.95	90.78	649.87	37792.44	45790.84	32593.48	0.000	3479.30	307.94
6	8018.40	129.17	291.94	32.99	415.92	54789.04	22995.40	41391.72	0.000	8778.24	347.93

On other hand, SEM has been widely used to characterize the morphology generated in field or laboratory column studies. In addition, discrete specific techniques, such as EDX in the SEM (Figure 1), allows to correlate pollutant data loads with a specific mineral fraction [11], by doing so results showed the presence of particle aggregates with a size less than 100 μm having a chemical composition of: Ca, O, Mg, Al, Si and K, whose relative percentage composition is 61.25, 1.97, 10.45, 22.83, 0.95 and 2.54 respectively. In EDX experiments compositional mapping was done to corroborate the general distribution for different elements in the sample, results showed a homogeneous coverage of the minerals over the soil sample (data not shown).

XRD technique was applied to the sample, it allowed to determine any As bearing mineral phase present in the soil, as arsenolamprite (Figure 2). In addition, the presence of sulfur, nitrogen, oxygen and methyl groups was verified by running an infrared spectrum (Figure 3), where the scissors vibration of $–SO_2$ were identified around 586 cm^{-1}. In the case of flexion vibration of –C-N- and –N-H, they were observed at 1190 and 3310 cm^{-1}, respectively. With respect to deformation and tension vibration of –C-OH, they were identified at 702 and 1060 cm^{-1}. The deformation of $–CH_2$ was showed at 1450 cm^{-1} and the tension of O-H between 3560 and 3730 cm^{-1}.

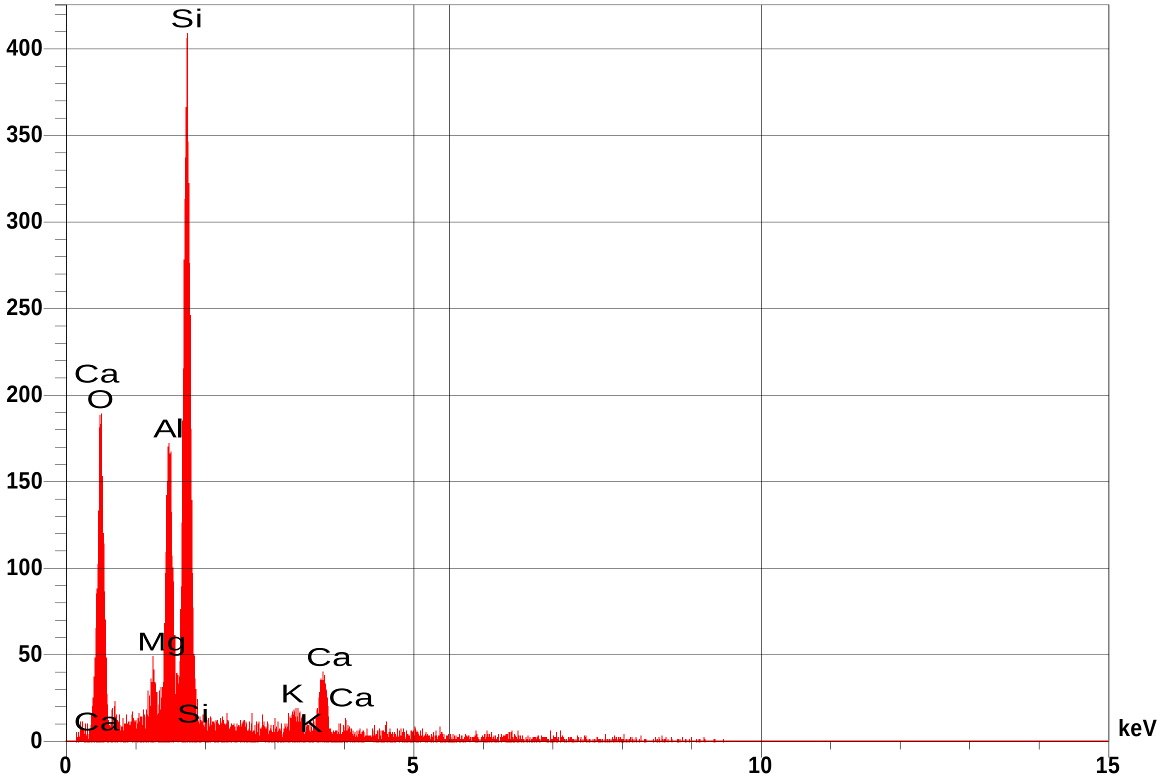

Figure 1. EDX analysis of polluted soil of Mineral de Pozos, Guanajuato, 15 kV of voltage acceleration and 150 *x*.

