Water-Soluble Polymer and Photocatalysis for Arsenic Removal

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ABSTRACT: In this study, the photocatalytic oxidation of hazardous arsenite (As(III)) to arsenate (As(V)) and the sequential removal of arsenate from aqueous solution by liquid-phase polymer-based retention (LPR) were investigated. The photocatalytic oxidation of arsenite was performed using TiO_2 (P25 Degussa, Germany) under UV-A light. The optimal photocatalytic conditions to oxidize 10 mg L^{-1} of arsenite solution were achieved using a 0.5 g L^{-1} of catalyst at a pH value of 2. The As(III) oxidation reached 100% after 30 min of illumination with UV-A light. A water-soluble polymer containing quaternary ammonium groups, poly(3-acrylamidopropyl)trimethylammonium chloride (P(ClAPTA)), was used as an extracting reagent in the LPR process. To obtain the optimized conditions, the removal experiments were performed at various polymer : As(V) molar ratios using 10 mg L^{-1} of arsenate solutions. After the oxidation of As(III) to As(V), the removal of arsenate by P(ClAPTA) was obtained in a 99% yield using a 20 : 1 polymer : As(V) molar ratio at a pH value of 9. The results demonstrate that the combination of these methods is highly useful for potential applications related to the treatment of wastewater contaminated with As(III). © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40871.

INTRODUCTION

Arsenic is classified as one of the carcinogenic elements of Group I.[1] Severe health effects have been observed in chronically exposed populations worldwide that consume water contaminated with arsenic.[1] Arsenic-contaminated groundwater has been found in aquifers in Bangladesh, Chile, Argentina, Mexico, and other countries.[2,3] Arsenic exists in four oxidation states: arsenate (+V), arsenite (+III), arsenic (0), and arsine (−III).[4] The forms, concentrations, and relative proportions of As(V) and As(III) in water vary significantly with changes in pH and/or the redox properties of natural environments.[5,6]

The toxicity of arsenite is 25–60 times higher than that of arsenate.[7] Long-term exposure to arsenic has been associated with cancer of the skin, lungs, kidneys, and liver.[2] Arsenic exposure can also produce various other noncancerous conditions including gangrene, limb loss, cardiovascular and pulmonary disease, and endocrine and hematological disorders.[7] The maximum permissible concentration of arsenic in drinking water is 10 μg L^{-1} as defined by the World Health Organization (WHO).[5]

Arsenic can be converted into its different forms or transformed into insoluble compounds in combination with other elements, such as iron.[8] Existing technologies for the removal of arsenic use various processes, such as coagulation/precipitation, adsorption, ion exchange, and membrane filtration, including reverse osmosis, nanofiltration, and others.[9] It is also important to note that As(III) is a neutral species in a wide range of pH values and is difficult to remove from solution. For this reason, As(III) is typically removed first by oxidizing it to As(V), which, in turn, is removed from solution.[2,5,7,10] Other strategies using sunlight combined with citrate or zero-valent iron have also been employed.[11,12] Ultraviolet radiation alone or in the presence of a suitable catalyst, such as TiO_2, can be a convenient and environmentally acceptable technique for the remediation of arsenite-contaminated water. However, the use of this procedure alone can generate arsenate-enriched solutions.[1]

The use of a heterogeneous photocatalyst involving TiO_2 is becoming a promising technology for the purification of water from various types of contaminants, such as dyes, chlorinated phenols, and pharmaceuticals.[13–15] The high photocatalytic activity of TiO_2, its physical and chemical stability at all pH ranges, and its low cost are recognized advantages of this compound. In the case of As(III)-contaminated water, such as underground or anoxic waters, a preoxidation step is commonly applied to improve the removal yield. In other oxidation processes, including oxidants, such as hydrogen peroxide, oxygen

