Electrosorption/Electrodesorption of Arsenic on a Granular Activated Carbon in the Presence of Other Heavy Metals

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Abstract

The adsorption, electrosorption, and electrodesorption of aqueous, inorganic arsenic on the granular activated carbon (GAC), DARCO® 12×20 GAC was investigated in solutions containing arsenic as the only contaminant, as well as with chromium, nickel and iron. Darco 1220 was selected for these investigations primarily because it is relatively ineffective as a normal (unassisted) arsenic adsorbent in the chosen electrolytes at the low loadings used. It is shown that the application of anodic potentials in the 1.0 – 1.5V range, however, result in enhanced uptake, most probably due to charging of the electrochemical double-layer at the electrode surface. 100% regeneration of electrosorbed arsenic was achieved *via* electrodesorption at a cathodic potential of 1.50V. The presence of ad–metal ions was observed to have a significant and complex effect on arsenic adsorption, electrosorption, and electrodesorption. In particular, the Cr:As ratio was shown to have complex effects, decreasing adsorption uptake when present as 3:2, but enhancing adsorption when present as 5:1. Nickel was found to have less of an effect than chromium except at the highest anodic potential used of 1.50V, where it exhibited better performance than chromium. The presence of iron significantly enhanced uptake. With a 1.50V anodic potential, the bulk arsenic concentration was reduced to less than detectable limits, well below the USEPA MCL for drinking water. Regeneration efficiency by electrodesorption for the As–Fe system was greater than about 90%.

1. Introduction

1.1. Background

There are many reports in the literature on the use of carbon adsorbents for the removal of metals and metal compounds,[1,2,3] but generally not to low $\mu g \cdot L^{-1}$ levels. Under certain conditions, however, the effectiveness of carbon adsorbents can be significantly improved by the application of electrical potential-controlled adsorption/desorption, or *ES/ED* (i.e., adsorption/desorption on solid adsorbents in an electric field) to enhance their capacity and to facilitate their subsequent regeneration.[4]

Most of the ES/ED data reported in the literature are for organic compounds. Alkire and Eisinger measured adsorption isotherms of some organic compounds on nonporous glassy carbon and graphite electrodes.[5,6] *ES* data for other organic species on carbon electrodes include quinines,[7] n-hexanol, cyclohexanol, and nitrobenzene,[8] and rhodamine B and tryptophan[9] on modified graphite electrodes. Related data are also available on activated carbon electrodes for phenol,[10,11] benzoic acid,[12,13] o-nitrophenol,[14] chloroform,[15] caprolactam,[16] ethanol and ethylacetate,[17] n-alcohols[18] and benzene.[19] Electrosorption has

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also been used to remediate water contaminated with a variety of inorganic salts,[20] and nitrate/nitrite.[21]

There are fewer reports of *ES* of metals. Jayson *et al.*[22] reported on the removal of Hg(II) acetate from aqueous solution by adsorption and *ES* onto an activated charcoal cloth (ACC) using shaking and flow-through techniques to improve mass transfer. Adsorption capacities of the ACC reached 2×10^{-3} mol·(g carbon)$^{-1}$ at pH 5.5. Application of an electric potential to the ACC during flow-through experiments significantly increased Hg(II) uptake. This was most marked when the applied polarity was -1 V. Afkhami and Conway examined the removal of Cr(VI), Mo(VI), W(VI), V(IV), and V(V) oxy-ions from industrial waste-waters by adsorption and *ES* on high surface area carbon cloth.[23] Farmer *et al.*[24] used *ES* to remediate water contaminated with chromium.

Adsorption equilibria of positive, negative and neutral species are dependent on the electrode charge. The polarization dependence of the surface loading is related to the potential of zero charge,[25] E_{PZC}, for a particular concentration of adsorptive in solution. Neutral species are most strongly adsorbed at, or close to E_{PZC}, and the loading of positively and negatively charged species increase as the surface becomes more cathodic or anodic, respectively. These interactions are well understood for nonpolarizable electrodes.[26,27] However, they are not directly applicable to activated carbon particles due to their well-known surface functional groups and their energetically heterogeneous surfaces,[28] as well as the complex potential distribution between particles. Acidic and basic functional surface groups on carbon surfaces (e.g., carboxylic, phenolic, etc.), exhibit buffering properties in aqueous media. Thus, the open circuit potential of carbon surfaces varies with pH and *vice versa*. This occurs up to a pH of about 12, where the buffering action is typically exhausted. [4] Bán *et al.* have measured isotherms for various species as a function of applied potential and demonstrated increases in equilibrium uptake from about a factor of 2–10 (depending on applied potential and concentration) with increasing positive potentials for anions of naphthoic and naphthalenesulfonic acids. In addition, adsorption/desorption cycles of methylquinolineum chloride cations were demonstrated with decreasing (adsorption) and then increasing (desorption) positive potentials.[4]

Narbaitz and Cen[11] measured efficiencies as high as 95% for electrochemical regeneration of a granular activated carbon loaded with phenol. Zhang[29] also investigated electrochemical regeneration of a coconut shell activated carbon loaded with phenol, and found regeneration efficiencies as high as 85%. It was also observed that cathodic was better than anodic regeneration by about 20% for phenol. A mechanism was hypothesized that included desorption and subsequent electrochemical oxidation of phenol by oxygen or chloride (from the NaCl electrolyte) to CO_2 and water. The superior cathodic electro-desorption performance was attributed to sodium cation migration to the cathode which aids phenol desorption in two ways: the formation of sodium phenolate, which does not adsorb very well onto carbon surfaces; and increasing the local pH in the vicinity of the cathode, which also decreases phenol adsorption capacity on carbon adsorbents. Mixing of the solution was also found to improve electrodesorption due to reduction of concentration polarization effects and improvement in external mass transfer.

García-Otón et al.[30] investigated the electrochemical regeneration of an activated carbon loaded with toluene. Regeneration efficiencies approaching 100% were measured, as well as almost complete electrochemical oxidation of the desorbed toluene in solution. In addition, no loss of adsorptive capacity of the carbon was found upon repeated adsorption/desorption cycles. Moreover, temperature programmed desorption experiments on the carbon following electro-regeneration were used to show that the carbon surface chemistry is significantly modified by electrodesorption. That is, following anodic regeneration, the surface complex

population increases, while for cathodic regeneration it decreases. It has been reported that decreased populations of surface functional groups increases the adsorption capacity of activated carbons for toluene.[31]

Weng and Hsu[32] reported on the effectiveness of an electrochemical process for the regeneration of a field-spent GAC. A regeneration efficiency of 91.1% was observed in a supporting electrolyte of 0.1 mol·L^{-1} NaCl with an applied electric field of 5 V/cm and the regenerated GAC, when evaluated as an adsorbent for methylene blue, exhibited similar performance to GAC samples regenerated using steam.

