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## Article

# Porous Polymers Based on PSU and PSU-TMA with Grafted Zirconium-Organic Moieties: Synthesis and Application for Removal of Arsenite and Arsenate Water Pollutants

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**Abstract:** Porous organic polymers (POPs), based on polysulfone (PSU) and covalently linked zirconium-organic moieties have been applied for the first time to Arsenic removal in wastewater. The synthesis involved anchoring a synthon molecule onto PSU, followed by MOF assembly and subsequent quaternization (QA) with trimethylamine (TMA). Two samples Zr-POP and Zr-POP-QA are characterized by NMR, FTIR, and titration. The efficiency of As uptake is revealed by ICP. The study is carried out at different pH (3, 7, and 12) to vary the charge of Zr-organic moieties and the charge of arsenite and arsenate species. Two concentrations (0.5 and 1 mM) of As (III) and As (V) are used. The results show that Zr-POP at pH 3 has a removal efficiency (RE%) of 77% for As (V), in agreement with the positive charge present in the Zr-framework at this pH. At neutral pH the As (III) sorption is also relevant. Zr-POP-QA at pH 12 shows, thanks to the positive charge on the ammonium moieties, a RE% of As (III) equal to 35%. The kinetic of processes, performed on the most promising system, i.e. Zr-POP at pH 3 for As(V), shows a plateau already after 8 hours with a second-order law. The regeneration of the material is also evaluated. According to the results, these materials are serious candidates in the removal of heavy metals in wastewater.

**Keywords:** POPs; polysulfone; water purification; As (III); As (V)

## 1. Introduction

Population growth requires an increasing quantity of drinking water, the consequent development of industries also leads to an increase in heavy metal in wastewater [1]. The presence of different toxic, carcinogenic heavy metals in the effluents makes their recycling very difficult and their removal became a crucial process [2–5]. Among them, arsenic is a potent cocarcinogen for some types of human organs, especially lung, liver, kidney, and bladder [6]. WHO 2004 provisional guideline value for arsenic in drinking water is  $10 \mu\text{g L}^{-1}$ ; it is generally found in higher concentrations in water. In Viterbo area (Italy) at Fabbrica di Roma, for example, arsenic is  $75 \text{ mg L}^{-1}$  and in Bagnoregio (UNESCO site)  $52 \text{ mg L}^{-1}$  [7]. As is presents in water at different oxidation states, most commonly as As (III) (arsenite) and As (V) (arsenate) form. Under oxidizing conditions, inorganic arsenic is predominantly present as As (V) and can be reduced to As (III) under moderately reducing environment [8].

Several treatment methods have been developed for the As removal as, ion exchange, sorption, membrane separation and precipitation, but most of these approaches are generally expensive, especially the membrane separation [9]. Metal-organic frameworks (MOFs), a highly porous materials formed by inorganic metal nodes connected by organic ligands are characterized by excellent tunability and well-ordered structure. These characteristics make MOFs promising candidates for several applications: 1) catalysis [10–12,13], 2) as fillers of mixed-matrix membranes (MMMs) [14] [15–17,18] and 3) in water pollution [19], using defective MOF, hierarchical-pore MOF and MOF

based composites (ref [20] and ref. therein). However, only MOFs displaying thermal and chemical stability under harsh conditions are considered suitable for industrial scale-up. In 2020, Feng et al. provided an overview of the factors affecting MOF stability under external stimuli, such as chemical, thermal, photolytic, radiolytic, electronic, and mechanical, offered guidelines to avoid unwanted framework degradation [21]. New emerging approaches to overcome these stability problems are the creation of hybrid composite materials combining “hard” metal-organic frameworks and “soft” polymers. The porous nature of MOFs and the flexibility and processability of polymers are synergistically integrated into MOF-polymer composite materials. The strong covalent bonds, create a robust molecular connections and facilitate the dispersion of the inorganic part in polymers. Different strategies of covalent connection are explored and summarized in ref [22]. One of them is the “polymerization of the framework” where organic ligands simultaneously constitute both MOF and the polymer chain, this method also doesn’t reduce the porosity [23–25]. Some examples of covalently linked MOF and commercial polymers are reported in different applications like: fuel cell [14,25], CO<sub>2</sub> separation [26,27], and heterogenic catalysts for organic transformation with stimuli response [28,29]. Among them, the Zr-MOF (UiO-66) have extraordinary thermal and chemical stability [30]. The effectiveness of UiO-66-based adsorbents, is due to a probable chemical bond with metals. In addition to the effect of electrostatic attraction, the effect of complexation and chelation between adsorbent and pollutants must be considered [31]. Wang et al. [32] reported for the UiO-66 an arsenate uptake capacity of 303 mg g<sup>-1</sup> at pH=2, much higher than that of currently available adsorbents (5–280 mg g<sup>-1</sup>, generally less than 100 mg g<sup>-1</sup>, see Table 2). This capacity was attributed to a high porosity, a large contact area and a plenty of active sites in the unit space. Two binding sites within the adsorbent framework are proposed for arsenic species, i.e., hydroxyl group and benzenedicarboxylate ligand. At equilibrium, approximately seven equivalent arsenic species can be captured by one Zr<sub>6</sub> cluster through the formation of Zr-O-As coordination bonds [32]. More efficient and faster absorption can be achieved by increasing pore sizes, increasing defect densities, and decreasing particle sizes [33].