and ozone, chlorine, manganese oxide, electrochemical oxidants, and Fe(III), TiO$_2$ has also been successfully used.[6,16,17] The oxidation reaction occurs on the surface of TiO$_2$, where photo-excited electrons react with adsorbed molecular oxygen, producing the superoxide radical (O$_2^-$•), which can act as an oxidant. Conversely, the hydroxyl radical adsorbed on the surface (•OH$_{ads}$), which is a powerful oxidant in aqueous media, is produced in holes (VB$^+$) by reacting with adsorbed water or hydroxide anions. Fei et al.[17] noted that in TiO$_2$ photocatalysis, the superoxide seems to be the dominant oxidant of As(III). More recently, Li and Leng[18] conclude that the main reactive oxygen species responsible by the oxidation of As(III) is hydroxyl radical with a weak participation of superoxide anion. Consequently, dissolved oxygen plays an important role in the oxidation of As(III). Reaction conditions have a great influence on the reaction rate and mechanism. Variables such as pH, dissolved oxygen, and the presence of organic compounds determine the absorption of As(III) and As(V) and the formation of reduced oxygen species.

Alternatively, it has been reported that liquid-phase polymer-based retention (LPR) has excellent separation that can be useful for the removal of arsenate.[19] In the LPR system, a water-soluble polymer and arsenate solution are contacted in the feed-side of a filtration cell; the arsenate ions are consequently bonded to the polymer and the macromolecular species formed is mainly retained by a size-exclusion mechanism. The unbounded species, with a diameter smaller than the cut-off diameter of the membrane, passes through the membrane to the permeate stream.[19] As previously described, the capacity of a polymer to bind to the arsenate anion is attributed to the anion exchange between the chloride and arsenate anions and the binding of these species to the quaternary ammonium cationic group.[19,20] Therefore, it is possible to assume that the combination of photocatalytic oxidation and the LPR method could be an effective method for the treatment of arsenic-contaminated solutions.

In this study, a photocatalytic preoxidation step was used to oxidize As(III) to As(V) in a synthetic solution to improve the removal efficiency of As(V) by LPR.

EXPERIMENTAL

Materials

Photocatalytic Oxidation of As(III) to As(V). Photocatalysis experiments were conducted with TiO$_2$ under UV-A irradiation (Philips HB 311 Solarium, 6 × 20 W lamps, $\lambda = 300$–400 nm). A 350-mL borosilicate reactor was used in the experiments. The initial concentration of As(III) was 10 mg L^{-1}, and it was prepared using deionized water from a Milli-Q water system (Millipore, USA). As(III) stock solutions were prepared using NaAsO$_2$ (Sigma-Aldrich). Experiments were conducted at different initial pH values and photocatalyst amounts to determine the optimum values.

The reaction solution was maintained under magnetic stirring and oxygen bubbling (1 L min^{-1}). The stirring rate was kept constant at 300 rpm. The schematic representation of the photocatalytic oxidation system is shown in Figure 1. Before irradi-
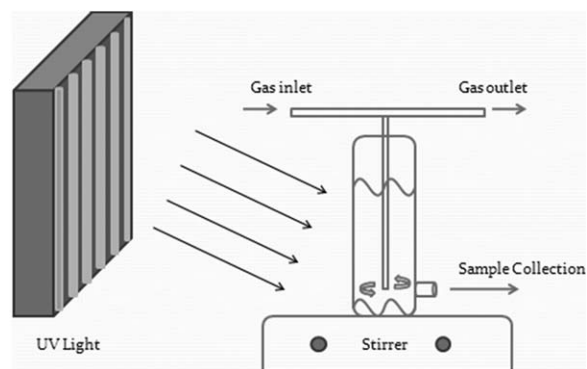

Figure 1. Schematic representation of photocatalytic oxidation system.

ation was initiated, As(III) solution interacted with the catalyst in the absence of light for 20 min to reach the adsorption equilibrium. Samples were taken at different periods of time and filtered with membrane filters with 0.22-µm pore diameters (Millipore) before analysis.

Synthesis of Water-Soluble Polymer. The monomer used to produce the water-soluble polymer was (3-acrylamidopropyl)trimethylammonium chloride (ClAPTA, 75 wt % in water; Aldrich). The polymer P(ClAPTA) was prepared by free-radical polymerization. Five grams of monomer and 1 mol % of ammonium persulfate (AP, Aldrich) used as an initiator were dissolved in 40 mL of deionized water in an inert atmosphere. The reaction mixture was kept at 70°C under N$_2$ for 24 h. The obtained polymer was dissolved in deionized water and fractionated by ultrafiltration membranes with a molecular mass cut-off of 50,000 Da. Collected retentate was lyophilized. The polymer structure is shown in Figure 2. The characterization of the polymer by NMR was reported previously.[21]