1.2. Arsenic Compounds on Carbons

Arsenic exhibits complex adsorption chemistry primarily due to its redox reactions. It exists primarily as an anion in natural waters, soils, and sediments. The common valences are +3 (arsenite) and +5 (arsenate) in inorganic hydrolyzed species such as H_3AsO_3 , $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}, and H_3AsO_4, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}.[33] Arsenate ($HAsO_4^{2-}$) is the primary anion in aerobic surface waters and arsenite (H_3AsO_3 or $H_2AsO_3^-$) is the primary species in groundwater.[34] As(III) is considerably more mobile and toxic than As(V).[35] Arsenate adsorbs onto iron oxides and hydroxides, especially at low pH when hydrous oxides have a positive surface charge.[36] Typically, no organic arsenic species are found in contaminated waters.[33]

Arsenic can be removed from water with certain activated carbons.[1,37,38,39,40] Pattanayak *et al*.[1] concluded that uptake of arsenic by carbon is dependent on the form of arsenic in solution (i.e., As(III) or As(V)), the degree of oxidation of the carbon surface, the metal concentration, and the pH and temperature of the solution. More highly oxidized carbon surfaces typically result in greater uptake of As(III) than As(V). Oxidation of As(III) to As(V) and its subsequent removal at pH < 7 was the proposed mechanism, and the optimum pH range depended on the carbon. The behavior with temperature was also complex. Uptake increased with temperature for one carbon, and decreased for another.[1] Another report of arsenate adsorption on various geological materials showed that both the capacity and the rate of adsorption decrease with increasing temperature.[34,41]

The amount of arsenate adsorbed typically increases with pH, but attains a maximum at a pH < 7.[34] Significant adsorption takes place at pH < pH$_{PZC}$ of the adsorbent due to electrostatic attraction when protonated surface species dominate. With increasing pH, the predominant form of arsenate in solution progresses from H_3AsO_4 to $H_2AsO_4^-$ to $HAsO_4^{2-}$ to AsO_4^{3-}.[34] Thus $H_2AsO_4^-$ typically predominates in the pH range of maximum adsorption.

It has been noted that arsenic adsorption can be improved by treatment of activated carbons with certain metals.[37,42,43,44,45] An order of magnitude improvement in arsenic adsorption over an untreated carbon was reported after treatment with ferrous salts, especially ferrous perchlorate.[42] Evdokimov *et al*.[45] reported improved arsenic adsorption by impregnating carbon with ferric hydroxide or tartaric acid from 1% solutions in aqueous KOH. Rajakovic′[44] found that carbon pretreated with Ag$^+$ or Cu^{2+} improved As(III) adsorption but reduced As(V) adsorption. Rajakovic′ and Mitrovic′[46] developed this approach further with multifunctional cellulose chemisorption filters (combining adsorption, ion exchange and filtration) treated with Cu(II), for which as much as a 1000-fold improvement in performance was reported. Initial concentration, pH, and arsenic in anionic form were all important factors. The removal of As(V) was more effective than As(III). Lorenzen *et al*.[43] found that carbon pretreatment with Cu(II) solutions resulted in more effective As(V) removal. It was concluded that parallel mechanisms are responsible for the experimental observations. Arsenic can form insoluble metal arsenates with the copper

impregnated in the carbon, and arsenic is also independently adsorbed on the carbon. The optimum pH for arsenic adsorption was found to be approximately 6. Arsenic desorption was easily achieved using strong acidic or alkaline solutions. However, copper was also eluted in strong acidic solutions.

Here we report the results of a series of experiments undertaken to investigate electrosorption and electrodesorption on a commercially available activated carbon as a means of remediating arsenic–contaminated water. Results are reported for systems in which aqueous arsenic is the single contaminant and also for systems containing chromium, nickel and iron.

2. Experimental

The adsorbent selected for this study was commercially available DARCO® 12×20 (Darco 1220, Norit Americas, Inc.); an acid washed, granular activated carbon (GAC) produced by steam activation of a lignite coal. The specific surface area, total pore volume, mean particle diameter and pH_{PZC} of this adsorbent are 650 $m^2 \cdot g^{-1}$, 0.95 $mL \cdot g^{-1}$, 1.3 mm and 6.3 respectively.[47]

The Darco series of activated carbons have been used as sorbents for heavy metals and other species in aqueous systems for over 40 years. For example, Emmett Holt, Jr. and Holz[48] reported favorable results with Darco G60 as an adsorbent for a variety of potential human poisons from aqueous solution. Corapcioglu and Huang[49] undertook detailed parametric studies of the adsorption of Cu(II), Pb(II), Ni(II) and Zn(II) from aqueous solutions using Darco HDC, Darco HD3000, Darco S-51, Darco G60 and Darco KB. Hall *et al.*[50] used Darco G60 to adsorb tungsten and molybdenum from natural spring waters to concentrate these species for analysis *via* ICP-AES and ICP-MS.

Batch uptake experiments were performed using 500 ml of 500 $mg \cdot L^{-1}$ NaCl (Fisher, ACS Grade) supporting electrolyte. Atomic absorption standards (Sigma-Aldrich) were used to prepare electrolytes of the requisite concentrations of arsenic and chromium. The arsenic and chromium standards were prepared using As_2O_3 and $(NH_4)_2Cr_2O_7$, respectively. Working electrolytes containing Ni(II) and Fe(III) were prepared using nickel(II) chloride and iron(III) nitrate (Fisher, ACS Grade). Acids used to prepare standards, blanks, and sample preservatives were ultra–pure from Sigma–Aldrich. All the water used was 18.2 MΩ·cm from a Barnstead apparatus. All solutions were prepared using Class A volumetric glassware that was quantitatively cleaned using standard laboratory procedures. In preparing the working electrolytes, atomic absorption standards were dispensed using an Eppendorf 10–100 Research pipette.

A schematic of the batch cell used for the experiments is presented in Figure 1. It consists of: two identical platinum mesh current collectors (99.9% metals basis, 100×100 mesh, 0.0762 mm diameter wire) with Pt wire leads (99.95% metals basis, 0.025 mm diameter) woven into the mesh for electrical connections; three PVC washers (9/16" i.d., 1.25" o.d., 0.0625" thickness); two polypropylene mesh discs (121×121 mesh, 1.25" o.d.); and two Viton rubber gaskets (9/16" i.d., 1.25" o.d., 0.0625" thickness). GAC adsorbent particles were loaded on to the lower–most platinum mesh as a monolayer within the central cavity of the lower–most Viton gasket. The cell was bolted together using four PTFE machine screws (#4–40, 5/8" length) and PTFE nuts (#4–40) located at 90° to one another around the circumference of the cell.