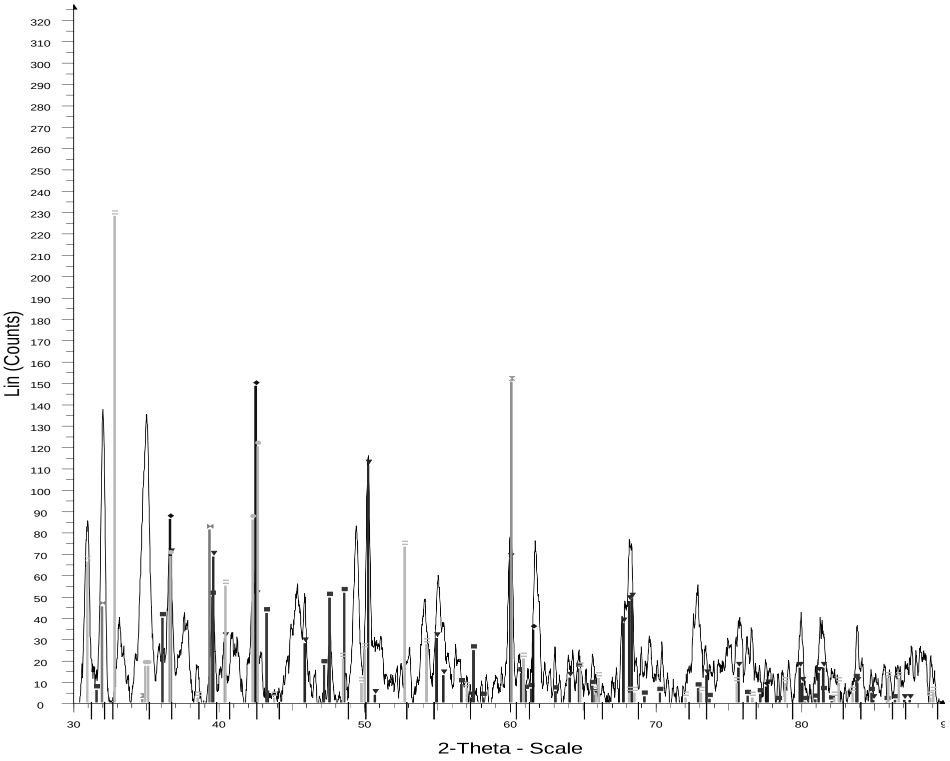

Figure 2. XRD analysis of the sample more polluted with arsenic, which shows the arsenolamprite (|).