In this study the covalently bonded MOFs make the polymer porous, therefore falling into the category of Porous Organic Polymers (POPs) that are characterized by their extensive porosity and surface area [34–38]. The high porosity of POPs combined with the metal center of the MOF and the ability of these polymers to be further functionalized with ionic groups, make it a versatile material that can be used in water treatment. In this work, we synthesized POPs covalently linked to metal organic moieties with ion conducting groups involved in the removal of arsenite and arsenate at various concentrations and at different pH.

## 2. Materials and Methods

### 2.1. Materials

Polysulfone UDEL P-1800 NT11 (PSU), terephthalic acid 98% (1,4-BDC), diethyl 2,5-dihydroxyterephthalate 97%, trimethylamine (TMA, 4.2 M in ethanol), 1-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), ZrCl<sub>4</sub> 99.5%, As<sub>2</sub>O<sub>3</sub> ACS reagent, Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O ≥98%, NaOH 98%, and other chemicals were used as received from Sigma-Aldrich without further purification.

### 2.2. Synthesis

#### 2.2.1. POP-Precursor

PSU-CH<sub>2</sub>Cl was obtained by the procedure described in ref. [39–41]. Two separated solutions were prepared. A) 2 g (3.8 mmol) of PSU-CH<sub>2</sub>Cl (1.7 degree of chloromethylation, DCM) was dissolved in 50 mL of anhydrous DMF under N<sub>2</sub> flux at 50°C, then 0.10 g of KI (0.64 mmol) were added under stirring. B) in 20 mL of anhydrous DMF were dissolved 0.82 g (3.2 mmol) of diethyl 2,5-dihydroxyterephthalate (in molar ratio 0.5 with respect to the chloromethyl groups) and 0.45 g, 3.2 mmol of K<sub>2</sub>CO<sub>3</sub>. The mixture was heated overnight at 80°C under nitrogen flux. The A and B solutions were combined and reacted at 70°C for 72 h. The solution was then treated with 10 wt% of NaOH in 50:50 H<sub>2</sub>O/MeOH at 60°C for 2 hours to hydrolyse of the residual esters. To obtain the H-form, the solution was precipitated with 30 mL of 2M HCl and 30 mL of ethanol and digested overnight. The

PSU-precursor was filterd and washed several times with water/ethanol and stored on P<sub>2</sub>O<sub>5</sub> at RT. Yield = 75 %.

2.2.2. Zr-POP

A) In 40 mL of anhydrous DMF, 1 g (1.74 mmol) of POP-precursor was dissolved under N<sub>2</sub> flux and 0.250 g (1.5 mmol) of terephthalic acid were added and mixed for 30 min. B) In 10 mL of anhydrous DMF, were added 0.1 mL of double distilled water and 0.4 g of ZrCl<sub>4</sub> (1.5 mmol) and stirred for 30 min. The two solutions were mixed for 30 min, placed in a Teflon bottle and put in the oven for 16 h at 120°C. The product was washed with HCl 0.1 N and acetone 3 times and stored on P<sub>2</sub>O<sub>5</sub>. Yield = 100 %.

2.2.3. Zr-POP-QA

0.8 g (1.2 mmol) of Zr-POP were dissolved overnight under N<sub>2</sub> flux in NMP, then 0.48 mL of TMA (2 mmol) were added and left to react at 80°C for 3 days under stirring. The product was dried under high vacuum and washed with H<sub>2</sub>O and dried again [25]. The degree of amination, stimated by NMR, was 1.15.

2.3. Batch Adsorption Studies

A weighted amount of As<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>HAsO<sub>4</sub> · 7H<sub>2</sub>O salts were dissolved in double distilled water (dd) to obtain concentrations of 0.5 and 1 mM. Several samples with 10 ± 0.3 mg in weight of Zr-POP and Zr-POP-QA powders, were prepared. pH was adjusted as reported in Table 1, varying the amount of 37% w/w HCl and 1M NaOH solution. The As (III) solutions at pH 12, was prepared under N<sub>2</sub> flux to avoid the carbonatation of OH<sup>-</sup>. The solutions at different concentrations and pH were used for the measurements adding Zr-POP and Zr-POP-QA powders. The resulting systems were left under stirring for 24 hours in closed vessels at room temperature. After that, each solution was filtered using a polyamide membrane filter (porosity: 0.2 μm, Whatman).

