Investigation of arsenic removal from aqueous solution through selective sorption and nanofiber-based filters

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Abstract

Background: This research paper focuses on removing of arsenic from contaminated water via a nanofibrous polymeric microfiltration membrane, applied in prospective combination with an inorganic sorbent based on iron oxide hydroxide FeO(OH).

Materials and methods: Nanofibrous materials were prepared by electrospinning from polyurethane selected by an adsorption test. The chemical composition (FTIR), morphology (SEM, porometry) and hydrophilicity (contact angle) of the prepared nanostructured material were characterized. The process of eliminating arsenic from the contaminated water was monitored by atomic absorption spectroscopy (AAS). The adsorption efficiency of the nanofibrous material and the combination with FeO(OH) was determined, the level of arsenic anchorage on the adsorption filter was assessed by a rinsing test and the selectivity of adsorption in arsenic contaminated mineral water was examined.

Results: It was confirmed that the hydrophilic aromatic polyurethane of ester type PU918 is capable of capturing arsenic by complexation on nitrogen in its polymer chains. The maximum *As* removal efficiency was around 62%. Arsenic was tightly anchored to the polymeric adsorbent. The adsorption process was sufficiently selective. Furthermore, it was found that the addition of even a small amount of FeO(OH) (0.5 g) to the nanofiber filter would increase the efficiency of *As* removal by 30%.

Conclusions: The presented results showed that an adsorption filter based on a polyurethane nanostructured membrane added with an inorganic adsorbent FeO(OH) is a suitable way for the elimination of arsenic from water. However, it is necessary to ensure perfect contact between the surface of the nanostructure and the filtered medium.

Keywords: Arsenic, Adsorptive filtration, Polyurethane, Iron oxide hydroxide

Introduction

Arsenic is an element that naturally occurs abundantly everywhere in the environment, but it is highly toxic and classified as a group 1 human carcinogen by the IARC (International Agency for Research on Cancer) [1–3]. Arsenic occurs also in natural water sources in both organic and inorganic forms. Organic species of arsenic have entered into waters e.g. from pesticides containing organoarsenicals, as well as via the mechanisms of biomethylation of microorganisms. Their toxicity is generally lower than reported for inorganic forms [4–6]. Inorganic forms of arsenic can enter waters by leaching from rocks [7]. The inorganic arsenic (arsenic anions) occurs as arsenate [As(V)] or arsenite [As(III)]. The trivalent form is far more toxic and harmful to humans [1, 8–11].

Numerous studies have proven that long-term exposure to arsenic in drinking water, particularly at concentrations exceeding 50 µg/L, causes health problems - skin lesions, diseases affecting the blood vessels, high blood pressure, reproductive disorders and cancer. Arsenic gradually accumulates in the human body. Long-term use of water even with a lower arsenic content can lead to a chronic poisoning referred to as arsenicosis [7, 9, 12–14]. As a consequence of its toxicity, the limits for the permitted concentration of arsenic in drinking water were set at 10 µg/L in Europe and the USA [14–16].

The removal of arsenic from water is now a major problem in many countries all over the world, especially in India, Bangladesh, Taiwan, Thailand, Argentina, West Bengal, Vietnam and Mongolia. Countries such as these have reported that much of their ground water is contaminated with arsenic at levels from 100 μg/L to over 2000 μg/L [17–22] and it is not easy to obtain drinking water or domestic water from such contaminated sources [23].

A number of methods and processes for the elimination of arsenic from natural, mineral and drinking waters have been described in the literature, several of which have been designed and improved in recent decades [1, 2, 24]. The most commonly used techniques for removing arsenic from water are oxidation (it must always be supported by another method), coagulation and flocculation (the most frequent method of removing arsenic followed by sedimentation or filtration [10, 12, 25–28]), adsorption [29–31], adsorptive filtration [32-34], ion exchange and membrane filtration [10, 23, 26, 29, 35–41].

The presented study focused on the use of combination of adsorption and microfiltration on nanofibrous filters. Adsorption is a method based on the principle of capturing particles (atoms and molecules) of one phase on the surface (phase boundary) of the other phase using interphase attractive forces. Commonly used adsorbent materials include activated carbon, activated alumina, carbon, fly ash, bauxite sludge, zeolites, titanium dioxide, ferric hydroxide, ferrous iron, chitosan, ion exchangers, etc. The most effective and available arsenic adsorbents are iron oxides and hydroxides, including nanoparticles having immense affinity for inorganic arsenic [29, 30].