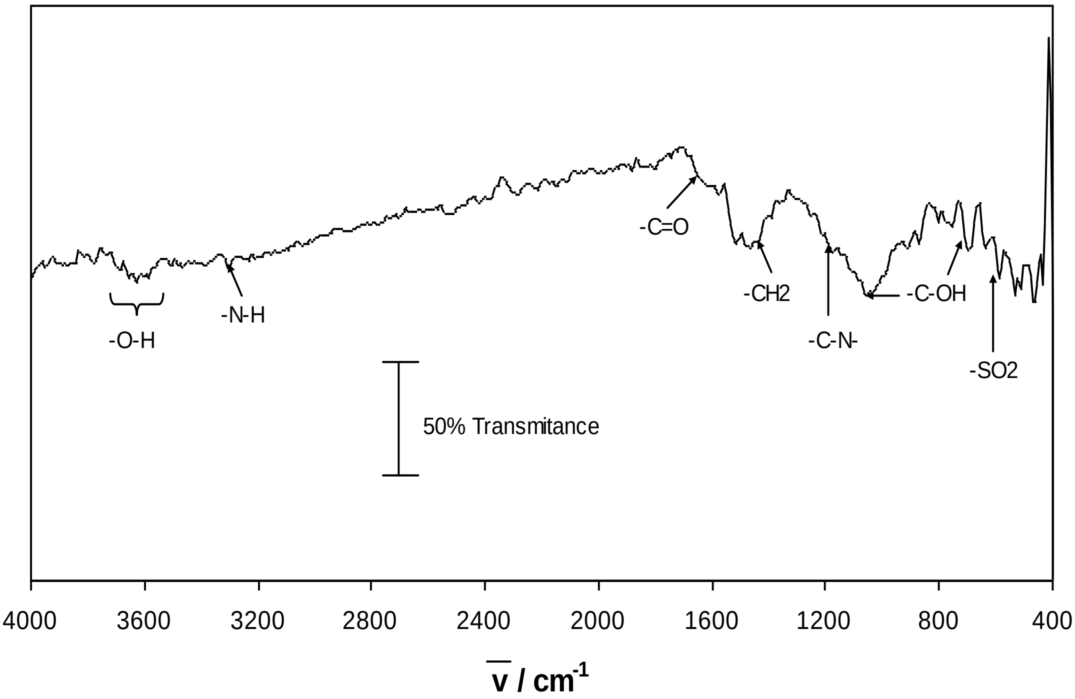

Figure 3. FT-IR spectrum of polluted soil, using 70 grades of incident angle light.

On other hand, chemiadsortion reactions were originated between clay active sites and the -OH groups from hydroxides. Such that $Fe(OH)_3$ precipitate is present between pH 3 and 13, and it is generated by the reaction: $Fe^{+3} + 3OH^- = Fe(OH)_3$. In this manner the clay – iron hydroxide complex occurring at pH < 6.5 has a positive charge, and the specie $H_2AsO_4^-$ is dominant; otherwise, at pH > 8.0 a negative surface charge is generated, and $HAsO_4^{2-}$ is the dominant specie. In the pH range between 6.5 and 8.0 the surface charge is mix; and the lower solubility of $Fe(OH)_3$ occurs at pH 8.0, since $Fe(OH)_2^-$ is the main iron specie when pH is between 5 and 7. At pH > 10.0 the predominant soluble species of iron and arsenic are $Fe(OH)_4^-$ and AsO_4^{3-} in order with the literature [2].

In this sense, a set of electrochemical experiments was set up , in order to verify for what specie of iron hydroxide the electrochemical process is favored, since fixing the pH at 7 and 11 provides conditions for $Fe(OH)_2^-$ or $Fe(OH)_4^-$ formation respectively; the first one occurs by the corrosion of Fe°, and an increase of pH produces $Fe(OH)_2$ precipitation at the start of the process according to the following reaction: $Fe° + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^-$ [12].

To define the reaction time between iron and arsenic, an iron powder sample of 0.6810 g was put in contact with 3 mL of a 10 ppm As aqueous solution, experimental conditions were pH 7 and 8 rpm stirring; reaction time was 24 h. At different reaction time, few samples were taken for UV-Vis analysis. Since the As signal was observed at 300 nm, then a calibration curve for As was defined using this UV-Vis value, where the coefficient of molar extinction (ε) was of 353.17 ppm^{-1} and a correlation coefficient of 0.90651, with this data the real concentration of As determined in all the experiments under similar conditions. In this manner, based on these series of experiments, 7 hours was defined as the best time to get the reaction between As – Fe because at this time there was practically the same concentration of As in the solution analyzed with UV-Visible spectrum (Figure 4-A).