In a typical experiment, 500 ml of the electrolyte was charged to the batch cell. The electrochemical potential was supplied with a Kepco DC power supply. Normal adsorption, electrosorption and electrodesorption were allowed to proceed while 1 ml samples were

taken with an Eppendorf Research 100–1000 pipette. All samples were preserved according to USEPA Method 200.951 by dilution with 1 ml of 0.5 mol·L^{-1} HNO$_3$.

Metals analysis was performed *via* Graphite Furnace Atomic Absorption Spectrometry (GFAAS) with a Perkin Elmer 4100 ZL Zeeman Atomic Absorption Spectrometer. The accuracy of the GFAA analysis was monitored *via* periodic analysis of Standard Reference Material 1640 (NIST) containing arsenic at 26.71±0.42 µg·L^{-1}. During a typical analysis of a series of experimental samples, the NIST standard was analyzed after every 5 samples. As an example of the typical precision obtained, the results of one analytical run yielded a mean NIST 1640 arsenic concentration of 25.9 µg·L^{-1}, based on 14 replicate analyses, with a standard deviation of 1.7%; these results are typical of all the analyses reported in this work.

3. Results and Discussion

3.1. Arsenic Alone

An example of the behavior of arsenic concentration in the bulk liquid as a function of time is presented in Figure 2 for a four-stage, adsorption/electrosorption/electrodesorption experiment (see Figure caption). As shown, the data for the initial adsorption stage are well approximated by a pseudo-zeroth order adsorption process in As at a rate of 0.30 µg·L^{-1}·h^{-1}, that resulted in only a very slight decrease in arsenic concentration from 100 to 91.0 µg·L^{-1}, at which point the uptake of arsenic by Darco 1220 was 0.036 mg·g^{-1}. In another normal adsorption experiment with the same electrolyte initial arsenic concentration, but with a lower adsorbent loading of 0.15 g·L^{-1}, adsorption for 42.25 hours resulted in essentially zero arsenic uptake. The mean value of the arsenic concentration in this latter experiment over this time was 99.7±1.6 µg·L^{-1}. From these results it is concluded that Darco 1220 is an ineffective adsorbent for aqueous arsenic in the current system. This is consistent with the observations of Pattanayak et al.[1], working at considerably higher arsenic concentrations and adsorbent loadings (157–992 mg·L^{-1} and 5 g·L^{-1}, respectively), who concluded that Darco S-51 (a powdered derivative of Darco 1220) did not perform well as an arsenic adsorbent from aqueous solutions ranging in pH from 2.2–9.3. Consequently, these authors reported no adsorption results for this material.[1]

Following the period of normal adsorption in Figure 2, application of a 1.00 V anodic potential to the carbon working electrode resulted in a slight increase in the rate of arsenic removal, that was found to be well described by a reversible, pseudo-first order adsorption process with an apparent forward rate constant, k_f = 0.018 h^{-1} and an equilibrium constant, K_c = 0.20. The 1.00V anodic potential was applied for 25.25 h, during which the arsenic concentration decreased from 91.0 to 83.7 µg·L^{-1}, for a total arsenic uptake of 0.066 mg·g^{-1}. The maximum uptake rate observed with the 1.00V potential was 0.87 µg·L^{-1}·h^{-1}, which represents a three-fold increase over the zeroth-order rate observed during the initial period of normal adsorption with no applied potential. The average rate of arsenic removal with the 1.00V anodic potential was 0.29 µg·L^{-1}·h^{-1}, which is still comparable to the zeroth-order rate observed for the initial normal adsorption stage.

The potential-pH equilibrium diagram for the aqueous arsenic system indicates that the predominant arsenic species present at pH 4.25 is the mono-ortho-arsenate anion, H$_2$AsO$_4^-$. [52] The equilibrium speciation of arsenic in the electrolyte was estimated to be 99.2% H$_2$AsO$_4^-$, 0.5% H$_3$AsO$_4$(aq) and 0.3% HAsO$_4^{2-}$.[53] The predominance of anionic arsenic species in the electrolyte supports the hypothesis that arsenic removal under a 1.00V anodic potential is *via* charging of the anion-rich electrochemical double-layer at the electrode surface.

Inversion of the polarity of the applied potential to 1.00V cathodic in Figure 2 resulted in an *increase* in the bulk liquid arsenic concentration. The cathodic potential was applied for 6 hours during which the concentration of arsenic increased at an approximately constant rate of 0.32 $\mu g \cdot L^{-1} \cdot h^{-1}$ from 83.7 to 85.7 $\mu g \cdot L^{-1}$. The similar rates of electrosorption and electrodesorption at $\pm 1.00V$, respectively, suggest a reversible process. However, the magnitudes of the electrosorption/electrodesorption rates at 1.00V were still similar to that of adsorption in the absence of an applied potential.

Application of a 1.50V anodic potential to the carbon working electrode after 49.25 hours resulted in considerably enhanced arsenic uptake *via* electrosorption. As observed with electrosorption at +1.00V, the response corresponded to a pseudo-first order, reversible sorption process. The optimized values of the apparent forward rate constant, k_f, and equilibrium constant, K_c, for the +1.50V electrosorption process were 0.25 h^{-1} and 5.2, respectively. The initial rate of arsenic removal for the +1.50V electrosorption process was 21 $\mu g \cdot L^{-1} \cdot h^{-1}$. 18.6 hours of electrosorption at +1.50V resulted in a decrease in the bulk-liquid arsenic concentration from 85.7 to 16.8 $\mu g \cdot L^{-1}$. It is noted that the latter value is quite close to the USEPA MCL for arsenic of 10 $\mu g \cdot L^{-1}$.

The data presented in Figure 3 demonstrate the effect of sorbent loading on arsenic uptake *via* electrosorption. Electrosorption was carried out at +1.50V in two experiments with adsorbent loadings of 0.15 $g \cdot L^{-1}$ and 0.25 $g \cdot L^{-1}$. As expected, and clearly shown in this figure, increasing adsorbent loading had a considerable effect, increasing both the uptake rate and equilibrium capacity. These results suggest that particular performance specifications for concentration/time can readily be met by use of the appropriate adsorbent loading.