Probably the most commonly used and effective adsorbent is iron oxide hydroxide (FeO(OH)), which is also able to adsorb antimony and other heavy metals from water. Granular adsorption materials based on iron hydroxides and oxides are sold under various trade names (GEH, Kemira CFH and Bayoxide E33). These adsorbents work on the principle of irreversible chemisorption of arsenic. The method is selective, undemanding, financially justifiable and very effective [31]. Nevertheless, an indisputable disadvantage of using adsorbents in general is the need to dispose of the spent sorbent material afterwards.

Nanofibrous polymeric membranes represent a group of microfiltration (MF) or ultrafiltration (UF) membranes. The pore size of these membranes is too large to remove dissolved contaminants from the water. Thus, before involving an MF or UF membrane in an elimination process, it is usually necessary to increase the arsenic particle size, e.g., by coagulation and flocculation. However, in the case of the presented study, the strategy of arsenic capture on the nanostructured membrane was somewhat different. The polymer nanofibrous membrane capable of adsorbing arsenic from contaminated water has been prepared by electrospinning process [42, 43]. The tests were further continued by combining a nanostructured microfiltration membrane, which introduces the advantage of a large surface area, with the inorganic adsorption material FeO(OH), which is considered to be an excellent selective arsenic sorbent. The adsorption efficiency was assessed in both model contaminated water and naturally contaminated mineral water.

Materials and methods

Materials
All chemicals used in the experiments were of reagent grade. N, N-dimethylformamide (DMF) used as solvent for polymer solutions was purchased from Brenntag, Germany. The chemicals for synthesis of polyurethane PU918 – 4,4'-methylene bis(phenyl isocyanate) (MDI), and 1,4-butanediol (BD) were obtained from Sigma-Aldrich, Germany and polyol poly(3-methyl-1,5-pentanediol)-alt-(adipic, isophthalic acid) (PAIM) was purchased from Kuraray, Japan. Sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7 H_2O$) for the preparation of arsenic contaminated waters was also obtained from Sigma-Aldrich. Arsenic contaminated water (CW) was prepared using deionized water. Nitric acid (HNO_3) for rinsing storage and sample bottles was purchased from Lachner, Czech Republic. Palladium modifier for stabilisation of samples before determining the arsenic concentration by atomic absorption spectroscopy (AAS) was obtained from Merck, Germany. The adsorption material iron hydroxide oxide – FeO(OH) (GEH 102) was from GEH Wasserchemie, Germany.

In addition to model contaminated water the real sample of naturally arsenic contaminated mineral water (NCMW) was used [44]. Concentrations of arsenic in CW was about 150 μg/L and NCMW from 60 μg/L to 160 μg/L. The pH for CW was about 6.5 and for NCMW 6.8, at room temperature (23°C).

Polymeric materials for nanofibrous adsorptive filters preparation

Many polymeric materials have been tested as adsorbents of arsenic in form of nanofibrous structures: polyvinylidene fluoride copolymer with hexafluoropropylene – PVDF (Kynar-Flex 2801-00, RESINEX Czech Republic s.r.o.); cellulose acetate with 40% acetyl groups – CA (Eastman CA-398-30, Eastman Chemical B.V.); polyacrylonitrile at the molecular weight of 150 000 – PAN (Polyacrylonitrile, Sigma-Aldrich); polyurethanes – PU (Permuthane SU-22-542 from Stahl Europe b.v., referred as PUSU; Elastollan EB95A from BASF Polyurethanes GmbH, referred as PUEL; and self-synthesized PU918). Two combinations of polymers were also tested: PAN with polyaniline – PANI (Panipol F, Panipol OY) in the proportion 2:1 and PUEL with PANI in proportion 2:1.

Polyurethane PU918 synthesis

The synthesis of polyurethane PU918 with a high content of nitrogen in its chains was carried out in a three-neck reaction vessel fitted with a thermometer and KPG stirrer. PU solution in dimethylformamide (DMF), based on 4,4'-methylene bis(phenyl isocyanate) (MDI), poly(3-methyl-1,5-pentanediol)-alt-(adipic, isophthalic acid) (PAIM) and 1,4-butanediol (BD), was synthesized in the molar ratio 9:1:8 (PU918) at 90°C for 6 hours. The per partes manner of synthesis was applied, whereby a prepolymer was synthesized from the MDI and polymer diol (at the molar ratio of 2:1), then all of the chain extender (BD) was added, followed by the remaining quantity of MDI after 1 hour of the polyaddition reaction. Requested concentration and viscosity of the PU solution was adjusted by gradually adding DMF into it. The density of PU918 equalled 1.1 g/cm^3.

