



## As(III) oxidation by MnO<sub>2</sub> coated PEEK-WC nanostructured capsules

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### ABSTRACT

PEEK-WC nanostructured capsules were prepared by the phase inversion technique and used as support for the coating of a manganese dioxide layer. The coating was done by a chemical treatment of the capsules followed by a thermal one. The presence of the MnO<sub>2</sub> layer was confirmed by scanning electron microscopy (SEM), back scattering electron (BSE), energy dispersive X-ray (EDX) and X-ray diffraction (XRD) analysis. The produced capsules were, then, tested for As(III) oxidation in batch. The experiments consisted in treating 165 ml of As(III) solution with 1 g of coated capsules at fixed temperature (15 °C) and pH (5.7–5.8). In particular, the efficiency of the system was investigated for different As(III) concentrations (0.1, 0.3, 0.7 and 1 ppm). For feeds at lower As(III) content (0.1–0.3 ppm), tests lasted for 8 h, while prolonged runs (up to 48 h) were carried out on more concentrated solutions (0.7 and 1 ppm). The produced capsules were able to oxidize As(III) into As(V) leading to complete conversion after 3 and 4 h for feed concentrations of 0.1 and 0.3 ppm, respectively.

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### 1. Introduction

Arsenic is a high toxic species that causes serious health problems, especially for long term exposure to contaminated drinking water and food. The maximum contaminant level (MCL) of arsenic in drinking water has been significantly lowered in last years and the new value of 10 µg L<sup>-1</sup>, recommended by the WHO [1], is today adopted by the European Union [2] and by USA [3].

In natural waters arsenic normally occurs in two oxidation states: (i) +III (arsenite) and (ii) +V (arsenate). It is well known that the reduced state is much more toxic than the oxidized one [4] and that its removal is more difficult. Therefore, many technologies applied for removing arsenic from water need a pre-oxidation step to convert As(III) into As(V). In the presence of air, the oxidation rate of As(III) is very slow [5,6]. Frank and Clifford [7] reported that 8% of As(III) was oxidized within 60 min by injecting with pure oxygen into the solution. Kim and Nriagu [8] treated a groundwater containing As(III) with air and pure oxygen and observed that 54% and 57% of As(III) were oxidized within 5 days, respectively. The oxidation rate of As(III) in the presence of oxygen can be increased by UV irradiation of the water, especially if ferric ions or citric acid or sulfites are also contained into the water [9–12]. The oxidation rate

of arsenite is high if oxidants such as ozone or chlorine compounds are used. For example, Kim and Nriagu [8] reported complete oxidation of arsenite in the presence of O<sub>3</sub> within 20 min. However, in most cases, the use of ozone is limited, due to the high cost, the high energy consumption and safety issues. Referring to chlorine compounds, they also are harmful and could lead to corrosion problems in the plant. Besides the use of liquid oxidants, arsenic oxidation can be also obtained by employing solid manganese oxides, that have an inert nature [13–19]. Most of the literature studies refer to the use of MnO<sub>2</sub> particles in batch or column tests and confirm its oxidation activity. MnO<sub>2</sub>-self has oxidative properties and does not act as a catalyst for the oxidation by dissolved oxygen; in fact, it has been observed that the amount of dissolved oxygen does not affect the oxidation rate of arsenic when MnO<sub>2</sub> is employed [18]. However, Ghurye and Clifford [19] confirmed this result only in the absence of interfering reductants in the solution, whereas a significant effect of the dissolved oxygen content was registered when interfering reductants, such as dissolved manganese, dissolved iron, sulfide and TOC, were present.

When using solid oxidants, their size plays an important role on the performance of the system. In fact, smaller particles lead to higher efficiency; on the other hand, the smaller is their size, the higher is the risk that they could be dispersed into the feed stream. The size of beads is usually around 80 µm [13,20,21]. The aim of this work was to produce a new type of solid oxidants, of bigger size, consisting of coated MnO<sub>2</sub> polymeric nanostructured capsules and to test them for As(III) oxidation. The polymeric capsules, used

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as support, were produced combining the phase-inversion technique and the membrane process as described in literature [22]. In particular, the capsule morphology, its shape, and size were easily adjusted by changing parameters such as polymer concentration, solvent and non-solvent. The production of capsules with a nanostructured surface is one of the key points for a successful deposition of the  $\text{MnO}_2$  layer. In fact, in presence of micropores,  $\text{MnO}_2$  could penetrate inside them, leading to an inhomogeneous coating of the external surface of the capsule. This would decrease the efficiency of the system, due to the lower  $\text{MnO}_2$  area available for the arsenic molecules.