LPR Procedure. The main components of the LPR system are the filtration unit (Amicon 8050 stirred cell with 50 mL volume), membrane filter with a known molecular mass cut-off (MMCO), reservoir, and pressure source, for example
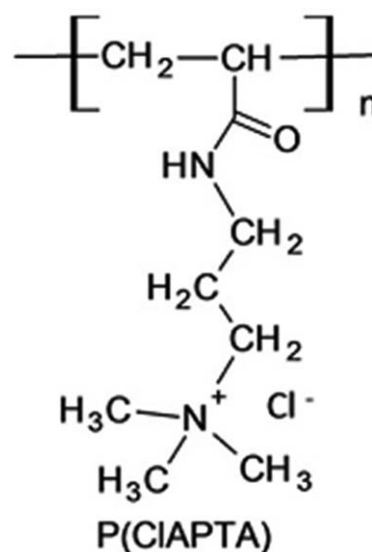

Figure 2. Structure of the P(ClAPTA).

pressurized nitrogen gas. In an ideal case, the system may be considered as a mixed flow reactor. The detailed description of the system was presented previously.[19]

The washing method used is a batch method where a liquid sample containing a water-soluble polymer and arsenate to be separated is placed in the ultrafiltration cell and washed at a given pH and ionic strength. Before carrying out the ultrafiltration, the pH of the solution was adjusted to the desired value. The polymer and arsenate solution were mixed and stirred for 15 min at room temperature and then placed in the ultrafiltration cell. The solution underwent ultrafiltration and was washed with reservoir water at the same pH. The pH was adjusted by adding $0.1M$ of NaOH or HNO_3 (from Merck) and it was measured by a pH meter (H. Jürgen).

The ultrafiltration process was performed under a total pressure of 1 bar using a membrane of regenerated cellulose with MMCO of 10 kDa, 1.55×10^{-3} m^2 (Millipore). Total cell volume (20 mL) was kept constant during the filtration process. Fractions of 20 mL were collected up to a total filtrate volume of 200 mL. Experiments were performed with a solution of polymer : As(V) molar ratios of 10 : 1, 20 : 1, and 50 : 1.

To determine the removal of arsenate from aqueous solution using the washing method, two factors should be defined: (1) retention (R) that shows the fraction of arsenate remaining in the cell and (2) filtering factor (Z) that demonstrates the volume exchange ratio.

$$R = [As_{cell}]/[As_i] \qquad (1)$$

where [As_{cell}] is the amount of arsenate retained in the cell and [As_i] is the initial amount of arsenate. The filtration factor (Z) is the ratio between the total permeate volume (V_p) and the retentate volume (V_r):

$$Z = V_p/V_r \qquad (2)$$

Arsenic Speciation Analysis. To determine the concentrations of As(III) and As(V) during the experiments, all samples from the photocatalytic reactor were filtered and analyzed using the coupled system of HPLC-HG-AFS (high-performance liquid chromatography-hydride generator-atomic fluorescence spectrophotometry). This procedure was adapted for the determinations of As(III) and As(V) according to the setup and analytical conditions that are reported previously.[22] The HPLC system consisted of a HPLC-pump from Merck-Hitachi, Germany (model L-7100 LaChrom), a six-port HPLC valve from Rheodyne, USA (model 7725i) with a 100-µL sample loop, and a HPLC-column Purospher® STAR RP-18 encapped (3 µm) from Merck, Germany (model LiChroCART® 30-4). The separation was performed at 45°C with a flow rate of 0.8 mL min^{-1}. The HPLC mobile phase contained 0.35 mmol L^{-1} of tetrabutylammonium hydrogen sulfate (ion pair reagent) purchased from Merck (Germany), and a pH value of 7.0 was regulated using an ammonia solution (Merck) prepared at 0.1 mmol L^{-1}. The column output was connected directly to the hydride generator system consisting of a homemade flow injection device with two PEEK$^{(R)}$ T-joints for continuous flow of HCl (20%) and NaBH$_4$ (0.15%, in KOH 0.05%). These solutions were pumped at a flow rate of 1 mL min^{-1} using a peristaltic pump. All
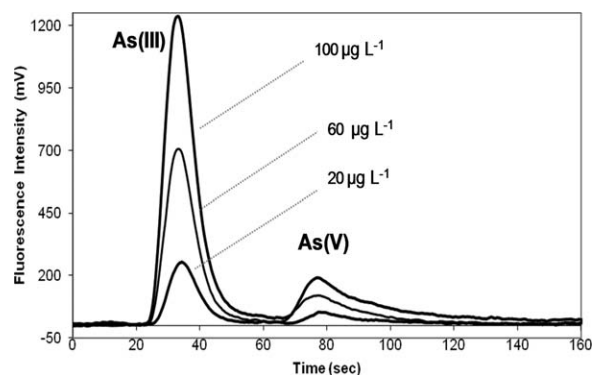