**Table 1.** Results of As (V) and (III) uptake by Zr-POP and Zr-POP-QA. The quantity added for each bach (15 mL) was 10 ± 0.3 mg. .

| System | Metal  | Sample    | pH/Initial concentrations As [mM] | RE % (±5%) |
|--------|--------|-----------|-----------------------------------|------------|
| a      | As V   | Zr-POP-QA | pH=3/[0.5]                        | 31.1       |
| b      | As V   | Zr-POP-QA | pH=3/[1.0]                        | 25.4       |
| c      | As V   | Zr-POP    | pH=3/[0.5]                        | 77.0       |
| d      | As V   | Zr-POP    | pH=3/[1.0]                        | 58.9       |
| e      | As V   | Zr-POP-QA | pH=12/[0.5]                       | 5.2        |
| f      | As V   | Zr-POP-QA | pH=12/[1.0]                       | 9.9        |
| g      | As III | Zr-POP    | pH=7/[0.5]                        | 27.2       |
| h      | As III | Zr-POP    | pH=7/[1.0]                        | 35.5       |
| i      | As III | Zr-POP-QA | pH=12/[0.5]                       | 34.5       |

The removal efficiency (RE) of each system is evaluated using the formula:

$$RE(\%) = \frac{c_0 - c}{c_0} \cdot 100 \tag{1}$$

where c<sub>0</sub> and c are the concentration, before and after sorption, respectively.

2.3.1. Kinetic measurements

The kinetic measurements were performed for the sample Zr-POP at pH 3 (0.5 mM, As V), at 30 min, 1 , 2 , 4 , 8 , 16 and 24 h of immersion.

2.3.2. Regeneration

The Zr-POP sample was chosen for the regeneration tests. The system was placed at pH 3 in 0.5 mM As (V); after 24 h the powder was filtered and regenerated with 1 M NaCl solution overnight.

The material was then filtered and washed with dd water several times, dried over  $P_2O_5$  and weighted. The renewed sample was inserted again into the same volume of fresh As (V) solution. The procedure was repeated 2 times.

#### 2.4. Characterization Techniques

##### 2.4.1. Ion Exchange Capacity

The IEC (milliequivalents per gram of dry polymer) was determined by potentiometric acid–base titration. For  $OH^-$  form, the finely ground powder of Zr-POP-QA was treated in NaOH 0.1 M solution for 24 h and washed with bidistilled water to remove the excess of NaOH for 48 h. After drying for 3 days over  $P_2O_5$ , the powder was weighed and immersed in 0.02 M HCl for 2 days. The acid solution was then back-titrated with 0.02 M NaOH. The IEC was 1.93 meq/g.

##### 2.4.2. $^1H$ -NMR Spectroscopy

$^1H$ -NMR spectra were recorded with a Bruker Avance 700 spectrometer operating at 700.18 MHz using deuterating solvents ( $DMSO-d_6$ ,  $CDCl_3$ ). A small portion of synthesized materials were treated under vacuum before NMR analysis.

##### 2.4.3. FTIR Spectroscopy

FTIR spectra were recorded in transmission mode in the range of 4000–500  $cm^{-1}$  using a Perkin Elmer Spectrum 2 IR spectrometer equipped with an ATR Zinc Selenide (ZnSe) crystals.

##### 2.4.4. Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES)

The heavy metal ion concentrations were determined by ICP-OES Perkin Elmer, Avio 200. The solutions were analyzed after a proper dilution.