An interesting aspect of the application of electrosorption as a remediation technique is the possibility of adsorbent regeneration by reversing the applied potential. In Figure 4 are presented results of a four–stage experiment in which the initial arsenic concentration was 100 $\mu g \cdot L^{-1}$ and the adsorbent loading was 0.15 $g \cdot L^{-1}$. In this series, no arsenic uptake was observed in the absence of an applied potential. Electrosorption at +1.25 V and +1.50V was well described by a first order process with apparent forward rate constants, k_f = 0.014 and 0.035 h^{-1}, respectively. At the conclusion of the +1.50V electrosorption stage, the concentration of arsenic in the bulk liquid was 54.6 $\mu g \cdot L^{-1}$, which corresponds to a nonequilibrium uptake of 0.30 $mg \cdot g^{-1}$. As shown, electrodesorption at $-1.50V$ resulted in complete regeneration of the carbon adsorbent.

3.2. Arsenic in the Presence of Other Metals

In addition to electrosorption and electrodesorption of arsenic alone on Darco 1220, the effects of the presence of other metals were also investigated.

The results of an experimental series in a solution that was only hexavalent chromium are summarized in Figure 5. As shown, unlike the case for arsenic alone, significant normal adsorption of chromium was observed without an applied potential. This response was well described by a first–order reversible adsorption process with an apparent forward rate constant, k_f = 0.071 h^{-1} and an equilibrium constant, K_c = 1.72. The concentration of 0.66 $\mu mol \cdot L^{-1}$ attained after 72 h of adsorption corresponds to a chromium uptake by of 0.220 $mg \cdot g^{-1}$. The application of a 1.00 V anodic potential resulted in a considerably accelerated rate of chromium removal that was well described by a first–order reversible adsorption process with a forward rate constant, k_f = 0.145 h^{-1} and an equilibrium constant, K_c = 8.53. 25.3 hours of electrosorption with an applied 1.00 V anodic potential resulted in the reduction of the chromium concentration to 0.11 $\mu mol \cdot L^{-1}$, which represents an equilibrium uptake of 0.295 $mg \cdot g^{-1}$.

The equilibrium pH-potential diagram for chromium for solutions containing chloride, given by Deltombe *et al.*,[54] indicates that the predominant forms of chromium in the liquid phase at pH 3.7 and an oxidation potential of +150 mV (typical of non-deaerated solutions) are Cr^{3+} and $CrOH^{2+}$. A CHEAQS[53] calculation gives an equilibrium chromium speciation of 65% $Cr_4(OH)_6^{6+}$, 22% Cr^{3+} and 13% $CrOH^{2+}$ (the pH-potential diagram of Deltombe *et al.* [54] does not include $Cr_4(OH)_6^{6+}$). These equilibrium results indicate a cationic speciation of chromium in the working electrolyte. Thus, the uptake of chromium observed with no applied potential indicates that Darco 1220 preferentially adsorbs cations. This conclusion is supported by work such as that of Huang and Blankenship,[55] for example, who reported 99–100% Hg^{2+} removal for 11 commercial activated carbons over the pH range of 4–5, as well as our own unpublished work with mercury on Darco 1220. In addition, as demonstrated in Figure 2 and Figure 4, Darco 1220 is not an effective adsorbent for anionic species without an applied potential. Having preferentially adsorbed cationic Cr(III) with no applied potential, the further removal of chromium upon application of a 1.00 V anodic potential might seem counterintuitive. However, the equilibrium electrochemical data suggest that at pH 3.7 and an oxidation potential of 1000 mV, essentially 100% of the chromium becomes $HCrO_4^-$. It is feasible, therefore, that upon application of the anodic potential, the adsorbed Cr(III) cationic species are oxidized to anionic Cr(VI) and retained electrostatically. The forced convection in the cell provides a continuous source of bulk Cr(III) that can interact with the carbon surface to be oxidized and retained electrostatically, resulting in the further removal of chromium as observed in Figure 5. This is consistent with the well known and problematic (with respect to electroplating) facile anodic oxidation of Cr(III) to Cr(VI) in electroplating baths.[56] Moreover, switching the potential from anodic to cathodic (not shown in Figure 5), caused the bulk chromium concentration to increase slightly, proceed through a maximum and then begin to decrease once again, consistent with the continued adsorption of cationic species. Similar behavior was also observed by Afkhami and Conway for *ES* of chromium on activated carbon cloth.[23]

In Figure 6 are presented the results of a similar two–stage adsorption process in which the initial concentrations of arsenic and chromium were both 100 µg·L^{-1} (1.33 mmol·L^{-1}, 1.92 mmol·L^{-1}, respectively) and the adsorbent loading was 0.3 g·L^{-1}. As shown in this figure, for the period of normal adsorption, arsenic uptake was described by a zeroth–order adsorption process occurring at a rate of 0.094 µg·L^{-1}·h^{-1}, while the chromium uptake was fit by a first–order reversible adsorption process with an apparent forward rate constant, k_f = 0.070 h^{-1} and an equilibrium constant, K_c = 1.44. In comparison to the normal adsorption process reported in Figure 2, the 20% increase in adsorbent loading from 0.25 g·L^{-1} to 0.30 g·L^{-1} did not accelerate the uptake of arsenic; i.e., the observed zeroth–order uptake rate in Figure 6 is almost 70% less than that reported for Figure 2. Chromium adsorption, however, was observed to occur at a similar rate to that in the absence of arsenic with a decrease in the equilibrium constant. The decreased arsenic uptake during normal adsorption is attributed to the preferential uptake of chromium by the adsorbent, which resulted in a decrease in chromium concentration from 100 to 40 µg·L^{-1}.

As shown in Figure 6, the application of a 1.00V anodic potential resulted in the uptake of chromium and arsenic at very similar and increased rates of about 0.0068 µmol·L^{-1}·h^{-1} (0.51 µg-As·L^{-1}·h^{-1} and 0.35 µg-Cr·L^{-1}·h^{-1}). This represents a significant deviation from the behavior exhibited by chromium alone in Figure 5. This is hypothesized to be indicative of an arsenic–chromium surface interaction. The constant rate of arsenic uptake at +1.00V in Figure 6 is ~ 67% greater than that reported for the same applied potential in Figure 2 in the absence of chromium. The observed 1:1, As:Cr molar removal ratio is consistent with the hypothesis that an insoluble arsenic–chromium compound with this stoichiometric ratio is being formed at the electrode surface. The solubility product of chromium(III) arsenate is pK_{sp} = 20.11,[57] which corresponds to an equilibrium arsenic concentration of 6.6 ng·L^{-1}.

As discussed above, it is feasible that a significant concentration of Cr^{3+} is present and, consequently, if there were a mechanism for the formation of the tri–ortho–arsenate ion, $AsO_4{}^{3-}$, it is feasible that $CrAsO_4$ may be formed by what may be described as "electrochemically-assisted precipitation."