Preparation and characterisation of nanostructured material

Nanofibrous materials were prepared from the polymeric solutions by electrospinning process using SpinLine 40 device (SPUR, Czech Republic) equipped with two sets of nanofibers forming moving jets. The formed nanofibers were layered on polypropylene (PP) spunbond (SB) nonwoven textiles (NT) or PU meltblown (MB) NT support. The solution and electrospinning process parameters have to be carefully adjusted for each polymer. The parameters for the selected polyurethane PU918 were as follows: solution concentration of 13 wt.%, viscosity of 1.5 Pa.s and conductivity of 150 µS/cm. The electric voltage applied to the polymer solutions was 55 – 75 kV, the distance between electrodes measured 190 mm, the dosage of polymer solution was 0,24 mL/min and the speed of supporting textile collecting nanofibers was 0.16 – 0.32 m/min. The ambient conditions comprised the relative humidity of 25 – 30% and temperature of 22 – 24°C.

The structure and surface morphology of the nanostructured materials were evaluated using a scanning electron microscopy (SEM – Vega 3, Tescan, Czech Republic). The samples of nanofibrous material were coated with a thin layer of palladium to increase the electric conductivity before SEM imaging.

The nanofibrous material surface hydrophilicity was determined via the water contact angle test using Surface Energy Evaluation System (SEE System, Advex Instruments, Czech Republic) equipment. A set of 3 samples was tested by water drop of 5 µL in volume. The angle was measured approximately 1 second after release from micropipette. An average of three measurements was reported.

The nanostructured material was further characterized by porometry. The measurement was performed on porometry device (SPUR, Czech Republic) according to ASTM F316-03 (2011). Galpor (Porometer, Belgium) was used as a wetting liquid. The dry and wet tests were done on three circular samples cut out from material and average values were reported. The results of the porometry measurements were medium diameter of pores in nanostructure, maximum pore diameter and permeability of nanostructure for the dry air. A pore size distribution was counted as well.

The chemical nature of the nanostructured material was evaluated using Fourier transform infrared spectroscopy (FTIR). It was performed by FTIR spectroscope Nicolet iS5 (Thermo Fisher Scientific, USA) equipped with Ge crystal in the range between 4000 cm^{-1} and 400 cm^{-1}, resolution 4 cm^{-1}.

## Arsenic removal experiments – arrangement and characterisation

Discontinuous adsorption test

In order to select an optimal nanofibrous sorbent a discontinuous sorption test was applied. Samples of nanostructured polymeric materials were immersed in 100 mL of mineral water contaminated with arsenic at a concentration of approximately 150 µg/L. The glass flasks (volume of 250 mL) containing the samples were intensively shaken for 1 hour (RT, 100 rpm; GFL 3005 shaker by GFL Gesellschaft für Labortechnik mbH). Afterwards, samples of the solutions were removed and analysed by the AAS method to determine the amount of arsenic absorbed by nanofibrous sorbent.

Very similar sorption tests were used to discern the optimal amount of the sorbent. Different amounts (0.1–2.0 g) of the given polymer (or FeO(OH) for comparison) were immersed in 100 mL of contaminated distilled water with a concentration of arsenic of 150 μg/L. The conical flasks with immersed samples were intensively shaken for 1 hour at 175 rpm. The samples were left to stand for 24 hours and arsenic concentration was determined by AAS. The procedure was repeated for 5 days, involving the replacement of fresh contaminated water in the conical flasks after withdrawing the samples for AAS analysis. The same procedure was applied for determining the sorption properties of the support materials used in the nanofibrous filters.