##### 2.4.5. Brunauer-Emmett-Teller (BET) Analysis

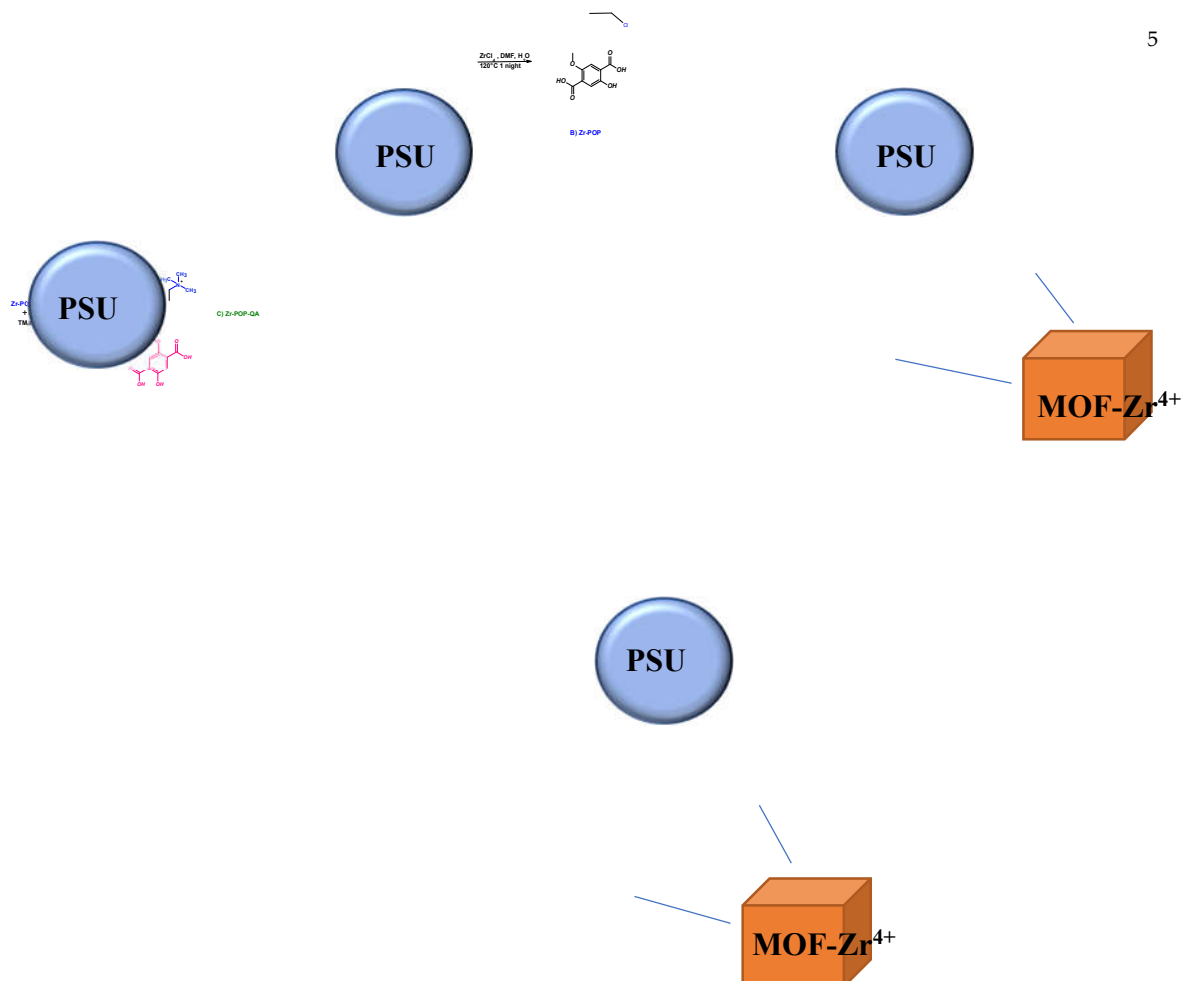
The BET surface area was determined via nitrogen gas sorption at 77 K. The samples were vacuum-degassed at 250°C before the analysis. The BET surface area of Zr-POP was 269  $m^2/g$  and for Zr-POP-QA 192.5  $m^2/g$ .

### 3. Results and Discussion

The covalent linkage of Metal-Organic Frameworks to polymers introduces a significant advantage in terms of stability and durability. When MOFs are covalently bound to polymers, the resulting composite material exhibits enhanced structural integrity, making it more robust in harsh environmental conditions. This increased stability ensures a prolonged lifespan of the material, crucial for sustained and effective heavy metal removal from water sources [22].

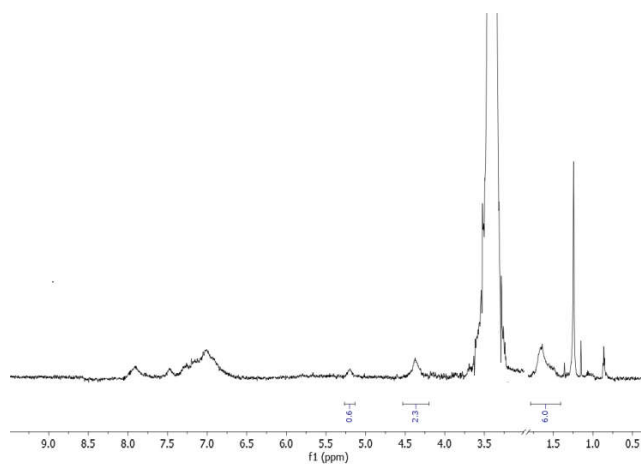
The synthesis of Zr-POP-QA is represented in Scheme 1 and reported in reference [25]. The POP-precursor synthesis (Scheme 1a) started with the deprotonation of phenolic groups of terephthalic ester by  $CO_3^{2-}$ , the resulting phenolate reacted with chloromethyl groups of polysulfone by a  $S_N2$  reaction. As described in the Experimental section, the stoichiometry is chosen so that only a fraction of the  $-CH_2Cl$  groups can react with the phenolate, leaving the remaining ones available for the successive quaternization reaction.