The effects of Ni(II) and Fe(III) ad-ions on arsenic adsorption were also investigated in a similar fashion as in Figure 6. The two additional selected cations are reported to form sparingly soluble arsenates: $Ni_3(AsO_4)_2$, $pK_{sp} = 25.51$; and $FeAsO_4$, $pK_{sp} = 20.24$.[57] For these experiments, the initial arsenic concentration, initial cation concentration and adsorbent loading were standardized at 1.33 µmol·L^{-1}, 6.67 µmol·L^{-1}, and 0.36 g·L^{-1}, respectively. Adsorption for 24 hours was followed by three 48 h periods of electrosorption at anodic potentials of 1.00V, 1.25V and 1.50V. Since the selected conditions differ from those used previously, chromium was also included in this series under similar conditions as Ni(II) and Fe(III). Results of these co–adsorption/electrosorption experiments are presented in Figure 7.

These data show that over the period of normal adsorption, the mixture containing an initial concentration of 6.67 µmol·L^{-1} chromium (i.e., As-Cr) exhibited the highest arsenic uptake rate of all the systems investigated of 1.1 µg·L^{-1}·h^{-1}, with apparent zeroth-order behavior. This enhancement in adsorption rate is attributed to a combination of the 20% increase in sorbent loading and the 500% increase in initial chromium concentration. The relative contributions of these effects are the subject of continuing investigations.

Upon application of a 1.00V anodic potential, the As-Fe system exhibited a significant enhancement in uptake. 24 h of electrosorption at this potential for this system resulted in reduction of the bulk arsenic concentration from 85.7 to 37.6 µg·L^{-1} *via* an approximately first–order, reversible adsorption process with an apparent forward rate constant, $k_f = 0.050$ h^{-1} and an apparent equilibrium constant, K_c, = 1.32. Application of a 1.25V anodic potential resulted in pseudo–first order responses for all three systems. However, the most significant result was the removal of arsenic to below the USEPA MCL of 10 µg·L^{-1} for the As–Fe system.

Continued electrosorption at 1.50V anodic again resulted in pseudo–first order responses from all systems. In this period the concentration of arsenic in the As-Fe system was reduced below the detection limits of the GFAA. The response of the As-Ni system at +1.50V caused the arsenic concentration to fall below that for the As-Cr system.

Uptake ratios consistent with the expected stoichiometry of the insoluble arsenates previously discussed were not observed in these As-Cr and As-Ni results, as they were under the conditions in Figure 6. Also, since the Fe analysis *via* GFAAS was problematic, the iron behavior is not reported here.

Upon completion of the electrosorption processes reported in Figure 7, a 1.75V cathodic potential was applied in order to investigate electrochemical regeneration of the sorbent. These results are presented in Figure 8. As shown, all three systems exhibited electrodesorption, but with varying efficiencies. The carbon adsorbents in the As–Ni and As–Cr systems were electrochemically regenerated with efficiencies of about 25% and 50%, respectively. As in the case of electrosorption, the As–Fe system exhibited the most interesting and significant behavior with an ultimate regeneration efficiency in excess of 90%.

The use of zero valent iron (ZVI; Fe(0)) as an arsenic remediation technique is well established and has been shown to be effective for the removal of As(III) and As(V) from aqueous solutions.[58,59] The underlying chemical mechanisms responsible for the complex

interactions between aqueous arsenic species and the corrosion products of Fe(0) are the subject of extensive research.[60,61] The data presented in this work show that the products of interactions between iron species and arsenic species at the carbon electrode surface may be electrodesorbed or decomposed by the application of an electrochemical potential. This observation suggests the possibility that ZVI systems may be electrochemically regenerated. This also raises he possibility that electrosorption/electrodesorption may be a viable means of concentrating low level influents for subsequent irreversible sorption using, for example, a high capacity adsorbent material.

4. Conclusions

In order to better investigate electrosorption/electrodesorption on carbon surfaces, Darco 1220 GAC, a relatively ineffective normal, unassisted adsorbent for aqueous, inorganic arsenic at loadings of 0.15–0.30 g·L^{-1}, was used in electrolytes containing *ca.* 100 µg·L^{-1} arsenic at pH 4.5. The application of anodic electrochemical potentials to Darco 1220 resulted in enhanced uptake *via* electrosorption associated with the charging of the anion–rich electrochemical double layer at the electrode surface. It was also demonstrated that close to 100% regeneration of the sorbent is possible upon application of a 1.50V cathodic potential.

The presence of other metal ad-ions has been shown to have significant and complex effects on normal, unassisted adsorption, electrosorption, and electrodesorption of arsenic on/from Darco 1220. The uptake mechanism in systems containing chromium has been shown to be a function of chromium concentration, and remains a subject of ongoing investigations. The presence of chromium resulted in greater uptake than in a system containing nickel, up to an electrosorption potential of +1.25V. However, increasing the anodic potential to +1.50V resulted in greater arsenic uptake for the As-Ni than the As-Cr system.

The presence of Fe(III) has been shown to have a significant enhancement effect on the electrosorption of arsenic on Darco 1220. Of the As–Cr, As–Fe, As–Ni systems studied, the As–Fe system exhibited the greatest uptake of arsenic and also was regenerated with the highest efficiency when subject to a 1.75V cathodic potential. The behavior observed for electrosorption in the presence of iron may have significant implications for the mechanism/application of ZVI remediation technologies.