Figure 3. Chromatogram of calibration curve for As(III) and As(V).

reagents used were of analytical grade. Chromatography grade water (Merck, Germany) was used for preparing all standard stock solutions. Standard stock solutions were prepared by the appropriate dilution of NaAsO$_2$ (Sigma Aldrich, Germany) and H$_3$AsO$_4$ (Merck, Germany) commercial standards. NaBH$_4$ was prepared daily in KOH (0.05%) owing to its low stability. The samples and standard solutions for analysis were stabilized using a phosphate buffer at a pH value of 7. All samples were filtered with membrane disks of 0.22 µm prior to analysis.

The chromatograms obtained for the speciation of As(III) and As(V) in aqueous solutions from using a HPLC-HG-AFS-coupled system are shown in Figure 3.

The total arsenic concentration in the LPR filtrate was measured by HG-AFS (Aurora, 3300). The flow rate of the carrier gas (Ar) was 600 mL min^{-1}, whereas the flow rate of air was 400 mL min^{-1}. Arsenic was measured at 193.7 nm, and the current intensity of the lamp was 100 mA.

Multivariate Analysis. For multivariate analysis, response surface methodology was used, as described previously for the photocatalytic processes.[23] This model is based on a central composite circumscribed design consisting of a factorial design and star points. The data were analyzed using Modde 7.0 software. The values of variable were coded and normalized in unitary values, -1 and $+1$, for the concentration of TiO$_2$ and pH, which ranged between 0.5 and 1 g L^{-1} and 2 and 5, respectively. From these ranges, the central point (coded 0) was set and determined in triplicate. The star points were distributed at a distance of $n^{1/2}$ from the central point, where n is the number of variables. The response factor was determined by the oxidation of As(III) after 30 min of irradiation. A second-order function that described the behavior of the system was determined by a multiple regression. The optimized values of the analyzed variables were obtained using Modde 7.0 software. Statistical validation was performed by an ANOVA test with a 95% of confidence level.

RESULTS AND DISCUSSION

Photocatalytic Oxidation of Arsenite

In our preliminary assays, the oxidation rate of arsenite under UV-light illumination was examined in a pH range of 3–9, the amount of TiO$_2$ ranged from 0.1 to 1 g L^{-1}. The results suggest that arsenite oxidation is considerably dependent on pH and
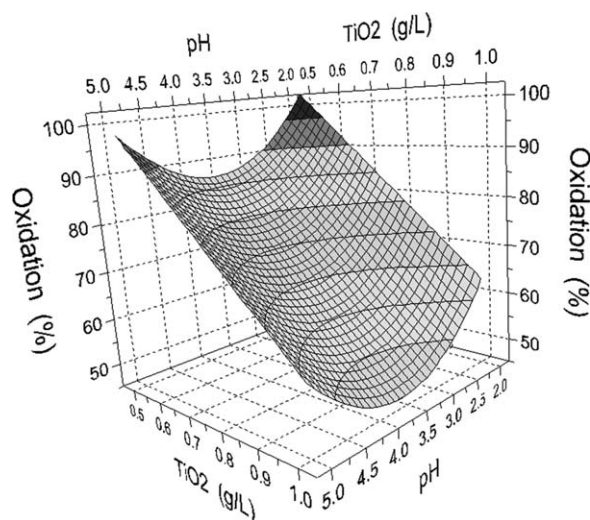
Figure 4. Response surface plot of As(III) oxidation (%), pH range 2–5, and TiO$_2$ amount, 0.5–1 g L^{-1}.