The study presented here includes three main parts:

1. The polymeric capsules preparation;
2. The  $\text{MnO}_2$  coating;
3. The As(III) oxidation tests in batch mode.

Concerning the oxidation tests, they were mainly devoted to investigate if there was any oxidation activity and were carried out without any optimization of the operating conditions.

## 2. Materials and methods

### 2.1. Materials for capsules preparation and $\text{MnO}_2$ coating

The capsules were made of PEEK-WC, a polymer supplied by the Chan Chung Institute of Applied Chemistry, Academia Sinica. PEEK-WC was chosen for the production of capsules due to the broad experience that the Institute on Membrane Technology (ITM-CNR) has on the production of PEEK-WC membranes by the phase inversion technique. In particular, PEEK-WC has been used for the preparation of membranes to be applied in water treatments [23,24] as well as in gas separations [25,26]. The acquired experience led to the preparation of capsules of controlled morphology, suitable to be used as support for the  $\text{MnO}_2$  coating. The solvent, *N,N*-dimethylformamide (DMF), was purchased from Merck. The dodecane was purchased from GPR Rectapur, VWR International, and used as oil phase. The isopropanol, purchased by Carlo Erba Reagents, was mixed with water and employed as a non-solvent. The surfactant, sodium dodecylsulphate (SDS) was added to the coagulation bath and was purchased from Sigma-Aldrich, Germany.  $\text{MnO}_2$  coating over capsules was done using manganese(II) chloride tetrahydrate and sodium hydroxide flakes from MERCK, India. All materials were used as received, without further purifications.

### 2.2. Materials for arsenic solutions preparation

The aqueous solutions of As(III) at different concentrations (0.1–1 ppm) were obtained by properly diluting a “mother solution” containing 1 ppm of As(III), prepared dissolving  $\text{NaAsO}_2$  (Sigma-Aldrich, Germany) in distilled water.

### 2.3. Methods for capsules preparation and characterization

The PEEK-WC polymer (10 wt%) was dissolved in DMF by stirring at room temperature. The polymeric solution (Phase 1) was, then, pressed through a polyethylene (PE) monoporous film (pore size, 600  $\mu\text{m}$ ) until the formed drop in the dodecane phase (Phase 2) precipitated in the rotating coagulation bath (Phase 3), consisting of a mixture of water/isopropanol 10:90 (v/v) and 1 wt% of SDS [22]. The experimental set-up is shown in Fig. 1.

The temperature of the coagulation solution was kept constant at room temperature using a thermostatic unit. The capsules were immersed and washed in the isopropanol bath for 24 h, and then dried in a vacuum oven at 60 °C overnight.

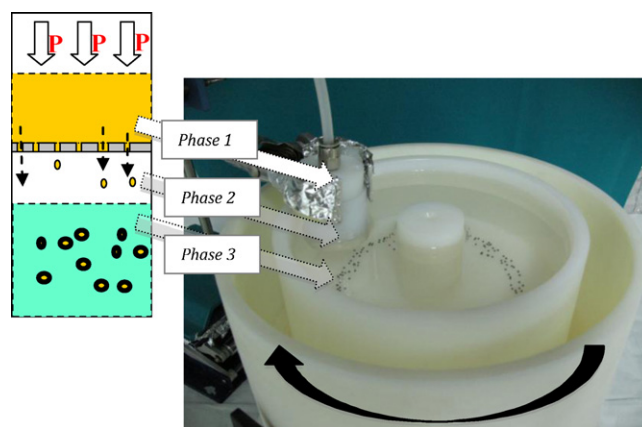


Fig. 1. Polymeric microcapsule experimental setup (dye was added to the polymer capsule for better visualise them in the system).

$\text{MnO}_2$  coating was done by chemical treatment of the capsules followed by heat treatment. In the first step, 3.0 ml 2.5 M Mn(II) salt solution was added to 3.0 g of capsules in a heat resistant pot and mixed thoroughly. After, 0.3 ml 8 N sodium hydroxide solution was added and well mixed. The mixture was then heated up to 150 °C in oven for 5 h. In the second step, it was first heated to 250 °C in oven for 3 h, and then cooled down to room temperature. Finally, coated capsules were washed with distilled water.