Acknowledgments

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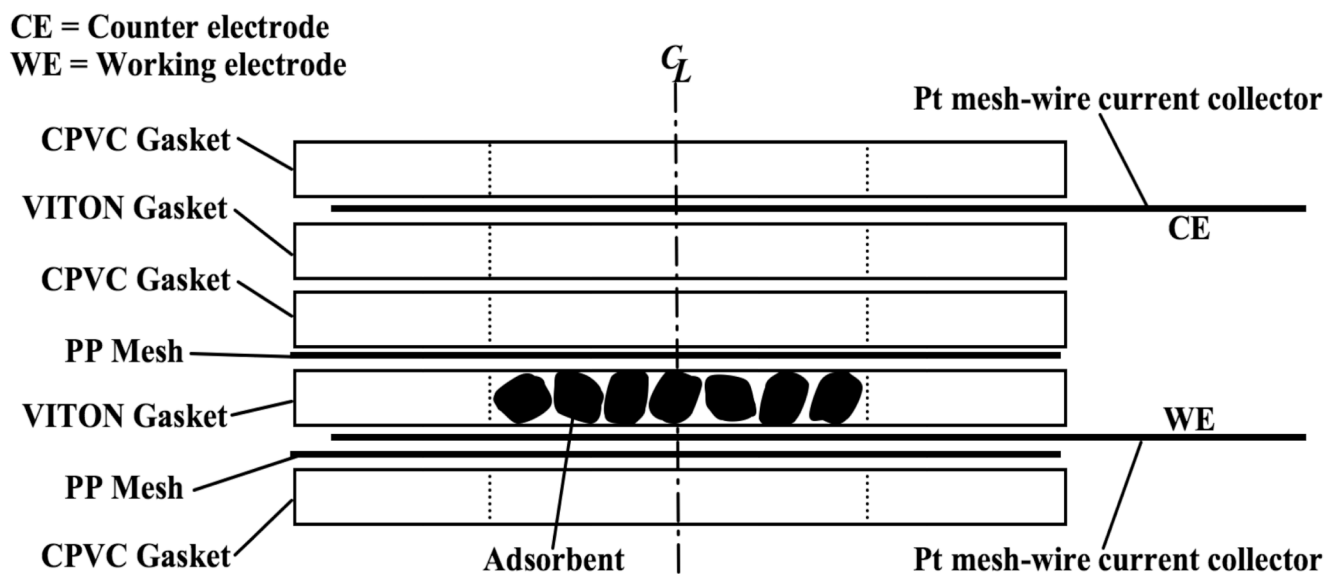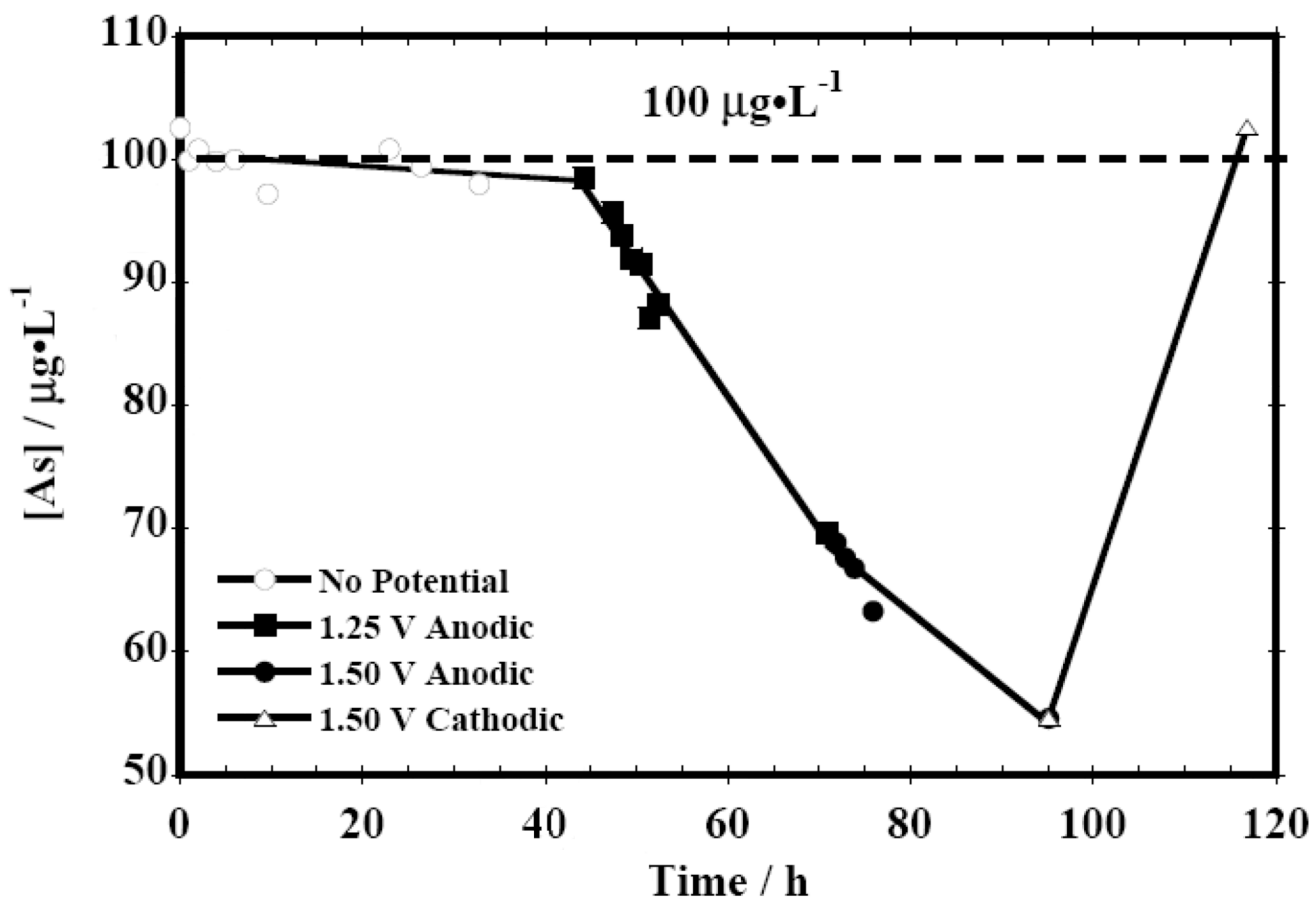
Figure 1.
Schematic of the batch adsorption cell.
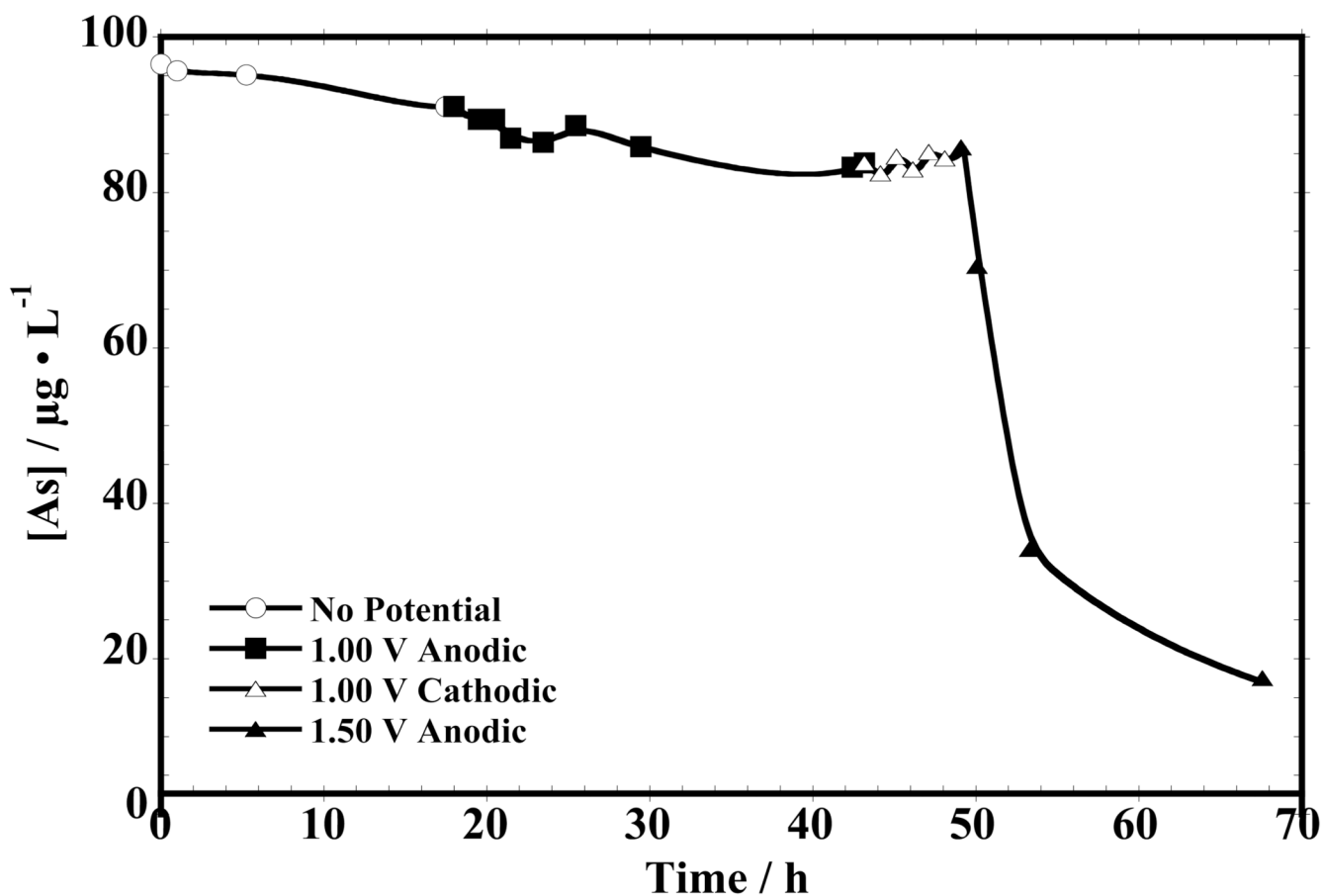
Figure 2.
Four-stage batch adsorption of arsenic from 500 mL of electrolyte containing 100 µg·L^{-1} As and 500 mg·L^{-1} NaCl at pH 4.5 with 123.4 mg of Darco 