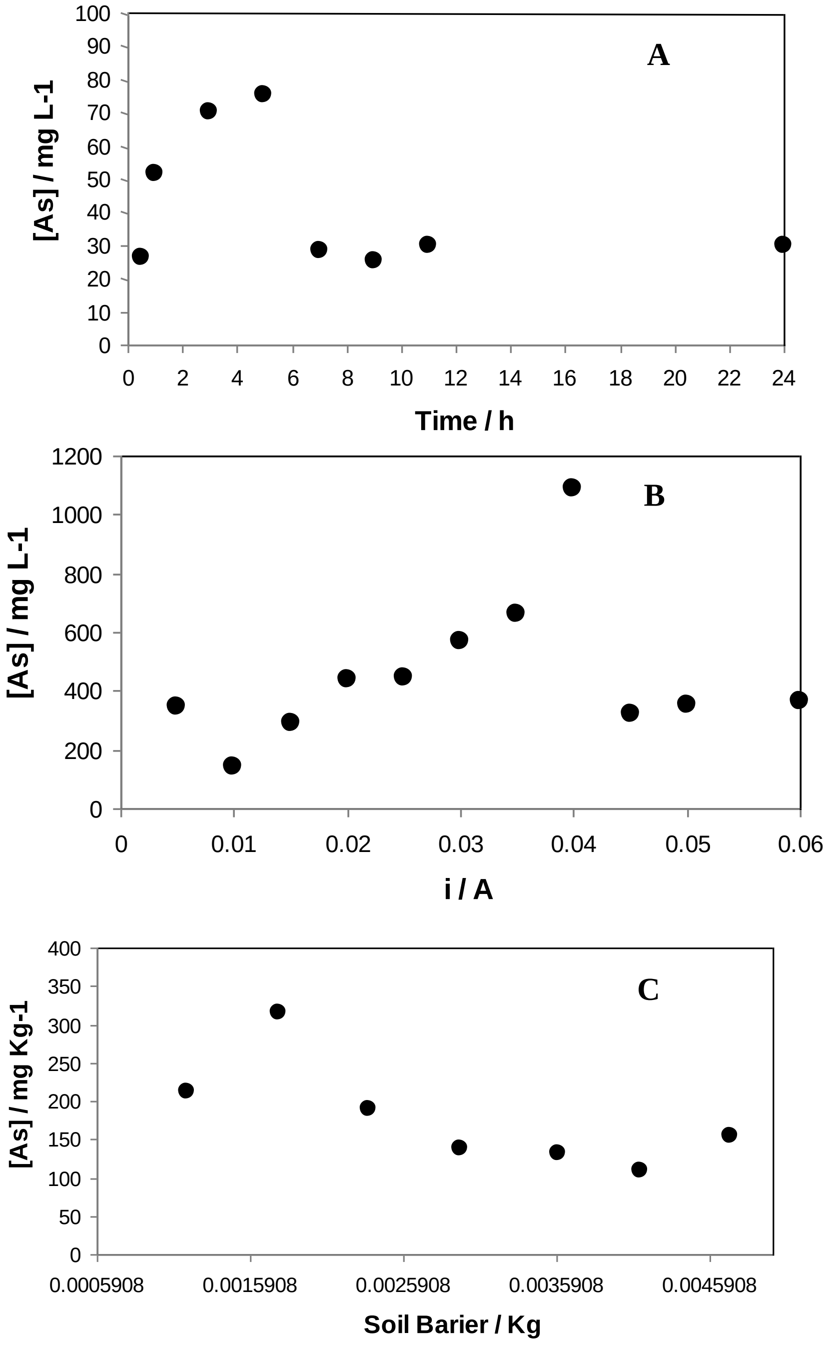

Figure 4. Graph of [As] vs. time of remotion with PRB (A), i (B) and soil barrier (C) used in the PRB treatment with electrochemical remotion of arsenic in pH 7 and 8 rpm of flow.

Once complexation time was defined (Figure 4-A), it was possible to stablish the required current to make electrochemical co-complexation take place. With the objective of enhancing permeability and in consequence increasing the hydraulic flow, for these experiments the column was packed with a mixture of 1.77 g of soil and 0.88 g glass-fiber. After running these experiments, it is observed that As concentration exhibits a maximum when the electrochemical process develops a 45 mA current, results are shown in Figure 4-B.

