



Easy and fast functionalization of polypropylene and its efficiency in arsenic (V) removal Fácil y rápida funcionalización del polipropileno y su eficiencia en la remoción de arsénico (V)

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Abstract

This article presents an easy functionalization of polypropylene with the ability to remove arsenic (V) upon contact with the aqueous solution, retaining it on its surface, being easy to remove, and complying with the WHO limit. Functionalized polypropylene requires 10 minutes of reaction in UV radiation. The maximum removal was 68% of As (V) at an initial concentration of 1 mg/L and 12 hours of contact time. We found that the removal percentage increased with increasing the number of functionalized membranes three in the arsenic solution reaching the removal of 80% of the initial concentration of 48 $\mu\text{g/L}$, achieving the maximum concentration of As (V) in water established by the WHO.

Keywords: Arsenic (V); grafting polymerization; functionalized polypropylene; Uv irradiation, carboxylic group.

Resumen

Este artículo presenta una fácil funcionalización del polipropileno con la capacidad de remover arsénico (V) al contacto con la solución acuosa, reteniéndolo en su superficie, siendo fácil de removerlo y cumpliendo con el límite establecido por la OMS. El polipropileno funcionalizado requiere 10 minutos de reacción en radiación UV. La máxima remoción fue del 68% de As (V) a una concentración inicial de 1 mg/L y 12 horas de tiempo de contacto. Se encontró que el porcentaje de remoción aumentó al incrementar el número de membranas funcionalizadas tres en la solución de arsénico alcanzando la remoción del 80% de la concentración inicial de 48 $\mu\text{g/L}$, logrando la concentración máxima de As (V) en agua establecida por la OMS.

Palabras clave: Arsénico (V); polimerización por injerto; polipropileno funcionalizado; Irradiación Uv, grupo carboxílico.

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1 Introduction

Arsenic has been considered one of the most toxic chemical elements present in groundwater and surface water (Armienta and Segovia, 2008; Osuna-Martínez *et al.*, 2021). The presence of arsenic derives from anthropogenic sources such as mining, agriculture, or natural sources such as volcanic emissions and the erosion of rocks that contain arsenic (Knappett *et al.*, 2020; Mahlkecht *et al.*, 2023). Arsenic in aqueous medium is found as oxyanions of As (V) and As (III), with As (V) being the most dominant species in surface waters and As (III) predominating only in anaerobic conditions such as groundwater (Nicomel *et al.*, 2015; Villa-Lojo *et al.*, 1997). It has been shown that the use and consumption of water with arsenic has harmful effects on human health that cause damage to the cardiovascular and nervous system, generate liver damage, and are associated with the development of different types of cancer (Fatoki and Badmus, 2022; Tchounwou *et al.*, 2019). That is why the World Health Organization (WHO) has established the maximum permissible limit of 10 $\mu\text{g/L}$ of arsenic in water for human consumption. Arsenic removal methods such as reverse osmosis, membrane filtration, ion exchange, electrochemical treatment, etc. have been used (Ali *et al.*, 2013; Altowayti *et al.*, 2022; Pal, 2015; Zeng *et al.*, 2020). These methods represent disadvantages such as the excessive use of reagents, the generation of toxic sludge, high energy demand, operating high costs, difficulty separating of the adsorbent material from the water, etc. (Bastida-Vázquez *et al.*, 2024; Mondal *et al.*, 2013). Therefore, it is important to research new materials that can remove arsenic (V) from aqueous solutions.

Derived from the limitations for the removal of arsenic with current technologies, it is important to carry out research in the design of new materials, for this reason, the functionalization of polymeric matrices is innovative, since depending on the functionalization, its applications can be expanded (Makvandi *et al.*, 2021). The functionalization of polymeric materials such as membranes allows the creation of materials with dual functionality by separating contaminants through filtration and adsorbing them on the surface (Chia *et al.*, 2023; Miller *et al.*, 2017). Different materials have been used to functionalize such as polysulfone (PSf), poly(ethersulfone) (PES), poly(vinylidene fluoride) (PVDF), polypropylene (PP), poly(acrylonitrile) (PAN) and polyamides (Janićijević and Radovanović, 2018; Mondal *et al.*, 2018; Nik-Abdul-ghani *et al.*, 2021; Shokri *et al.*, 2016; Zhu *et al.*, 2018). Polypropylene is a versatile material low cost, and chemical resistance that has limited applications due to its lack of reactive functional groups (Jasinska-