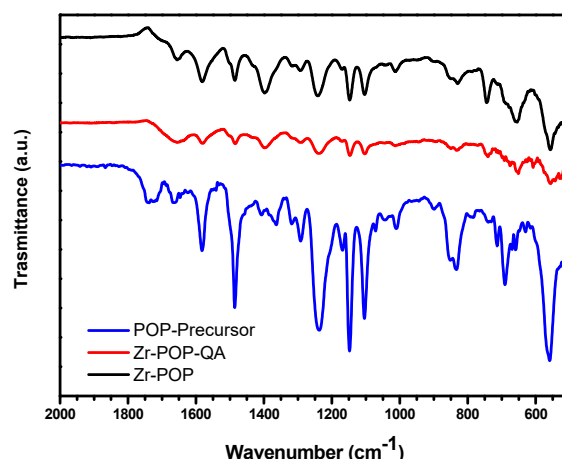
**Scheme 1.** Reaction sequence of the synthesis of: A) POP-precursor, B) Zr-POP, C) Zr-POP-QA.

The PSU linked with the synthon molecule is used to assemble the MOF by reaction with further terephthalic acid via solvothermal method (Scheme 1b), adapting the procedure used in the synthesis of UiO-66 [17]. Scheme 1c reports the formation of Zr-POP-QA. The quaternization of unreacted -CH<sub>2</sub>Cl groups is carried out following the procedure in ref. [33]. The <sup>1</sup>H-NMR spectrum of Zr-POP is shown in Figure 1 despite its low solubility. The signal ascribed to the ether bond between the phenolic group of terephthalic ester and the chloromethyl groups of PSU appears at 5.2 ppm evidencing the formation of the covalent link. The residual chloromethyl moieties are at 4.4 ppm. The other signals belong to PSU, in particular the methyl groups linked to quaternary carbon (1.6 ppm), and the aromatic region between 6.7-8.1 ppm. Considering 6 H for the methyl groups of PSU, the ether bond amounts to 0.6 H, i.e. a degree of functionalization equal to 0.3.



**Figure 1.** <sup>1</sup>H-NMR of Zr-POP in DMSO-d<sub>6</sub>.

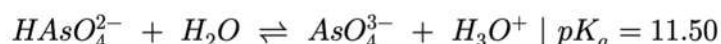
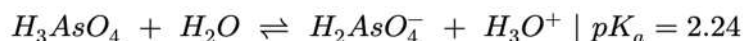
The Figure 2 compares the FTIR spectra of POP-precursor, Zr-POP and Zr-POP-QA. In the POP-precursor the presence of the peak at 1730  $\text{cm}^{-1}$  is due to the C=O stretch of terephthalic acid linked by ether bond to PSU. Other signals are due to the typical absorptions of PSU [34] and terephthalic acid. For the Zr-POP compound, the peak at 1730  $\text{cm}^{-1}$  disappears, and the shift of the signal from 1670  $\text{cm}^{-1}$  (carboxylate) to 1650  $\text{cm}^{-1}$  is observed. In fact, as a result of the Zr coordination, carboxylates present two peaks, asym and sym stretches at 1650 and 1400  $\text{cm}^{-1}$ , respectively [35]. The peaks at 750 and 650  $\text{cm}^{-1}$  belong to Zr—O bonds [36]. The methyl groups link to nitrogen ion ( $-\text{N}^+\text{Me}_3$ ) overlap with the methyl groups of PSU [37].



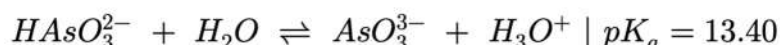
**Figure 2.** FTIR spectra of POP-Precursor, Zr-POP, Zr-POP-QA.