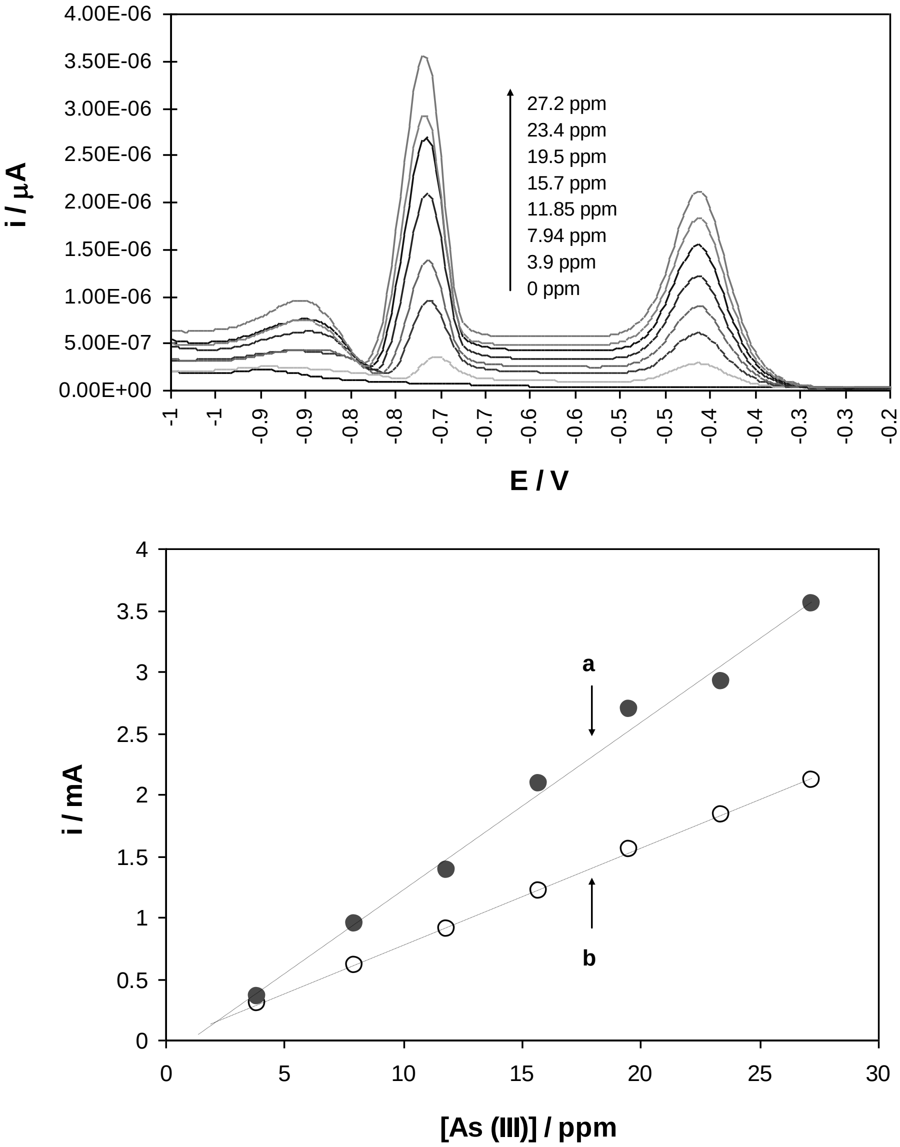

Figure 5. Polarograms of different concentration of As(II) (A) to construct the calibration curve (B), observing the first signal around -0.415 (a) and -0.71 V (b).

A

From data in Figure 6, it can be affirmed that major As removal across the iron barrier was attained with pH 7 rather than pH 11 (93.64 % and 40.57 % at -0.71 V vs. Ag / AgCl respectively), this phenomena can be due to the combination of superficial mixed charge and the few presence of $Fe(OH)_3$ and $Fe(OH)_2$ [2, 10 – 11]. Percentage removal across the PBR was calculated with the equation: $\%R = ([As(III)]_{inicial} - [As(III)]_{final}) / [As(III)]_{inicial}) * 100$.