Walczak *et al.*, 2022). However, its reactivity can be enhanced by functionalizing its surface with reactive functional groups such as -OH, -C=O, -NH₂, SO₄⁻², etc. (Himma *et al.*, 2016). This process can expand the applications of polypropylene, especially in the field of water treatment. The functionalized polypropylene surfaces act as ligands, which can remove various contaminants from the aqueous environment, making it a promising material for water treatment. Several studies have been conducted on the effectiveness of functionalized polypropylene surfaces in removing contaminants from water. Some of these studies include (Lee *et al.*, 2017; Mishra and Ramaprabhu, 2011; Pal, 2015; Picón *et al.*, 2022; Rowley and Abu-Zahra, 2019; Zeng *et al.*, 2020). Some of the techniques used for the functionalization of polymers are plasma, UV radiation, γ rays. UV radiation has many advantages over other techniques since it does not require specialized equipment, and free radicals are generated at room pressure and temperature, resulting in a low-cost and environmentally friendly process (Sangermano and Razza, 2019; Yang and Yang, 2013).

Photografting is a technique for functionalizing polymeric surfaces using vinyl monomers. This process forms C-C covalent bonds between the surface and the functional group, as described by Hernández *et al.* in 2016. This method is not only easy to use but also has the added benefit of not leaching contaminants into the aqueous environment, making it an attractive option for surface modification.

The functionalization of polymeric surfaces with acrylic acid has been reported using different methodologies, some require controlled atmospheres (nitrogen), while others require the use of toxic reagents or sophisticated infrastructure (Abudonia *et al.*, 2018; Ang *et al.*, 2020; Vandenbossche *et al.*, 2014). The methodology used in this research work was graft polymerization, which is easy and fast, does not require sophisticated infrastructure, and is highly efficient. By functionalizing polypropylene with acrylic acid, a pH-sensitive material is obtained; the carboxyl groups can be protonated or deprotonated (Purkait *et al.*, 2018), acting as an intelligent material, which may have the ability to remove cations or anions depending on the pH of the solution.

COOH-functionalized polypropylene was synthesized using a green chemistry approach, which involves reacting at room temperature, using a minimal amount of reagents and without generating side products. The process requires only 10 minutes of irradiation. The manuscript was sectioned into functionalization, characterization, and evaluation of polypropylene with COOH groups in the removal of As (V). The objective is to understand and explain its performance in removing arsenic by analyzing the effects of parameters such as; pH of

the solution and degree of grafting. In addition, factors such as the initial concentration of As (V) and the contact time were studied, using the response surface methodology. The study focused on the physicochemical characteristics of functionalized polypropylene and its impact on the adsorption of As (V). The key contribution of this article is the easy and rapid obtaining of functionalized polypropylene with groups COOH and its potential application as an efficient material to treat water contaminated with As (V) achieving the limits established by the WHO.

2 Methods and materials

2.1 Materials

Microporous polypropylene membrane with a pore size of 0,45 μm , width of 114 μm and 84,6% porosity, provided by 3M Company, deionized water, acrylic acid, benzophenone, hydrochloric acid, sodium hydroxide, sodium iodide (KI), stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), silver diethyldithiocarbamate (AgDDTC), pyridine, granular zinc (net 20), sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$), and all of the reagents used without prior purification. The As (V) solutions were prepared using $\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$ from a solution of 100 mg/L in deionized water and diluted to the desired concentration.

2.2 Functionalized polypropylene (PPAA)

The polypropylene membrane was modified using the grafting photopolymerization method with UV radiation. A 4x4 cm area (0.02g in weight) of the polypropylene was placed in a benzophenone solution at 5% p/v (photoinitiator). Afterward, it was placed in a 20% p/v acrylic acid solution and exposed to a photoreactor at 300 nm for 10 minutes (Palacios-Jaimes et al., 2012). The excess monomer was then removed with water at 65°C for 5 minutes, washed in acetone, and dried until a constant weight. The grafting degree of PPAA was calculated using the following equation.

$$GD = \frac{P_1 - P_0}{P_1} \times 100 \quad (1)$$

Where:

- GD= grafting degree of the adsorbent membrane
- P_1 = final weight of the adsorbent membrane
- P_0 = initial weight of the polypropylene membrane.

2.3 Analysis of the Functionalized polypropylene (PPAA)

2.3.1 Fourier Transform Infrared Spectroscopy (FT-IR-ATR)

The Fourier Transform Infrared Spectroscopy (FT-IR) analysis was performed on a Perkin Elmer Septum Two spectrophotometer using attenuated total reflectance (ATR) with four sweeps per sample in the absorption interval of 4000 to 500 cm^{-1} .