1220, or 0.25 g·L^{-1}. Program: (1) adsorption for 18 h with no applied potential; (2) electrosorption at +1.00V for 25.3 h; (3) electrodesorption at −1.00V for 6 h; and (4) electrosorption at +1.50V for 18.6 h.
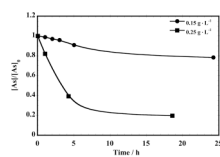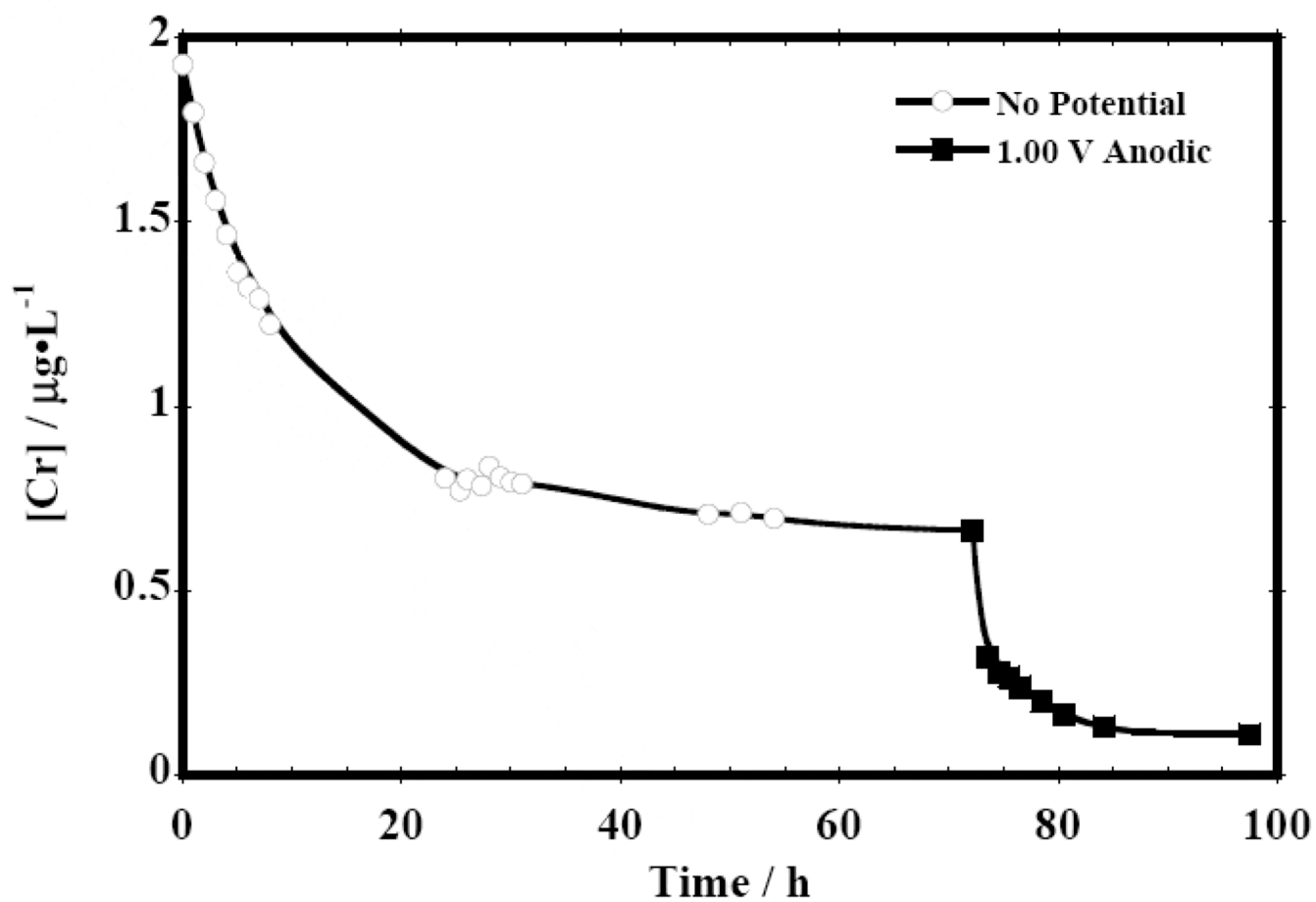
Figure 3.
Effect of adsorbent loading on arsenic electrosorption with +1.50 V applied potential at pH 4.5.