Figure 5. Oxidation profile of As(III) under optimal conditions. As(III) concentration, 10 mg L^{-1}; initial pH, 2; and TiO$_2$, 0.5 g L^{-1}.

that acidic conditions are more favorable. On the other hand, Bissen et al.[24] reported that pH did not influence the arsenite oxidation rate in a pH range between 5 and 9 for 0.1 mg L^{-1} of arsenite solution. Moreover, Zhang and Itoh[25] conclude that the complete oxidation of 100 mg L^{-1} of As(III) was achieved at a pH value of 3 using 0.02 g L^{-1} of TiO$_2$. This behavior was explained, considering that under acidic conditions, the generation of H$_2$O$_2$ would be favored which in turn indirectly produces •OH radicals. In terms of the amount of TiO$_2$, the strongest oxidation was achieved using 0.5 g L^{-1} of TiO$_2$. In addition, the photocatalytic oxidation of arsenite is greatly affected by the amount of catalyst. According to our preliminary results and reported studies, the ranges of variables such as pH and TiO$_2$ were adjusted to new ranges. The initial pH was adjusted to a value between 2 and 5, and the concentration of TiO$_2$ ranged from 0.5 to 1 g L^{-1}. To determine the optimal reaction conditions, the experimental values associated with the pH and the concentration of TiO$_2$ were simultaneously changed. This alteration allowed for the identification of the optimal conditions for the oxidation of As(III) by performing a limited number of experiments. In our study, with two variables and two levels (-1 and $+1$), the number of experiments was 11 including the central points (3) and the star points (4). Using multiple linear regression (MLR), it was possible to obtain a polynomial describing the influence of each variable in the oxidation ratio of As(III). This polynomial is shown in eq. (3) and validation was performed using the ANOVA test.

$$Y = 64.8(\pm 2.8) - 5.7(\pm 2.1)\,\text{pH} - 12.6(\pm 2.1)\,\text{TiO}_2 + 3.3(\pm 2.4)\text{pH}^2$$

The values in parentheses in the polynomial represent the standard deviation of each codified coefficient. If the standard deviation is higher than the associated coefficient, then this term is eliminated, reducing the size of the polynomial. In the studied domain, the most significant variable is the amount of TiO$_2$, where the reaction is favored at lower amounts of TiO$_2$, having a maximum value of approximately 0.5 g L^{-1}. The pH
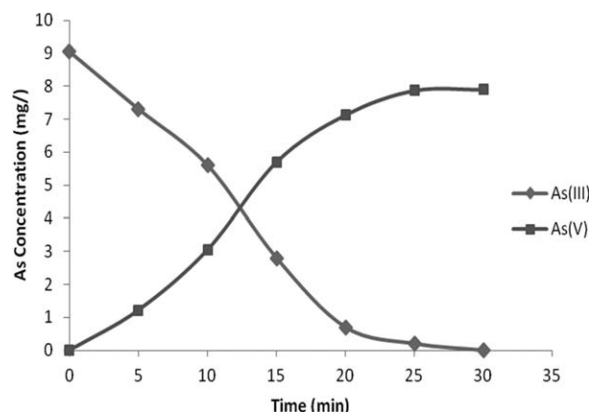
affects the oxidation yield to a lesser extent, increasing the oxidation yield by a lower amount and reaching a maximum at a pH value of 2 (quadratic behavior). No synergies or antagonism between the variables was found in the studied range.

A 3-D representation of the polynomial is shown in Figure 4, illustrating that 10 mg L^{-1} of arsenite solution is completely oxidized to arsenate after 30 min of irradiation at a pH value of 2 and 0.5 g L^{-1} of TiO$_2$. An increased amount of catalyst should make the suspension quite opaque to favor light penetration, which is necessary for photocatalysis. On the contrary, it is possible that using lower amount of catalyst the same results can be attained; however, under the present conditions, a 100 % oxidation was reached and in consequence no further explorations were done.