2.3.2 Water absorption test (swelling)

The water absorption capacity test for the polypropylene functionalization (PPAA) and polypropylene (PP) was done. The membranes were placed in deionized water, evaluating their hydration capacity every 5 minutes. The initial weight of the dry membrane (W_0) and wet membrane (W_s) were registered. The swelling percentage (% S) can be calculated following equation 2.

$$\%S = \left(\frac{W_s - W_0}{W_0} \right) \times 100 \quad (2)$$

2.3.3 Point of zero charge

Point of zero charge analysis was performed by placing PPAA (4x4 cm) in 50 mL flasks of deionized water; pH was adjusted using 0.1M NaOH and HCl solutions at 3, 4, 5, 6, 7, 8, 9, and 10 values, stirring at 150 rpm for 48 hours at room temperature. The final pH was measured after reaching equilibrium time (Verma et al., 2020).

2.3.4 Atomic Force Microscopy (AFM)

AFM was performed noncontact using an MFP-3D Origin AFM apparatus equipped with Igor Pro 6.34A. The sample was attached to a glass slide using a double-sided tape then scanned the surface by a silicon nitride probe in air at ambient conditions. The scanning was performed at a speed of 0.24 Hz and scan sizes of 90, 60, 30, and 15 μm . A sampling resolution of 448 points per line was selected.

2.4 Adsorption experiments of arsenic (V)

As (V), adsorption experiments were performed in a discontinuous system of 125 mL flasks. A 4x4 cm of PPAA in 50 mL of As (V) solution at room temperature was placed under magnetic stirring at 400 rpm. The pH influence was evaluated by keeping the pH of solutions from 1 through 7, adding HCl (0.1M) or NaOH (0.1M). The effect of the grafting degree of the functionalized membranes on As (V) adsorption was studied using PPAA with a grafting degree from 40 to 102% for As (V) adsorption (0.2 mg/L).

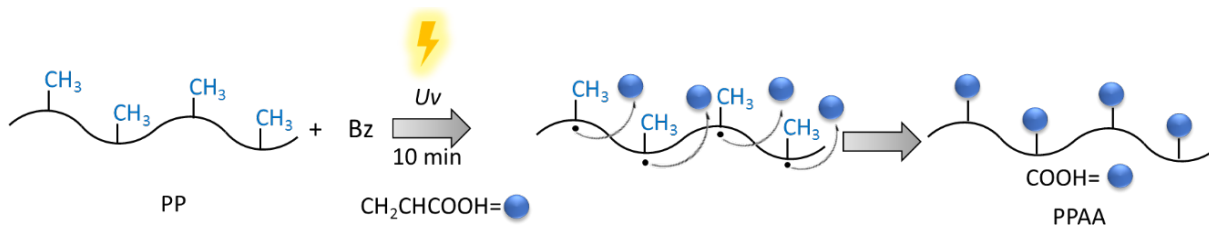


Fig. 1 Schemes of modification membrane by photografting polymerization.

Table 1. Numerical values and variable levels.

Variables	Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
X ₁ : [As] (mg/L)	0.034	0.2	0.6	1	1.147
X ₂ : t (h)	1.136	3	7.5	12	13.86

In all the experiments, the As (V) residual concentration was measured by an indirect spectrophotometric method using silver diethyldithiocarbamate (AgDDTC).

Removal percentage of As (V) was calculated with the following equation:

$$\% \text{ As removal} = \frac{C_0 - C_f}{C_0} \times 100 \quad (3)$$

Where: C_0 is the initial concentration and C_f is the final concentration.

2.5 Experimental design

Two independent factors were considered in the experiment design: initial concentration of arsenic in the water [As] and contact time of the membrane (t); DOE methodology was applied to device a compound 2×2 central experiments design. The inferior, central, superior, r, and axial levels of each factor are shown in Table 1, codified as $-\alpha$, -1, 0, +1 and $+\alpha$, in the same order.

3 Results and discussion

3.1 Obtained functionalized polypropylene (PPAA)

Graft polymerization is a process that generates radical reactive sites on the surface of polypropylene using UV radiation. These reactive sites then form a covalent bond through the polymerization of the acrylic acid monomer from α , β -unsaturated bonds of the monomer generated (Fig 1).