The produced  $\text{MnO}_2$  coated PEEK-WC capsules were characterized by the following methods:

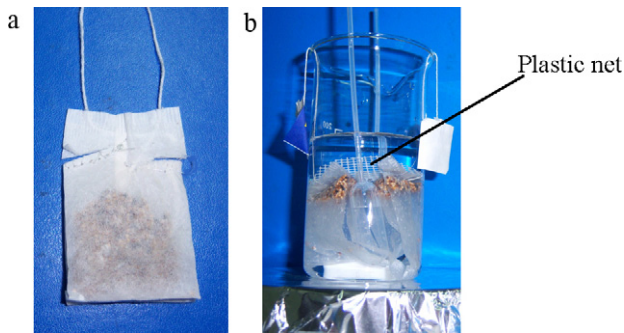
1. The morphology was evaluated by means of scanning electron microscopy (SEM) at 20 kV (Cambridge Instruments Stereoscan 360).
2. The success of the  $\text{MnO}_2$  coating and its uniform distribution on the surface of the PEEK-WC capsules was evaluated by X-ray diffraction (XRD) (Philips PANalytical X'Pert Pro XRD), energy dispersive X-ray (EDX) (Philips EDAX analysis system) and back scattering electron (BSE) (Cambridge Instruments Stereoscan 360) techniques.
3. The diameter was determined by a digital micrometer (Carl Mahr D 7300 Esslingen A.N.) and by SEM observation of the freeze-fractured cross-sections.

### 2.4. Methods for arsenic oxidation tests

The lab set-up used for carrying out the oxidation tests mainly consisted of a tank containing the feed, connected to a thermostatic bath for controlling the temperature. The feed was mixed by a magnetic stirrer. The coated capsules were immersed inside the solution. To avoid their floating and, therefore, to ensure a more effective contact with the solution, the capsules were placed in tea bags (Fig. 2a) and forced to be totally immersed by placing a plastic net at the top of the solution (Fig. 2b).

In all experiments (carried out for 8 h), the temperature was kept constant at 15 °C, which is an average value for natural waters, and the pH value was around 5.7–5.8. This pH (measured by a pHmeter, Hanna Instruments 213) was obtained by simply dissolving the arsenite salt in distilled water and no further adjustments were made. In each test, 165 ml of As(III) solution were treated with 1 g of coated capsules.

The degree of the As(III) oxidation was calculated by determining by a spectrophotometer (UV-160, Shimadzu) the content of As(V) in the solution. In particular, a colorimetric method has been used for preparing both samples and standards [27]. To each sample (5 ml), 400  $\mu\text{l}$  of colorimetric solution was added and the absorbance was measured at the wavelength of 840 nm.



**Fig. 2.** (a) Coated capsules into a tea bag. (b) Immersion of the tea bags into the solution.

Fig. 3 shows the calibration line obtained.

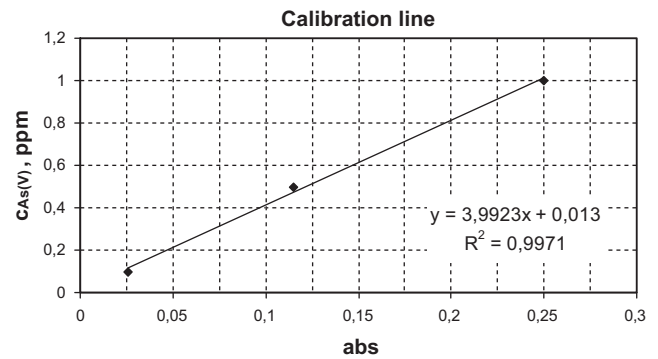
The manganese content in water was analyzed by using the inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 2100 DV, Perkin Elmer).

### 3. Results and discussion

#### 3.1. Capsules

A picture of the produced capsules is reported in Fig. 4. It can be noticed that they are quite uniform in size and shape. The brownish color of these capsules is due to the coated  $\text{MnO}_2$  layer on the external surface; in fact, uncoated PEEK-WC capsules are generally white in color.

Fig. 5 shows the XRD analysis of the polymeric capsules and of the polymeric coated capsules, before and after the oxidation. It can be noticed that for both types of coated capsules, the characteristic peaks of  $\text{MnO}_2$  (at  $2\theta$  values of 36 and 32) are present and their intensity does not change after the oxidation. Some other peaks are registered that are due to the polymeric support and that become of lower intensity moving from the polymeric capsules to the coated capsules and from the coated capsules to the coated capsules after oxidation.