Arsenate exists in several forms, such as  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$ .  $\text{H}_2\text{AsO}_4^-$  is the predominant species at pH from 2 to 6, while  $\text{HAsO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$  are the main ions at pH increasing from 7 to 10 [38]. As (III) exists in neutral form ( $\text{H}_3\text{AsO}_3$ ) at pH < 8.0 and negatively charged ( $\text{H}_2\text{AsO}_3^-$ ) at pH > 8.0 [38,39]. The dissociation reactions and the corresponding equilibrium constants ( $pK_a$ ) of  $\text{H}_3\text{AsO}_4$  and  $\text{H}_3\text{AsO}_3$  are shown below [40]:

**As (V)**



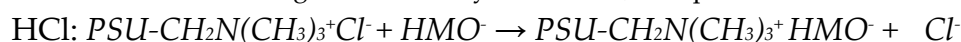
**As (III)**



Different factors can affect the sorption capacity of Zr-POP and Zr-POP-QA systems:

1) The charge present on MOF can affect the interaction and then the sorption of As. In the literature a pKa value of 3.52 for UiO-66 is found [30]. The isoelectric point (pH<sub>iep</sub>) and the point of zero charge (pH<sub>pzc</sub>) are 5.5 and  $\approx 5$  [41] respectively, which indicates a positively charged outer surface of UiO-66 when pH is below 5, where anions could get sorbed. When pH is above 5 a negatively charged outer surface is expected [42,43]. The maximum intake of 300 mg g<sup>-1</sup> for As (V) with UiO-66 at pH = 2 is found in ref. [32] as reported before.

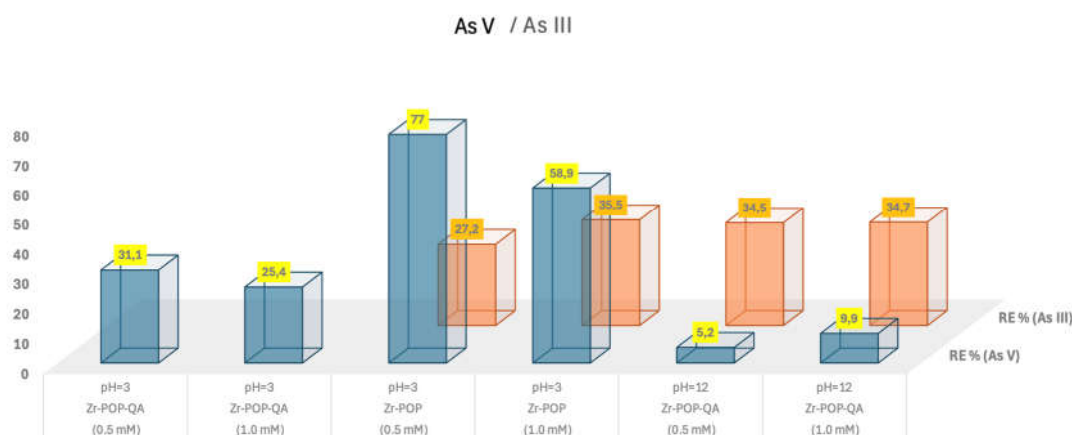
2) The anion exchange mechanism. In Zr-POP-QA, nitrogen is quaternized and presents a positive charge. The Donnan effect is then always favorable (except for the neutral As species). The ion to exchange is a function of pH: in HCl environment is the chloride ion, similarly at neutral pH, while in basic conditions the exchanged ion is the hydroxide ion, as reported below:



3) The porosity of the systems. As reported in the literature, the PSU polymer presents a low surface area of 6.1 m<sup>2</sup>/g, and volume of pores of 0.025 cm<sup>3</sup>/g [44]. In ref. [17] the UiO-66, shows a BET specific area of 665 m<sup>2</sup>/g and micropore volume of 0.16 cm<sup>3</sup>/g. Zr-POP exhibits a 269 m<sup>2</sup>/g of specific area and total pore volume of 0.39 cm<sup>3</sup>/g; for Zr-POP-QA, a 192 m<sup>2</sup>/g specific area and total pore volume of 0.30 cm<sup>3</sup>/g are found. The presence of MOF generated a consistent porosity in the pristine polymer. The average diameter of the pores goes from 5.8 (Zr-POP) to 6.2 nm for Zr-POP-QA, probably due to the steric effect of the ammonium group [25].

Previous studies, carried out in our laboratory with PSU-TMA (IEC=1.6 meq/g) show a RE for As (V) at pH = 7 less than 3% using similar As concentrations, indicating a low removal efficiency of the polymer in the absence of MOF.