This process takes only 10 minutes at room temperature, and it requires minimal energy expenditure and a short reaction time. This method does not involve a complex infrastructure and reduces operating expenses, making it an easy

and fast method. This information is based on studies conducted by (Hernández-Aguirre *et al.*, 2016). The functionalization of the polypropylene with the polar groups was obtained cleanly and uniformly, obtaining COOH grafts of 40% to 104% (around 0.04 g, depending of final grafting) in the polypropylene. This surface modification method is more homogeneous than conventional chemical initiation methods because the radiation area of the electron beam is wide and the penetration power is safe, facilitating the polymerization of polypropylene by free radicals. Polypropylene, when functionalized, favors its degradation process. Studies carried out in our research group showed that polypropylene when degraded using a mixed method (ultrasound-Phanerochaete chrysosporium) (Hernández-Aguirre and Gómez-Espinosa, 2017) reduces the degradation time, proposing approximately 100 hours, so We suggest that modification with carboxyl groups will accelerate this process, proposing the PPAA as an eco-friendly material, contributing to the circular economy of the material.

3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopy FTIR-ATR of the polypropylene (PP) functionalized with acrylic acid (PPAA) to confirm the grafted reaction. Figure 2, the unmodified polypropylene spectrum (PP) was used as a control to evaluate polypropylene functionalization (PPAA). In the PP spectrum, vibrations of 2920 cm^{-1} and 2845 cm^{-1} can be observed that match the stretching vibrations, symmetric and asymmetrical of methyl, methylene groups, the scissor vibration was showing in the digital footprint region for methyl in 1454 cm^{-1} and 1380 cm^{-1} . The acrylic acid functionalized membrane (PPAA) presents a new peak at 1708 cm^{-1} , which matches the tension vibrations of C=O of carboxylic acid, and two peaks at 1454 cm^{-1} and 1377 cm^{-1} that match the flexion vibrations of OH carboxylic acid grafted in polypropylene (García-García *et al.*, 2022).

3.3 Water absorption test (swelling)

Polypropylene is a hydrophobic material. However, when hydroxyl groups are added to the polypropylene,

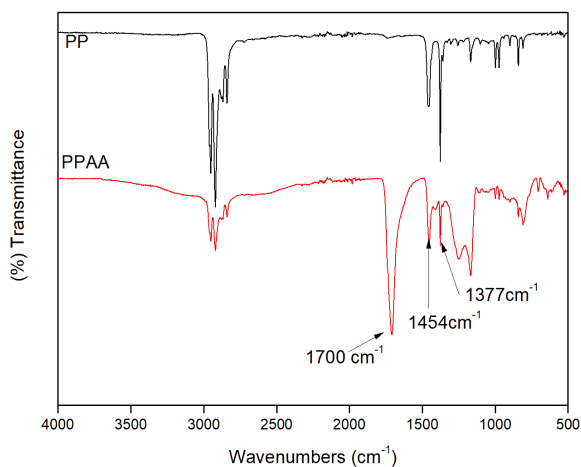


Fig. 2 FT-IR spectrum of functionalized polypropylene (PPAA) and polypropylene (PP).

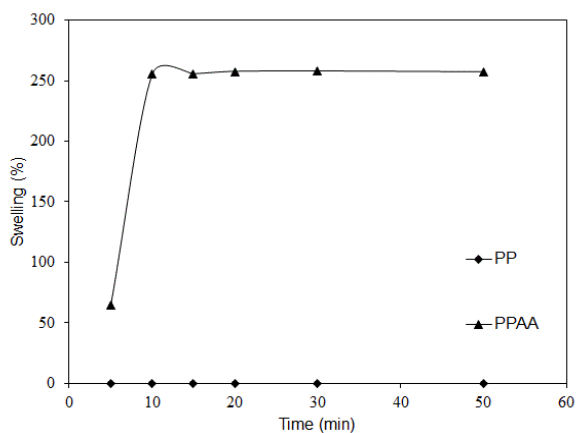


Fig. 3 Kinetic water absorption to the functionalized polypropylene PPAA and PP.

it becomes more water-friendly due to the incorporated polar groups (Erceg *et al.*, 2021). To evaluate the water absorption capacity of the functionalized polypropylene (PPAA), it was put in contact with deionized water, and the kinetic of water absorption was analyzed. The membranes were placed at different time intervals until they reached equilibrium. Polypropylene, due to its hydrophobic quality, did not present water absorption, whereas the PPAA showed at 30 minutes the maximum of 257% water absorption.