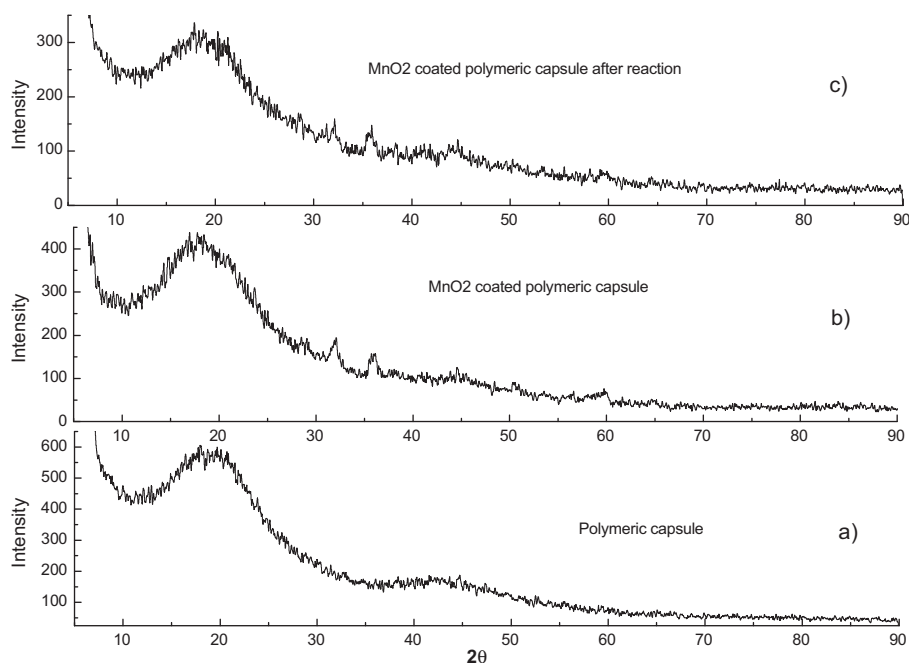
**Fig. 3.** Calibration line obtained with the As(V) standards.



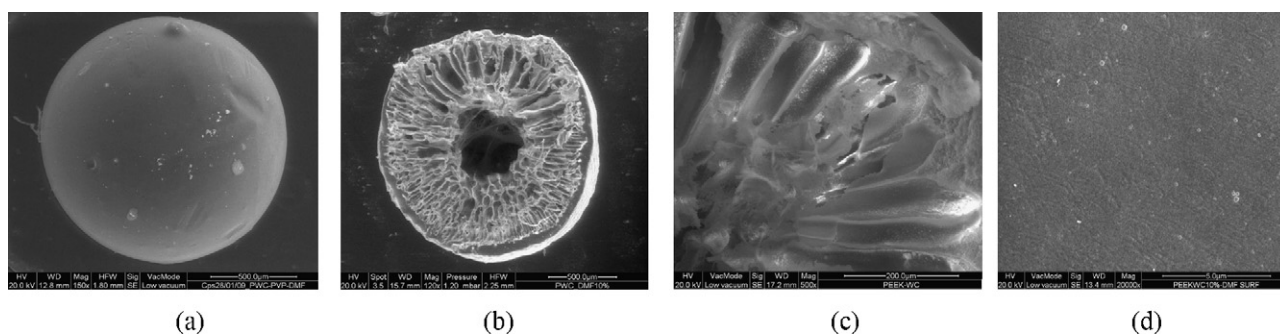
**Fig. 4.** Picture of the produced capsules.

The produced capsules were characterized by SEM analysis and their pictures, with and without coating of  $\text{MnO}_2$ , are reported in Figs. 6 and 7, respectively.

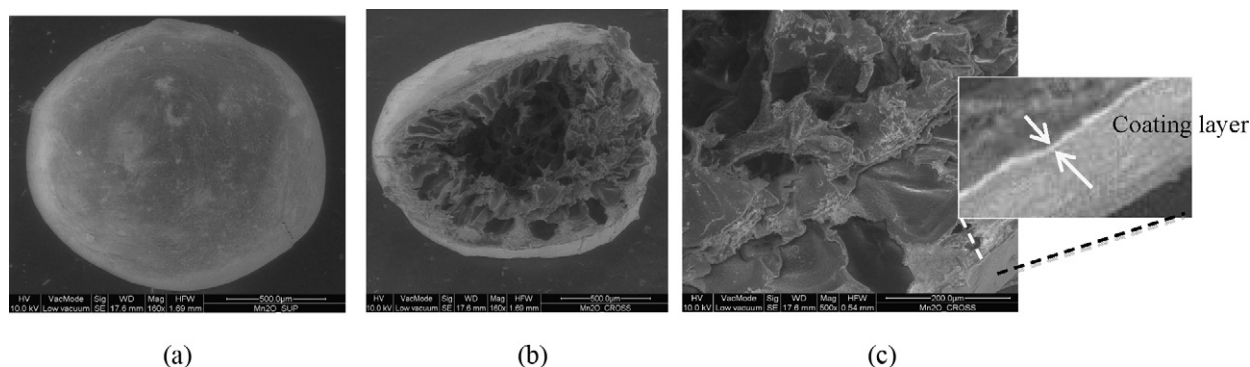
The PEEK-WC capsules have a spherical shape and a smooth surface (Fig. 6a). They present a central cavity and an asymmetric