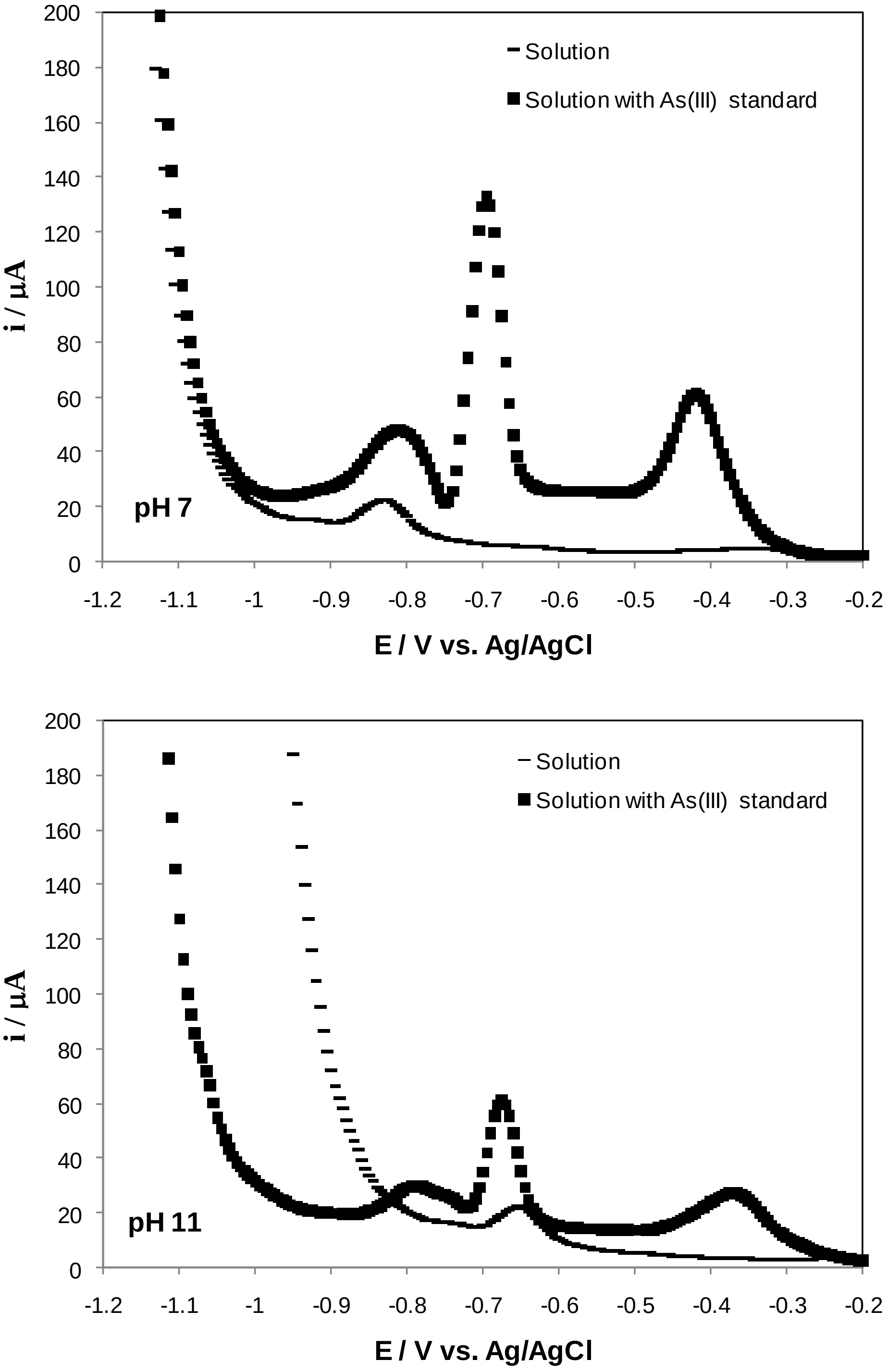

Figure 6. Polarograms of the As(III) of the solution after the electroremediation in presence of PRB with and without As(III) standard at pH 7 and 11.

In electrochemical experiments performed in neutral conditions, after two hours of treatment, it was observed an increase of pH up to about 11 (see Figure 7); and after the five hours it occurred a decrease around pH 6. This effect can be a consequence of the current increase due to the ions removal, occurring in the soil close the electrodes [13]. In this manner, all Fe(II) formed during reduction of As^{3+} to As^{5+} with zero-valent iron, it becomes oxidized to Fe(III), and subsequently precipitated inside the column as insoluble mixed As – $Fe(OH)_3$ phase, via corrosion of the elemental Fe [14].

In contrast, at basic conditions, after seven hours of treatment the pH remained approximately constant around 8.5. In these experimental conditions, the anodic reaction, originated an acid profile which allows for a lixiviation of Fe and As; also, the co-complexation was not evident since the electromigration of iron and arsenic ionic species was present, and detected in the pore fluid, as:

$$Fe^{\circ} + 2H_2O \rightarrow Fe^{+2} + H_2 + 2OH^-, \text{ and, } As^{+5} + 2H_2O \rightarrow As^{+3} + H_2 + 2OH^-$$