3.4 Point of zero charge analysis

Functionalizing the membrane is to attract arsenic oxyanions through adsorption to achieve their removal. By functionalizing the polypropylene, the surface chemistry of the membrane changes due to the graft of carboxyl groups (COOH); this causes the membrane to acquire acid sites, making it pertinent to analyze the surface charge of the membrane. The surface charge of the membrane was established by the point of zero charge (PZC); at the point of zero

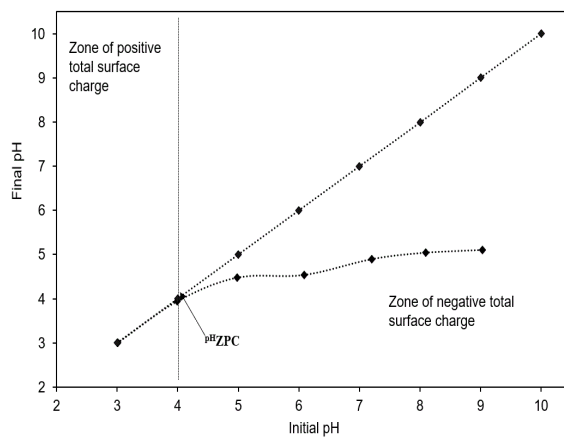


Fig. 4 PZC of functionalized polypropylene, PAA.

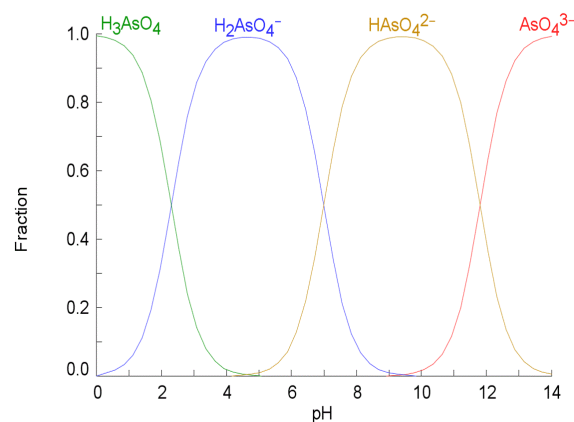


Fig. 5 Distribution diagram for As(V) species at different pH values.

charge (pHPZC), the surface charge of the membrane on an aqueous solution is neutral, whereas the surface charge of the membrane surface will be positive when the pH of the solution is lower than pHPZC and will be negative at a pH above pHPZC (Ateia *et al.*, 2020). In Figure 4, the pHPZC of the PAA is shown at a value of 4 on the pH scale; this suggests that beneath the value of 4, the membrane is positively charged, and above 4, it is negatively charged.

3.5 Study of pH effect in adsorption As(V)

pH is a determining factor in the process of arsenate adsorption since the speciation of As(V) is controlled by pH and the redox potential in bodies of water (Figure 4) (Lu and Zhu, 2011). That is why the influence of initial pH in the As(V) solution was studied in the removal capacity of PPAA as an adsorbent surface, varying the pH from 1 to 7. The removal of arsenate anions in the solution depends on the pH of the medium since the PPAA, due to its ionic nature, can be protonated or deprotonated at different pH values, as shown in the PCZ study. The impact of pH in As (V) is shown employing a PPAA; it is shown that at pH 7, there was no removal because the polar groups grafted in the membrane

at that pH value deprotonated leading to electrostatic repulsion between the ions and the membrane surface. However, at pH 5, the membrane could remove 18%, and at pH 3, it removed 43%; at this pH range, the dominant arsenic (V) species is H_2AsO_4^- , therefore, it is assumed that the removal at this range occurs because of electrostatic attraction between the positively charged membrane and the negatively charged arsenate. On the other hand, at pH 1, the removal increased to 48%; this suggests that at pH under 3, the dominant species is H_3AsO_4 . Therefore, the interaction between the COOH functionalized surface and the species of arsenic (H_3AsO_4) can happen through the formation of hydrogen bonds between the hydrogen atoms of H_3AsO_4 and the oxygen in the adsorbent surface; however, in this scenario, the creation of hydrogen bonds between arsenates and water molecules in the solution can occur (Dzade and De Leeuw, 2018; Meza-González *et al.*, 2024).