**Fig. 5.** XRD analysis of the capsules (a) uncoated, (b) coated, and (c) coated after the oxidation.



**Fig. 6.** SEM of the prepared PEEK-WC capsules: (a) surface of the whole capsule; (b) cross-section; (c) magnification of the cross-section (shell side); and (d) magnification of the outer skin.



**Fig. 7.** SEM of the PEEK-WC microcapsule coated with  $\text{MnO}_2$ : (a) surface of the whole capsule; (b) cross-section; and (c) magnification of the cross-section (shell side).

(finger type) structure but with a dense nanostructured skin layer at the outer surface (Fig. 6b and c). To better underline the nature of the skin layer, a zoom of the surface it is also reported (Fig. 6d). The morphologies are similar to those of membranes obtained using the same polymer, operating conditions and coagulation medium. In particular, the production of membranes or capsules with a thicker top-layer, as in this case, is generally due to the use of non-solvent which delays the demixing rate between the solvent and non-solvent [22].

The coated PEEK-WC capsules maintain a similar asymmetric structure of the PEEK-WC uncoated ones, although they have been treated at a temperature of about  $250^\circ\text{C}$  (Fig. 7a and b). In Fig. 7c, a thin coating layer on the capsule surface is visible. The coating thickness varies along the sample and from samples to samples and an average value of  $5 \pm 2\ \mu\text{m}$  was estimated.

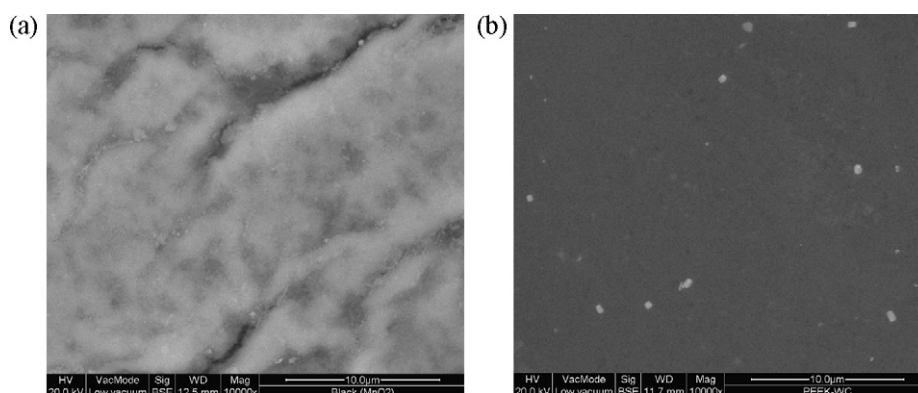
BSE images of the coated and uncoated capsules were made and they are shown in Fig. 8. The  $\text{MnO}_2$  particles could be visualised as

a homogeneous white layer (a) and compared with the uncoated darker PEEK-WC capsule surface (b).

The identification of the  $\text{MnO}_2$  on the capsules surface and cross-section was carried out by EDX analyses (Fig. 9). The intensity of the Mn and O signals is high on the surface while at the cross-section both signals are significantly reduced. This result shows that the  $\text{MnO}_2$  coating only partially penetrate the polymeric capsule, confirming that the nanostructured skin layer was able to ensure an homogeneous coating of the external surface.

In Fig. 10 the distributions of the PEEK-WC capsule diameters with and without coating are reported.

For the PEEK-WC capsules, the size distribution ranges from 1.3 to 1.6 mm with a maximum at about 1.4 mm. PEEK-WC capsules coated with  $\text{MnO}_2$  showed a lower size ranging from 0.8 to 1.4 mm, probably due to a polymer shrinking caused by the high temperature needed during the coating procedure.