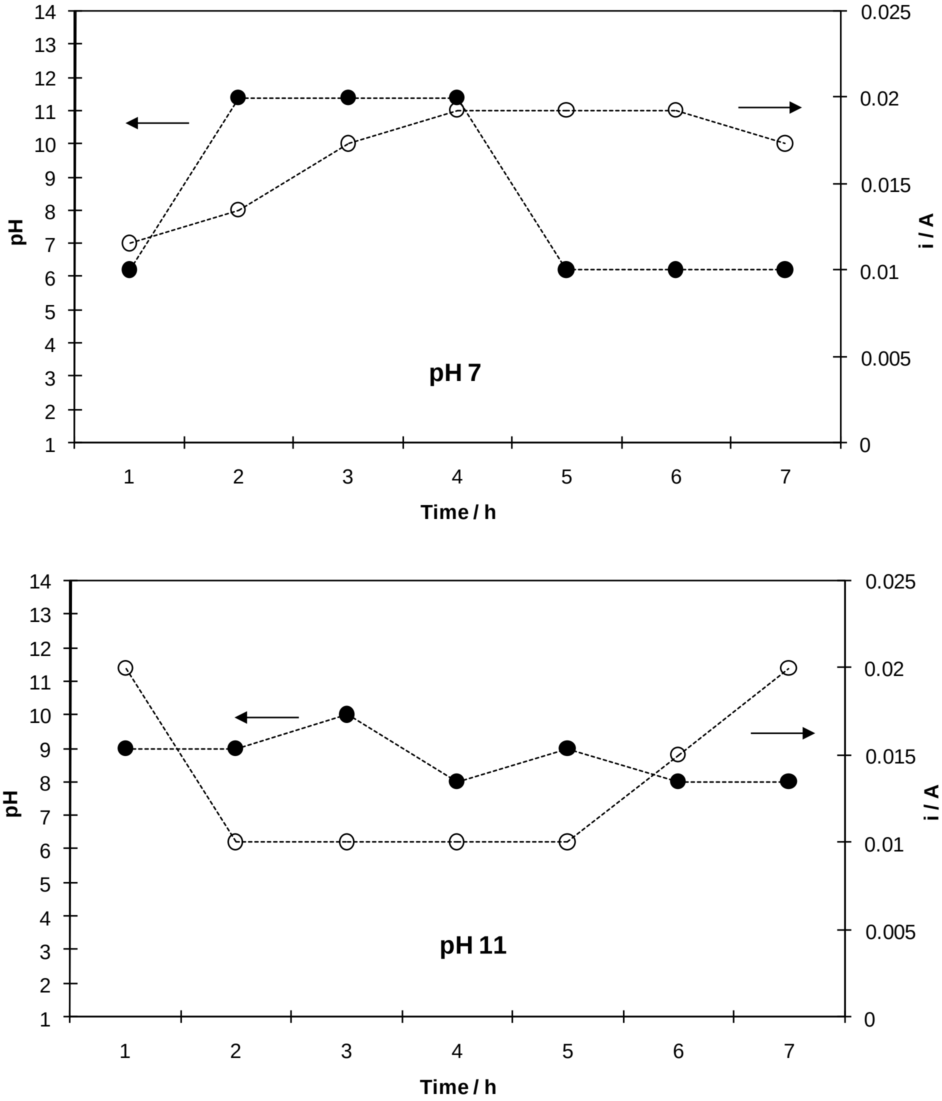

Figure 7. Graphs of pH and i vs. time of electrochemical treatment with PRB at pH 7 and 11.

In neutral and basic electrochemical treatments run at 296 ± 2 K, the cell potential was around 31 V, and the pH during the electrochemical experiment in basic conditions had the minor variation. In addition, SEM image of clean glass-fiber does not shown aggregate presence (Figure 8-A); and it is assumed that at basic conditions oxidation of As^{3+} to As° could be present, because it was observed the presence of aggregates whose minor size corresponds to pH 7 (Figure 8-B), and major size was observed for pH 11 (Figure 8-C) by the possible interaction Si – As [15], Si of the glass and As of the soil – As. The presence of As over the fiber was confirmed by polarography (Figure 5).