To understand the fate of arsenic during the photo-oxidation process, the total amount of arsenic in solution was determined after the completion of the photocatalytic assays. The As(V) produced can be dissolved in solution or adsorbed on the catalyst surface. Considering the mass balance of total arsenic (As(III) + As(V)) during the oxidation process, it was established that a portion of the As(V) produced remain adsorbed (17%) on the TiO$_2$, whereas no adsorption of As(III) was detected. This can be explained by the fact that the surface charge of TiO$_2$ is positive at a pH value of 2 (pzc = 6.2 for P25 TiO$_2$). Because As(III) and As(V) are neutral at a pH value of 2, a weak interaction between the catalyst and these species is expected at a pH value of 2.[16,26]

Figure 5 shows the oxidation profile of As(III) at a pH value of 2 with 0.5 g L^{-1} of TiO$_2$ as a catalyst. After 25 min of irradiation, all of the arsenite was oxidized to arsenate.

Removal of Arsenic Using the LPR Technique

The effect of pH on the retention of arsenate was studied by LPR using the washing method. The removal of As(V) in the form of mono and divalent oxoanions was determined using the LPR with P(ClAPTA) in a pH range from acidic to basic with varying polymer : arsenic (10 : 1, 20 : 1, and 50 : 1) molar ratios. The samples were analyzed using atomic absorption spectroscopy. The results are expressed in retention percentage (R) versus filtration factor (Z) of the water-soluble polymer
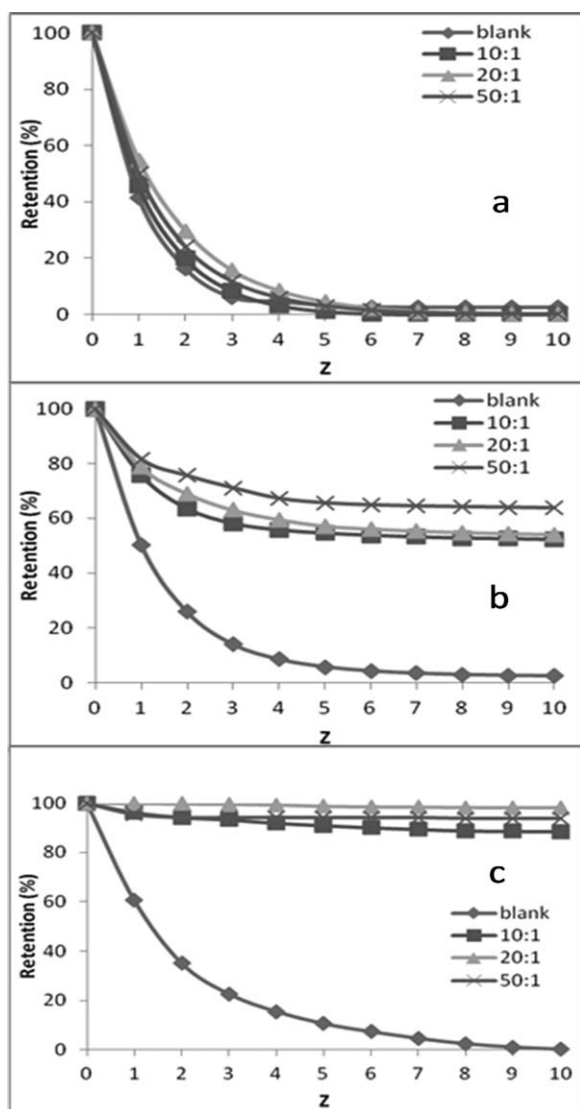
Figure 6. Retention profile of As(V) 10 mg L^{-1} using P(ClAPTA) (a) pH 3, (b) pH 6, and (c) pH 9 at different polymer : arsenic molar ratios.

Figure 7. Retention profile of oxidized arsenite solution of 10 mg L^{-1} at pH 9 and 20 : 1 polymer : As molar ratio.

molar ratio was 50 : 1 as shown in Figure 6(b). It can be owing to the conformational changes of the polymer that depend on the ionic strength at given pHs.[20]

At a pH value of 9, divalent As(V) species are predominant. The results demonstrate a higher retention capacity of predominantly divalent species at a basic pH by the polymer. Figure 6(c) shows the high affinity of the polymer to interact and remove As(V). The retention of As(V) at a pH value of 9 and a polymer : arsenic (20 : 1) molar ratio reached 99% under 1 bar of pressure while using regenerated cellulose as membrane filter.