**Fig. 8.** BSE images of the surface of the PEEK-WC capsules (a) coated with  $\text{MnO}_2$  and (b) uncoated.

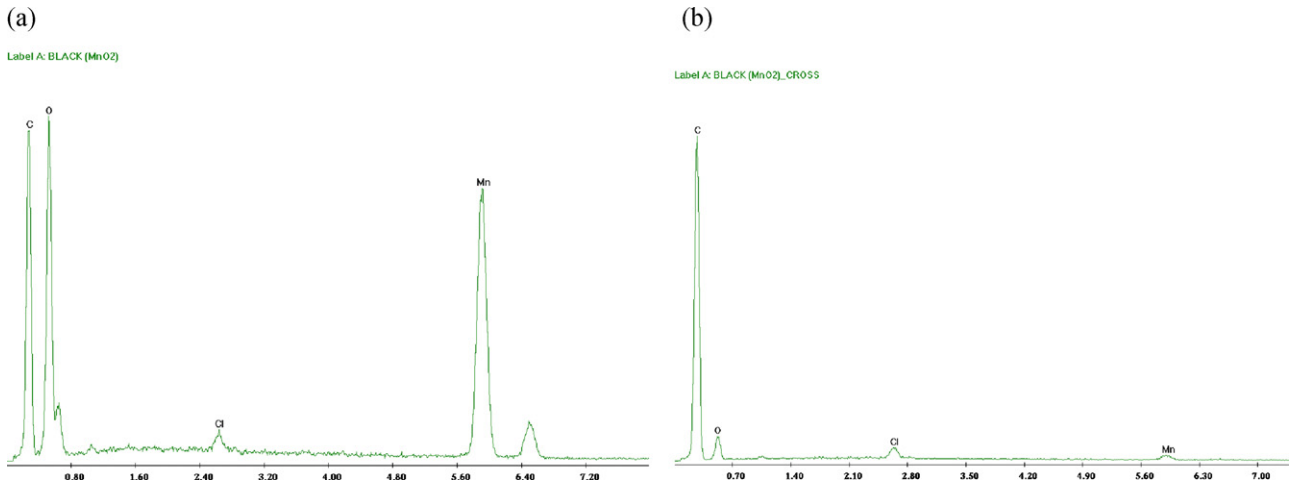


Fig. 9. EDX analysis PEEK-WC coated capsules (a) surface and (b) cross-section.

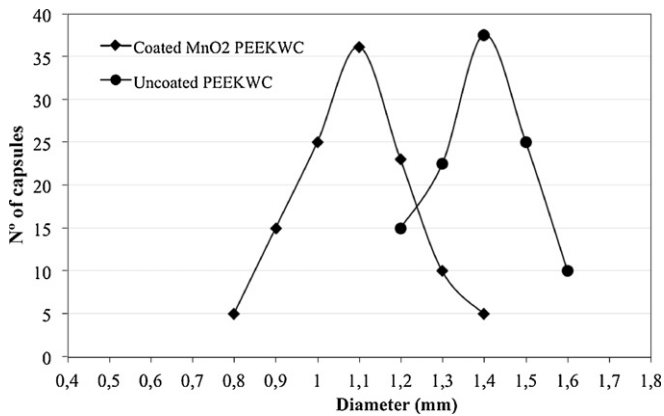


Fig. 10. Pore size distribution of the PEEK-WC capsule uncoated and coated with MnO<sub>2</sub>.

The coated capsules were heavier than uncoated ones, as reported in Table 1, and the ratio of the grams of MnO<sub>2</sub> per gram of capsule was 0.37.

3.2. As(III) oxidation tests

Experiments have been carried out with both coated and uncoated capsules. With the uncoated capsules no oxidation was observed, while the coated ones were able to oxidize arsenite into arsenate. In the following figures the main results achieved during the experimental tests with coated capsules are summarized. Each experiment was repeated at least two times and the plotted data are the average of the obtained results.

During the experiments, the performance of the system at different As(III) concentrations was analyzed. Fig. 11 shows the degree of oxidation obtained for four As(III) concentrations (0.1, 0.3, 0.7 and 1 ppm), after 8 h of test. For a content of As(III) of 0.1 and 0.3 ppm, complete oxidation was obtained, whereas a 33% and 26% of oxidation was registered for a content of 0.7 and 1 ppm, respectively. The observed behaviour could be due to the fact that at lower

Table 1 Increase of weight of the coated capsules.