Figure 4.
Four-stage batch adsorption/electrosorption of arsenic from 500 mL of electrolyte containing 100 µg·L^{-1} As and 500 mg·L^{-1} NaCl at pH 4.5 with 75 mg of Darco 1220. Program: (1) adsorption with no applied potential for 44.25 h; (2) electrosorption at + 1.25V for 26.6 h; (3) electrosorption at + 1.50V for 24.25 h; and (4) electrodesorption at −1.50V for 21.75 h.
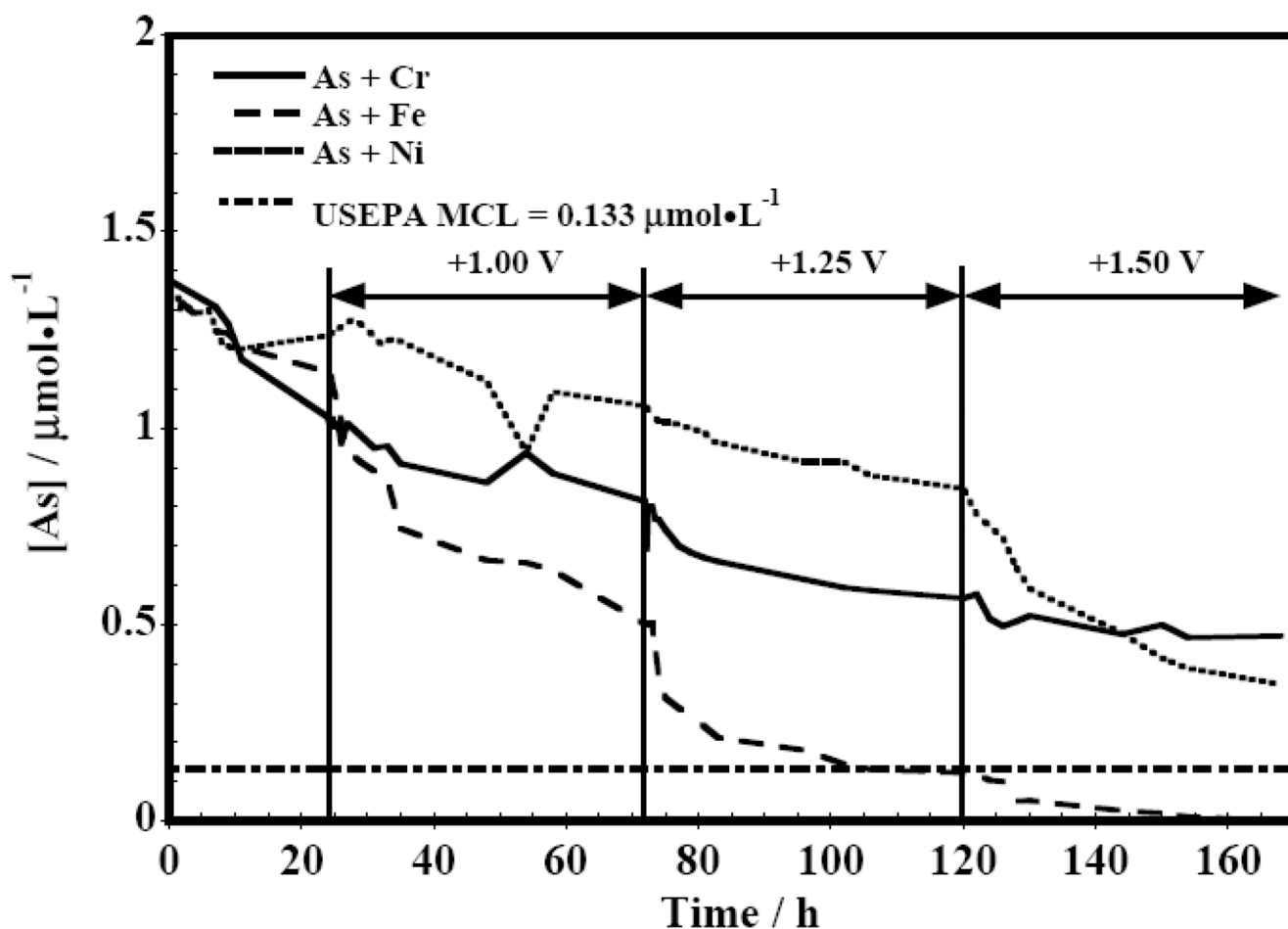
Figure 5.
Two-stage batch adsorption/electrosorption of Cr from 500 mL of electrolyte containing 100 $\mu g \cdot L^{-1}$ Cr, 500 $mg \cdot L^{-1}$ NaCl at pH 3.7 using 150 mg of Darco 1220 (0.3 $g \cdot L^{-1}$). Program: (1) normal adsorption for 72 h with no applied potential; and (2) electrosorption at +1.00V for 25.3 h.
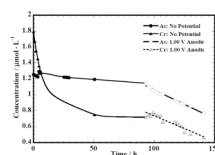
Figure 6.
Two-stage batch adsorption/electrosorption of As and Cr from 500 mL of electrolyte containing 100 µg·L^{-1} As, 100 µg·L^{-1} Cr and 500 mg·L^{-1} NaCl at pH 3.7 using 150 mg of Darco 1220 (0.3 g·L^{-1}). Program: (1) normal adsorption for 93 h with no applied potential; (2) electrosorption at +1.00 V for 48 h.

Figure 7.
Four-stage batch adsorption/electrosorption of As from 350 mL of electrolyte containing 100 µg·L^{-1} As and 500 mg·L^{-1} NaCl at pH 3.7 using 125 mg of Darco (0.36 g·L^{-1}). The metal ad-ions were present at an initial concentration of 6.67 µmol·L^{-1}. Program: (1) adsorption for 24 h with no applied potential; (2) electrosorption at +1.00V for 48 h; (3) electrosorption at +1.25V for 48 h; and (4) electrosorption at +1.50V for 48 h.
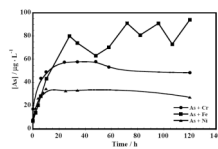
Figure 8.
Electrodesorption at −1.75V after completion of electrosorption program presented in
Figure 7.