3.6 Effect of Grafting Degree of PPAA in adsorption As(V)

Functionalized polypropylene was produced with grafting degrees ranging from 40% to 105%. The highest degrees of grafting were achieved when the acrylic solution was prepared immediately (Wang *et al.*, 2020). The effect of the grafting degree was studied, and different functionalized membranes were evaluated. They were analyzing whether there is a relationship between the degree of grafting and the arsenic removal capacity. Membranes with low (40%), intermediate (85%) and high (100%) grafting degree were selected. When the GD was 46%, As (V) removal was 20%. The PPAA with a GD of 85% led to a 50% removal. However, the PPAA with GD greater than 100%, the arsenic removal was 60%. This led us to the conclusion that increasing the degree of grafting does not necessarily increase

the reactivity of the functionalized membrane. We suggest that as there is more carboxyl group on the surface, these can form hydrogen bonds between them, reducing their availability and therefore reducing the removal of arsenic. For that reason, the functionalized polypropylene with 80% grafting degree was used in this work.

3.7 Topographical Analysis by AFM

It is important, to note that the adsorption process is achieved when the arsenic solution comes into contact with the functional groups of the polypropylene, acting as ligands, and coordinating with the arsenic ions. Analyzing the surface of the functionalized polypropylene was decisive in corroborating said coordination. The determination of the surface roughness by AFM allowed us to know the topology of the surface membranes, where the lighter areas represent the highest regions of the structure and the darker areas represent the deepest ones. This analysis allows us to observe the differences in the surface of each of the membranes, confirming the graft reaction (PP-PPAA) and the presence of As (V) (PPAA-As) on the surface of the modified membrane. Figure 6, represents 2D, and 3D topographic changes of A) PP, B) PPAA, and C) PPAA-As. The AFM analysis demonstrated an increment in the roughness of the membranes having the following order: PPAA-As > PPAA > PP. The above suggests that arsenic interacts with the polar groups found in the modified membrane PPAA-As, showing 173 nm of roughness. However, the most significant increase was between the polypropylene membrane PP and the adsorbent membrane PPAA. This suggests that the polymerization of the acrylic acid forms layers between them, generating greater roughness of 170 nm and thickening of the fibers compared to PP, which presented a roughness of 109 nm, corroborating with this analysis the retention of arsenic on the surface of the adsorbent membrane.

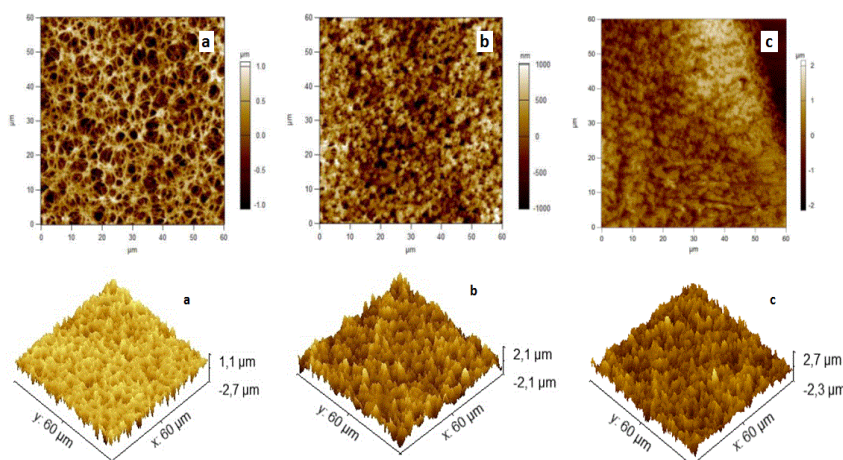


Fig. 6 AFM images of the membranes 2D and 3D; a) PP, b) PPAA and c) PPAA-As.

Table 2. Experiments design CCD at different de arsenic concentrations (X_1) and time (X_2).

Block	Experimental unit	Design in space	Actual variables		Coded variables		Result R (%)
			X_1 (mg/L)	X_2 (H)	x_1	x_2	
Day 2	1	Factorial	0.2	3	-1	-1	31.5
Day 2	2	Factorial	1	3	1	-1	2.91
Day 2	3	Factorial	0.2	12	-1	1	30
Day 3	4	Factorial	1	12	1	1	55.73
Day 1	5	Central	0.6	7.5	0	0	43.97
Day 2	6	Axial	0.0343	7.5	-1.4142	0	25
Day 3	7	Axial	1.1657	7.5	1.4142	0	21.65
Day 3	8	Axial	0.6	1.136	0	-1.4142	0
Day 1	9	Central	0.6	7.5	0	0	62.79
Day 1	10	Central	0.6	7.5	0	0	67.79
Day 1	11	Central	0.6	7.5	0	0	51.56
Day 2	12	Central	0.6	7.5	0	0	18.75
	^a 13	Axial	0.6	13.864	0	1.4142	-

^a Experimental unit 13 was not considered due to its contamination during analysis.