Material	Initial weight	Weight after coating	Weight gained
PEEK-WC capsules	3.0 g	4.10 g	1.10 g

As(III) concentrations the system is working with an higher excess of MnO<sub>2</sub>.

Fig. 12 shows the oxidation trend with time for the investigated feed concentrations of As(III). For a concentration of 0.1 and 0.3 ppm, it was possible to obtain a complete oxidation (100%) already after 3 h and 4 h, respectively, whereas for higher As(III) contents, although the degree of oxidation increased with time, after 8 h less than 40% was oxidized.

To investigate the effect of time on the feeds at higher concentration (0.7 and 1 ppm), prolonged tests (up to 48 h) were also carried

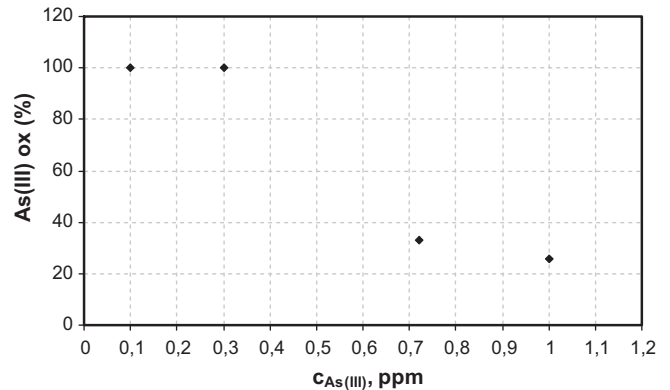


Fig. 11. As(III) oxidation vs feed concentration. V<sub>feed</sub>, 165 ml; T, 15 °C; pH, 5.7–5.8; 1 g coated capsules; t, 8 h.

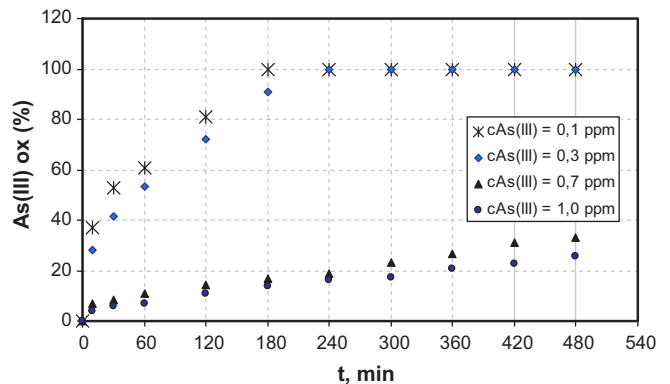


Fig. 12. As(III) oxidation vs time for different feed concentrations. V<sub>feed</sub>, 165 ml; T, 15 °C; pH, 5.7–5.8; 1 g coated capsules.

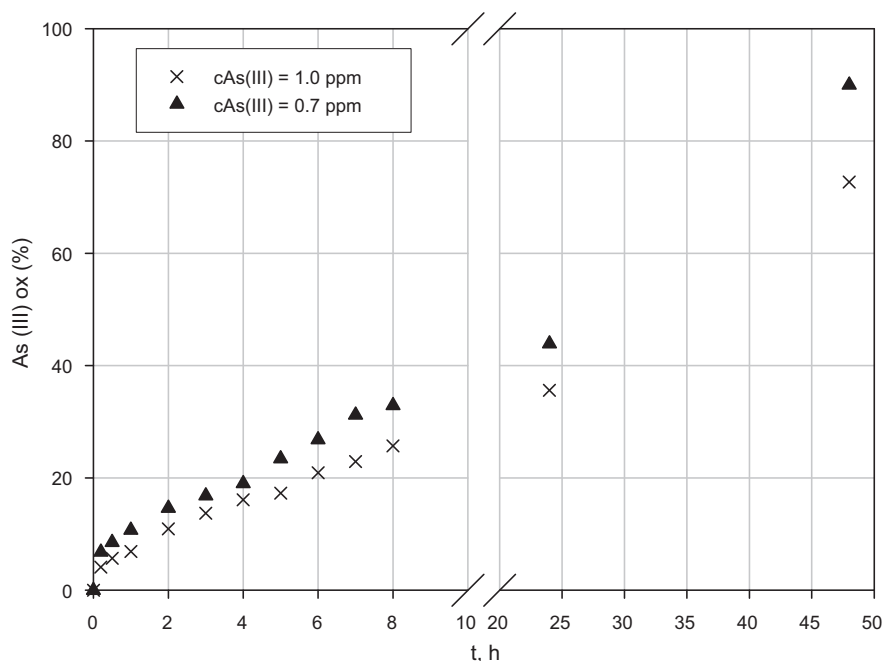


Fig. 13. As(III) oxidation vs time for the more concentrated feeds.  $V_{\text{feed}}$ , 165 ml;  $T$ , 15 °C; pH, 5.7–5.8; 1 g coated capsules.