Figure 3 shows a comparison between the uptake of As (III) and As (V). According to the results showed in Table 1 and Figure 3, the most efficient system for arsenic uptake was Zr-POP (sample c) at pH = 3 with an initial concentration of 0.5 mM As (V). The positively charged MOF, the predominant H<sub>2</sub>AsO<sub>4</sub> specie at this pH, and the high porosity of the system increases the arsenic capture, due to interaction with hydroxyl and carboxyl groups. Zr-POP-QA gave low adsorption, although the ion exchange mechanism is possible, probably due to the less porosity of the system. Increasing the pH, the MOF became negative and the uptake of As (V) decrease, as we can see in the Table 1 for the system “e/f” (Zr-POP-QA) at pH=12 (Figure 3 blue). In this case the MOF moiety does not participate in the capture due to the negatively charged –COO<sup>-</sup> and only the ammonium part should absorb. At pH 12, As (V) exists as arsenate ions (AsO<sub>4</sub><sup>3-</sup>); the high negative charge density of these species leads to a strong electrostatic repulsion between the arsenate ions and the negatively charged functional groups on the MOF surface.



**Figure 3.** Comparison of the uptake of As (III) (red) and As (V) (blue) by Zr-POP and Zr-POP-QA (acid and basic pH).

For neutral As (III) species at pH 7, the adsorption by the Zr-POP could be due to surface  $\pi$ - $\pi$  interactions according also to the large porosity of the material. The As (III) uptake (i sample, Table 1



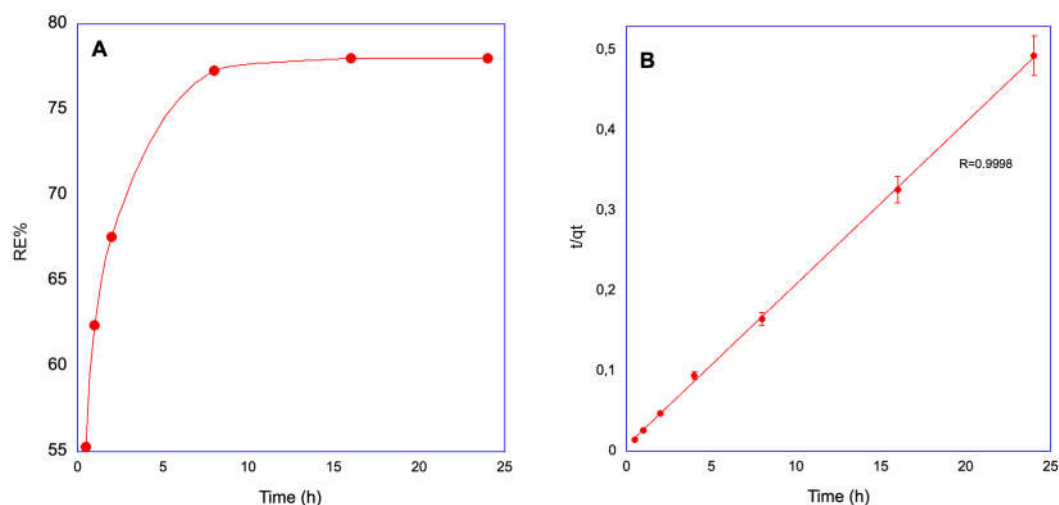
and Figure 3 red) is a favorite process at high pH, differently from As (V) (e, f). For As (III) at pH 12 the equilibrium between the species  $\text{H}_2\text{AsO}_3^-$  and  $\text{HAsO}_3^{2-}$  are established, the species are less charged and less hydrated, consequently the electrostatic repulsion is lower [44]. The reduced repulsion facilitates a more effective interaction and subsequent adsorption of As (III) onto the QA-MOF's active sites, compared to As (V) under this condition, as showed in Figure 3. Additionally, the smaller size and reduced hydration of As (III) facilitate a better diffusion and access to adsorption sites within the polymer matrix, while the larger and more hydrated As (V) species encounter steric hindrance. In all cases is evident that the increase in porosity of the system makes the capture of arsenic more effective.

To investigate the behavior of arsenic sorption process, kinetic studies are carried out on the best performing system: Zr-POP at pH=3 for As (V) adsorption. From Figure 4a, it can be observed that increasing the contact time, increases the RE%, as expected, and already after 30 minutes, Zr-POP reaches 55% As (V) removal. Furthermore, already after 8 hours the Zr-POP reaches its maximum sorption towards As (V). To study the uptake mechanism in more depth, the following calculations are performed, assuming a Pseudo Second Order (P-S-O) kinetic model [45].

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k} + \frac{t}{q_e} \quad (3)$$

where  $q_e$  is the concentration (mg/g) of arsenic adsorbed onto the MOFs at the equilibrium and  $q_t$  the concentration at time  $t$ . By plotting the values  $t/q_t$  versus  $t$ ,  $q_e$  can be extrapolated from the value of the slope. From the intercept, the rate constant for the P-S-O kinetic model,  $k$ , can be obtained.