Table 3. Variance analysis (ANOVA) for the quadratic reduced model.

Source	Sum of squares	df	Mean Square	F-value	p-value
Block	2968.7	2	1484.35		
Model	2117.93	3	705.98	11.34	0.0069
X_1	34.09	1	34.09	0.5477	0.4872
X_2	1317.27	1	1317.27	21.16	0.0037
X_1X_2	884.21	1	884.21	14.21	0.0093
Residual	373.45	6	62.24		
Lack on Fit	25.02	3	8.34	0.0718	0.9712
Pure Error	348.43	3	116.14		
Cor Total	5460.08	11			

3.8 CCD experimental design

Parameters such as initial As (V) concentration and contact time of PPAA on arsenic removal capacity (V) were analyzed using Central Composite Design (CCD). The experiments design CCD, regression analysis, and model adjustment were done using Design Expert ® V.13.0 software. The execution of the experimental design was carried out for three days using a blocking tool; each group could become a homogeneous unit and reduce external disturbances that could generate variations. The results of the experimental design are shown in Table 2.

3.8.1 Variance analysis

The adequacy of the fitted model and the importance of the polynomial terms was performed using an analysis of variance (ANOVA), as shown in Table 3. The results showed that the two-factor interaction model is the best statistical fit for eliminating arsenic, using PPAA in the variable range of the studied process p (0.0001) (Cabrales-González *et al.*, 2022; Gugushe *et al.*, 2019). In this study, x_1 , x_2 , x_1x_2 , are significant terms in the model since the value of p is close to or less than 0.01. This is not

significant regarding the lack of adjustment, which is to be expected since it was specified to adjust the experimental response to a two-factor interaction model.

3.9 Regression model evaluation

The experimental results obtained for the response of As (V) percentage removal and the variables of the PPAA process, a two-factor interaction model was specified. The model was adjusted to equations 4 and 5 for real and codified factors. Where y represents the modeled response, β the polynomial coefficients x_1 and x_2 , the encrypted independent variables. Equation 4 shows positive values of x_1x_2 , which indicates a favorable effect in the interaction between the initial concentration of As (V) and time.

Equation to codified factors

$$y = 36.10 + 2.71x_1 + 15.25x_2 + 16.61x_1x_2 \quad (4)$$

Equation to non-codified factors

$$y = 48.154 - 62.441X_1 - 2.149X_2 + 9.23X_1X_2 \quad (5)$$

Equation (4) can predict the response for the levels given to each factor. It can be employed to determine

the relative importance of the elements due to it presenting a determining coefficient of 0.8501. To evaluate the appropriateness of the model, the concurrence between adjusted R^2 and the predicted one was verified since R_{adj}^2 diminishes as terms are added to the model without value to it, and R_{pred}^2 gives information on data variance; therefore, predicted R square and adjusted R square must show a difference of 0.20 between each other (Dotto and Pinto, 2011). On the contrary, if the difference is more significant, it indicates problems with the data or the model. Therefore, for the proposed model, values of R_{adj}^2 (0.7752) and R_{pred}^2 (0.6758) were obtained, noting that the difference between both is under 0.2, which points to the reliability in the precision of the predictions generated by the model (Dávila-Parra *et al.*, 2022). To compare the range of predicted values at the design points with the average prediction error. The value of adequate precision (signal-noise relation) was obtained at 10.44, which implies a good signal, since relations above four-point towards an acceptable discrimination of the model (Dakhil *et al.*, 2021). Therefore, the adjusted polynomial can be employed to model the response within the bounds of the model (Ba and Boyaci, 2007; Karimifard and Alavi Moghaddam, 2018).

3.10 The main effect of the variables and interaction

Figure 7, shows the main effect of the variables: initial As (V) concentration, contact time, and concentration-time interaction. Figure 6a, shows the main effect of the initial arsenic (V) concentration, with the concentration showing no significant effect in removal, which is evident on the coefficient of x_1 since the increase in the response represents only 2.71% of the removal at the level change. On the other hand, the contact time in Figure 6b shows that the removal percentage increases by 15.255, going from a low level to a high level with an upward slope.

Experimental results (Table 2) show that at a low concentration of As (V) (0.2 mg/L), time is not relevant, with similar removal at 3 and 12 hours of contact time. However, when concentration increases to 1 mg/L, contact time influences the removal of As (V), with 3% removal at 3 hours and 56% at 12 hours of contact. This is further confirmed by the significance of the factor interaction, as shown in Figure 6c. At a higher concentration of arsenic, more contact time with the membrane is needed. On the contrary, low arsenic concentration does not require extended contact times.