out (Fig. 13). An increase of the oxidation degree was obtained for both feeds, reaching values of 44% and 36% for an As(III) content of 0.7 and 1 ppm, respectively, after 24 h. Tests were continued for 24 h more and the oxidation degree was of about 90% and 73% for the 0.7 and 1 ppm solution, respectively. The long time needed for obtaining significant oxidation values, could be due the fact that during tests not all the  $\text{MnO}_2$  is easily available for the As(III) (the capsules are contained in tea bags and they are also close each other) and, therefore, the accessible reaction sites are reduced.

For all the experiments, the reproducibility of the results was confirmed by repeating each test at least two times. As example, Fig. 14 compares the oxidation values obtained in two experiments carried out at the same operating conditions. It can be noticed a good overlapping of data for the two tests, with a maximum variation of 5%.

The same capsules were employed in all tests, showing a good efficiency. After tests, samples of the water solution were analyzed by ICP-OES to determine the presence of manganese. For concentrations of 0.1 and 0.3 ppm of As(III) (time of experiments, 8 h), the Mn content was of about 0.3 ppm, while for the solutions containing 0.7 and 1 ppm of As(III) (prolonged tests up to 48 h), the Mn amount was around 1 ppm.

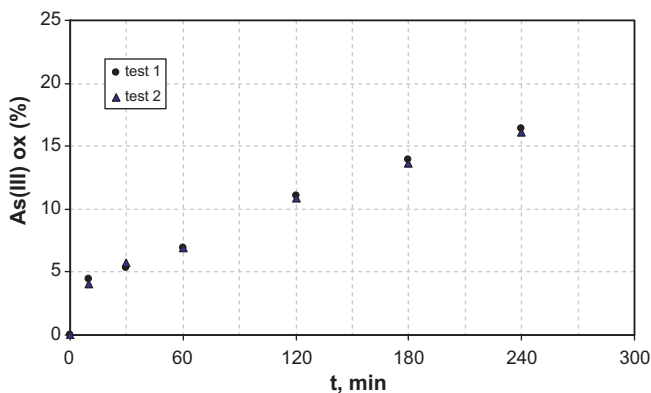


Fig. 14. As(III) oxidation vs time for two different tests.  $V_{\text{feed}}$ , 165 ml;  $T$ , 15 °C, pH, 5.7–5.8;  $C_{\text{As(III)}}$ , 1.0 ppm; 1 g coated capsules.

The maximum value of Mn allowed in drinking water is 0.05 ppm, then, if the produced capsules are used for drinking water treatments, a successive stage for removing both As(V) and manganese must be considered. However, for treatments of industrial waters, the amount of manganese within the imposed limit being of 1 ppm, no further stages for its removal are required.

#### 4. Conclusions

PEEK-WC capsules coated by a  $\text{MnO}_2$  layer were successfully prepared. They had a spherical shape and were asymmetric, with a central cavity and a nanostructured skin layer at the outer surface. Their size ranged from 0.8 mm to 1.4 mm and the coating layer on their surface had a thickness of about  $5 \pm 2 \mu\text{m}$ . Tests of As(III) oxidation were also carried out in batch by immersing the capsules in water solutions containing different concentrations of As(III). For feed concentrations of 0.1 and 0.3 ppm, complete oxidation was achieved after 3 h and 4 h of test, respectively; whereas, for feed with 0.7 and 1 ppm of As(III), longer time was needed (48 h) to obtain 90% and 73% of oxidation, respectively. Moreover, the data were reproducible. These results are promising, showing that the investigated system is able to efficiently oxidize As(III) into As(V). The amount of Mn into the treated solutions ranged between 0.3 and 1 ppm, in line with the imposed limits for industrial water processing. However, for drinking water treatment, an Mn removal step must be considered. Based on the positive results obtained, a study to optimize the system in terms of operating conditions and to evaluate the performance of the process in presence of interfering ions (also working on real solutions) will be carried out as future research. The optimization of the system will be at the basis of a cost-benefit analysis on the developed material with respect to other synthesized materials reported in literature.

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