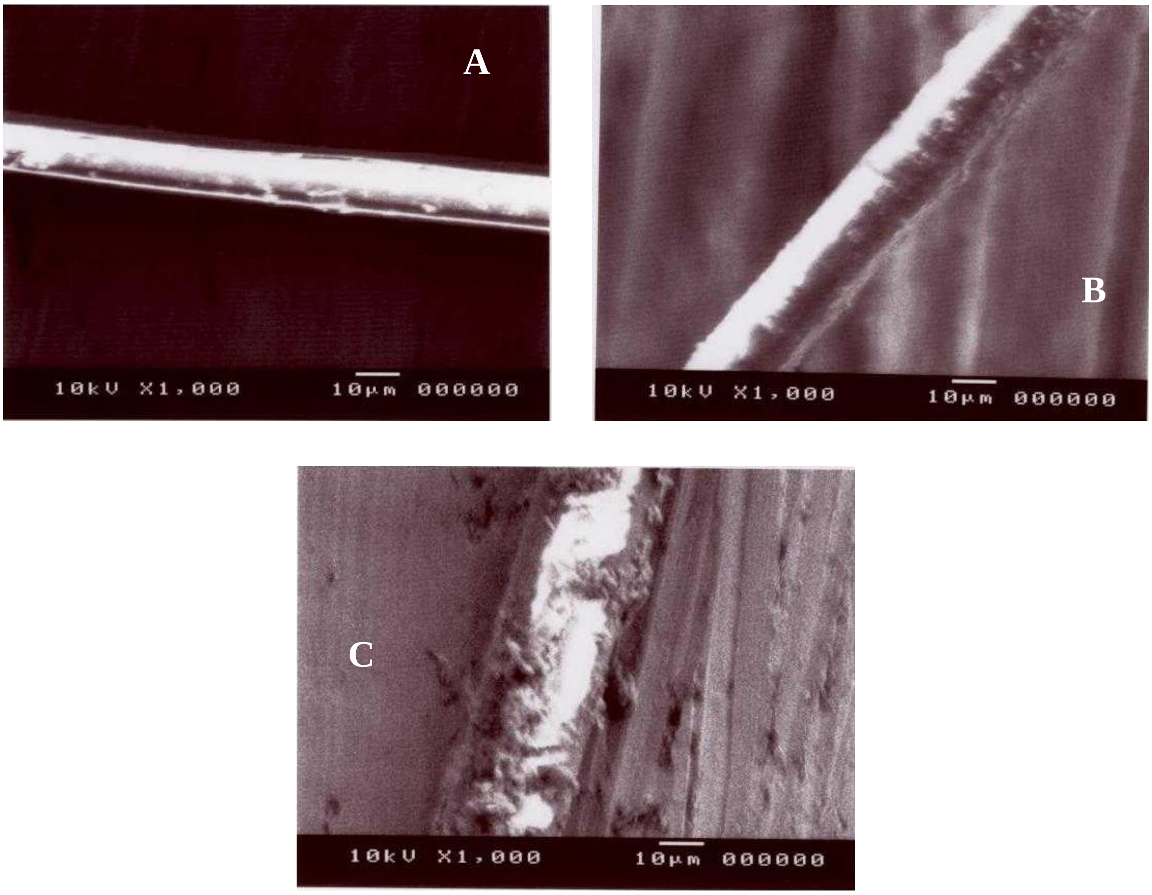

Figure 8. SEM analysis of glass-fiber before (A) and after the PRB with electrochemical treatment at pH 7 (B) and 11 (C). Experimental conditions: 10 kV with 1,000 x.

4. CONCLUSIONS

The permeable reactive barrier with zero-valent iron barriers in presence of an electrochemical process can be used for the decontamination of arsenic polluted soil, since neutral experimental conditions allowed increasing the co-complexation of Fe – As, and so far to eliminate As in polluted soil of Mineral de Pozos, Guanajuato.

The best conditions for arsenic electro-removal, with an electrochemical cell of 112 g of soil in presence of 56 g glass-fiber and 43 g of iron powder, took place in aqueous solution at pH 7, using a current of 45 mA during 7 h, the obtained efficiency was about 93.63 %, and it is enhanced by the interaction of $Fe(OH)_{3(s)}$ - AsO_4^{3-} as polarography experiments showed it.

This treatment has great expectative because the electro-remotion of arsenic in polluted soil with permeable reactive barrier of iron at pH 7 can be a good alternative to be applied on-site for a contaminated place with metallic pollutants.

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