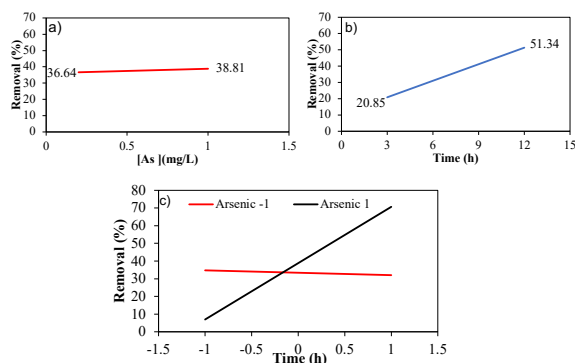


Fig. 7 Effects of the variables a) initial concentration of As (V), b) contact time, and c) interaction.

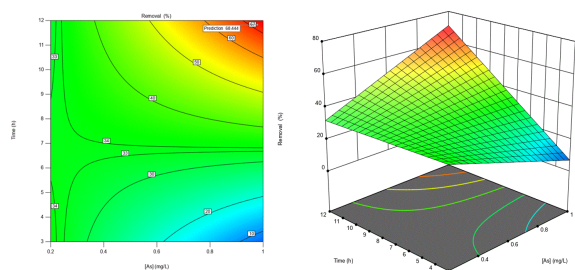


Fig. 8 Estimated values for removing As (V), considering contact time and initial concentration of PPA.

3.11 Maximum As(V) removal prediction

The design of experiments allows for obtaining a regression model based on the variables under study, which allows for predicting values according to the conditions of the studied process (Gonzales-Condori *et al.*, 2023). By the most pronounced slope method, 46 solutions were obtained with a desirability of one, which averages an initial concentration of As (V) of 0.98 mg/L and a contact time of the membrane of 11.8 hours to achieve a maximum removal percentage of 68.4%. Figure 8, shows the outlines where the estimated values for removal are emphasized through a color variation (cold blue for unfavorable results and warm yellow for favorable results).

The observed results concluded that a low concentration of arsenic results in a lower removal percentage. Therefore, it was suggested to increase the number of membranes to increase the number of available sites and achieve greater removal. To test this proposal, an experiment was carried out in which the number of membranes was increased to three and the initial concentration of arsenic was 48 ppb. The mixture was stirred until a final concentration of 10 $\mu\text{g/l}$ (+/-2) was reached. The data obtained from this experiment demonstrated that, under the conditions of the given model, the final concentration of arsenic could be reduced to the limits established by national and international organizations.

Conclusion

Graft polymerization by ultraviolet irradiation was an easy and rapid method to functionalized polypropylene. This method allowed the generating of a C-C covalent bond between polypropylene and acrylic acid, functionalizing it. The graft is not released during the removal process, so no byproducts were generated in the aqueous system. The use of functionalized polypropylene is easy and efficient in the removal of arsenic (V), since it only requires being in contact with the aqueous solution, without requiring additional treatment to recover it, it is enough to remove it from the solution, ensuring that the arsenic remains retained on its surface. Obtaining the maximum removal of arsenic (V) at an initial concentration of 1000 $\mu\text{g/L}$ and a contact time of 12 hours, using functionalized polypropylene (0.04 g weight, 4x4 cm area). However, to achieve the WHO limits for arsenic in water, it is recommended to increase the number of membranes (three). This increase allows for working at low concentrations (48 $\mu\text{g/L}$), removing arsenic, and reaching the limit established by the WHO. To enhance its performance, it is suggested to increase the number of membranes, reduce the contact time, and control the pH. This ensures a material that improves water quality, obtaining safe water, complying with international standards and contributing to the development of new materials and strategies that allow us to care for and heal this vital liquid.

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Nomenclature

ANOVA	Analysis of variance
ATR	Attenuated total reflectance
CCD	Central Composite Design
FT-IR	Transform Infrared Spectroscopy
KI	Sodium iodide
PP	polypropylene membrane
PPAA	functionalized polypropylene
PPAA-As	functionalized polypropylene with arsenic
pHPZC	Zero charge point

RSM	Response Surface Methodology
AgDDTC	silver diethyldithiocarbamate
WHO	World Health Organization
UV	Ultraviolet
GD	Grafting degree

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