**Figure 4.** Kinetic Uptake of: A) As (V) by Zr-POP (acid pH) and B) P-S-O kinetic model.

From uptake data is possible to approximately calculate the theoretical uptake of the POP systems. The value obtained from the kinetic at pH 3 for As (V) is about 50 mg/g. A Zr-POP cluster should theoretically absorb 7.5 As atoms by one  $\text{Zr}_6$  cluster, as reported in the work of Wang et al. [32]. The molecular weight of the system is 955 g/mol (with 1 cluster of  $\text{Zr}_6$ ) and 1.0 g of Zr-POP corresponds to 1.0 mmol and 0.35 meq. The theoretical mg of As absorbed by the system, can be calculated as follows:

$$\begin{aligned} \text{meq}_{\text{MOF}} &= \frac{g_{\text{Zr-POP}}}{PM_{\text{Zr-POP}}} = \frac{1.0 \text{ g}}{955.0 \text{ g/mol}} = 1.0 \text{ mmol} \\ &\rightarrow 0.35 \text{ meq (Active Zr - POP)} \end{aligned} \quad (4)$$

$$\begin{aligned} meq_{theoretical(As)} &= meq_{MOF} \times 7.5_{As} = 0.35\ meq \times 7.5 \\ &= 2.62\ meq\ (As\ for\ 1g\ Zr - POP) \end{aligned} \tag{5}$$

$$\begin{aligned} mg_{theoretical(As)} &= meq_{theoretical(As)} \times PM_{As} = 2.62\ meq \times 75\ \frac{g}{mol} \\ &= 196.5\ mg\ (As) \end{aligned} \tag{6}$$

Giving us the maximum theoretical amount that can be absorbed for 1 gram of system at pH 3. This high theoretical value gives us the possibility to improve the total absorption value in the future. Preliminary studies have also been done for the regeneration of Zr-POP. The system showed an 77±5% RE as reported in Table 1, while at the first cycle of regeneration the system continues to show activity in the uptake process with 79±5% RE.

Table 2 compares various arsenic adsorption systems based on MOFs, highlighting parameters such as removal efficiency (RE%), adsorption capacity (mg/g), initial arsenic concentration, and pH. Among them, the UiO-66 system achieves very high adsorption capacity compared to other materials. The system presented in this article showed a capacity of 50 mg/g in line with other UiO-66 polymer composites despite different experimental conditions. In other cases in Table 2 such as Magnetite, MIL-53, etc. the values are lower.

**Table 2.** Different systems used for arsenic removal and their capacity.

| System          | RE%   | mg/g | Initial Concentration | As species        | pH   | Ref.     |
|-----------------|-------|------|-----------------------|-------------------|------|----------|
| PSU             | 20%   | -    | -                     | As(V)             | 2.6  | [46]     |
| PPO/UiO-66      | 85%   | 68.2 | -                     | As(V)             | 7-10 | [47]     |
| PAN/UiO-66      | 92%   | -    | -                     | As (III)<br>As(V) | 4-9  | [48]     |
| PMMA/UiO-66     | 89%   | 110  | -                     | As(V)             | 7-11 | [49]     |
| Magnetite       | -     | 17.2 | 1.0 mM                | As (V)            | 5-9  | [50]     |
|                 |       | 18.7 |                       | As (III)          |      |          |
| Organic Biochar | -     | 16.2 | 50 ppm                | As (V)            | 2-19 | [51]     |
| MIO-CNTs        | -     | 24.1 | -                     | As (V)            | 2-10 | [52]     |
| MIL-53(Fe)      | -     | 21.3 | -                     | As (V)            | 5    | [53]     |
| Fe3O4@UiO-66    | -     | 73.2 | 150 ppm               | As (V)            | 7    | [54]     |
| Fe-BTC          | -     | 12.3 | unknown               | As (V)            | 4    | [55]     |
| Fe3O4@TA@UiO-66 | 80%   | 97.8 | -                     | As (III)          | 3-11 | [56]     |
| Zr-POP          | 77±5% | 50   | 60 ppm                | As (V)            | 3    | Our work |

4. Conclusions

For the first time, covalently linked Zr-POP and Zr-POP-QA systems are used for the removal of As (III and V) at different pH and different concentrations. The covalent bond between MOF and polymer enhances the properties of these materials for the application in water purification. The best results in terms of removal efficiency are obtained with the Zr-POP system at pH 3 with As (V), while at neutral pH the same material shows a moderate As (III) uptake. At alkaline pH the Zr-POP-QA has a consistent As (III) uptake due to the quaternized ammonium moieties on the matrix that play a crucial role for the uptake at these pH. The stable integration of MOFs within the polymer matrix minimizes the risk of leaching or detachment of MOF particles over time, ensuring sustained and reliable heavy metal adsorption capacities throughout the lifespan of the material.

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