Simultaneously, the analysis of flux was conducted in both the absence and the presence of water-soluble polymer. As we expected, the permeate flux in blank in all water samples was higher than the flux permeate in the presence of P(ClAPTA). The permeate flux of diafiltration without P(ClAPTA) was 60 L h^{-1} m^2, and the permeate flux of the diafiltration with P(ClAPTA) was 40 L h^{-1} m^2. This could be attributed mainly to interactions between the polymer and the membrane.

Removal of Arsenic by Sequential Photocatalytic Oxidation and the LPR Technique

After the oxidation of As(III) to As(V) (10 mg L^{-1}) at a pH value of 2 with 0.5 g L^{-1} of TiO$_2$, the pH of the oxidized solution was adjusted at 9 with NaOH. The resulting solution was placed into the filtration cell under optimized conditions for separation (pH = 9 and polymer : As(V) of 20 : 1 molar ratio). Depending on the experimental results shown in Figure 7, the maximum retention was reached from combining photocatalytic oxidation with ultrafiltration. This result indicates that the application of this sequential technique could be a valuable tool for removing arsenic from contaminated solutions.

The results indicate that the main drawback of the sequential treatment proposed in this article is the required adjustment to achieve optimal conditions for the photocatalytic process (pH = 2) and LPR technique (pH = 9). Nevertheless, considering the results shown in Figure 6(b), it is possible that the sequential treatment can also proceed at a pH close to neutrality, thereby avoiding pH adjustment altogether.

CONCLUSIONS

This study demonstrated that photocatalytic oxidation combined with water-soluble polymers and ultrafiltration is an

(Figure 6). Various inorganic As(V) species (H$_2$AsO$_4^-$, HAsO$_4^{2-}$, and AsO$_4^{3-}$) can coexist in an aqueous medium according to pH (pK_{a1}, 2.2; pK_{a2}, 7.0; and pK_{a3}, 11.5, respectively). The first arsenic retention experiment was performed at a pH value of 3 at various polymer : arsenic (10 : 1, 20 : 1, and 50 : 1) molar ratios using the LPR washing method technique with 10 mg L^{-1} of As(V) [Figure 6(a)]. The retention of the As(V) species was very low at a pH value of 3 because monovalent anionic species (H$_2$AsO$_4^-$) are in equilibrium with the arsenic acid at that pH.[5] Furthermore, the influence of the polymer concentration was investigated at a pH value of 3 as shown in Figure 6(a). Almost all of the polymer : arsenic mol ratios demonstrated the same behavior at a pH value of 3.

At a pH value of 6, the monovalent (H$_2$AsO$_4^-$) and divalent (HAsO$_4^{2-}$) oxoanionic arsenic species coexist in equilibrium. According to the results shown in Figure 6(b), the retention of As(V) increased at a pH value of 6 owing to the existence of divalent anions. At a pH value of 6, the optimum polymer : As
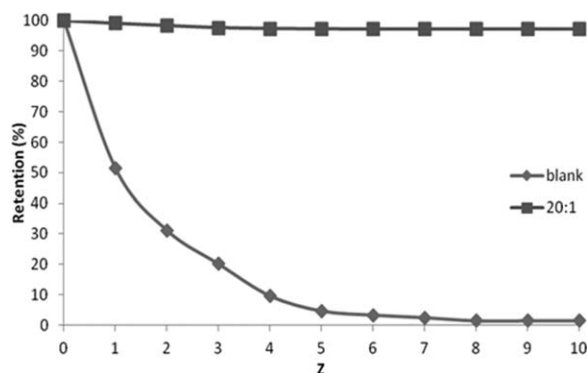
effective process to remove hazardous As(III) from aqueous solutions.

Arsenite can be rapidly oxidized using a TiO_2 photocatalyst under UV-A light irradiation to arsenate, which is less toxic and less mobile in aquatic environments. The results indicated that a complete conversion of As(III) to As(V) was achieved through photocatalytic oxidation using 0.5 g L^{-1} of TiO_2 at a pH value of 2 for 25 min of irradiation.

The synthesized polymer was able to separate arsenate efficiently using the LPR technique at a pH value of 9 with a polymer : As molar ratio of 20 : 1, thereby reaching a retention capacity approaching 97–99%.

ACKNOWLEDGMENTS

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