Continuous filtration-adsorption test

The continuous filtration-sorption experiment was carried out on a laboratory filtration device (Fig. 1). The filtration column was equipped with a semi-transparent tube with an inner diameter of 28 mm, permitting visual inspection of the process, wherein a sorption filter (different arrangements) was placed in the bottom part. The filtered media was passed into the tube by a hose pump via the upper part of the column. The device operated at a constant water column of 0.75 m (7.35 kPa), and the flow rate of permeate was controlled by a valve on the outlet of the filtration column. The filtrate was collected in a measuring beaker so as to evaluate the volume filtered.
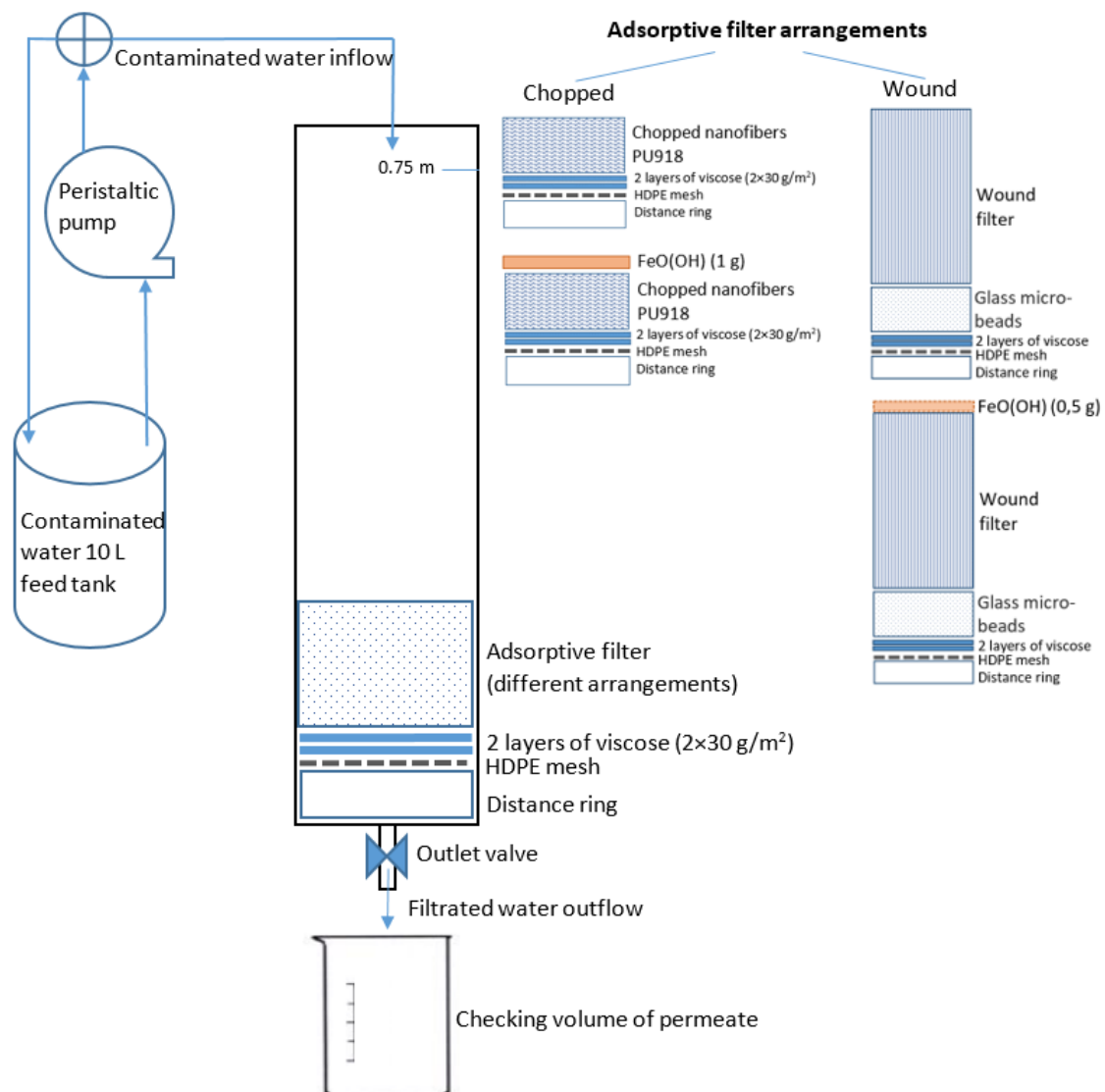
Fig. 1 Laboratory filtration device and arrangement of adsorptive filters used

During these experiments, either chopped or wound arrangement of the sorption filter was used. When the tube of the filtration column was inserted with the chopped filter, the arrangement of the filtration cartridge comprised (from the bottom upwards): an air gap of approx. 1 cm (achieved by the distance ring), a polyethylene (HDPE) mesh (for fixing the layers above the air gap), 2 layers of viscose spunbond (basic weight 30 g/m², preventing

penetration of the released nanofibers into the filtrate) and 8 g of chopped PU918 nanofibers. Testing also covered the combination of the chopped nanofibrous filter with addition of FeO(OH) (1 g). The flow rate for filtration was 10 mL/min.

The arrangement for the wound filter constituted a filtration cartridge as following (from the bottom upwards): an air gap of approx. 1 cm, an HDPE mesh (for fixing the layers above the air gap), 2 layers of 30 g/m^2 viscose spunbond, 10 g of fine glass beads (preventing penetration of fine fractions of the alternately added FeO(OH) into the filtrate) and a roll of the wound filter, which contained 0.5–0.8 g of PU918 nanofibers on supports of PP SB or PU MB. Testing also covered the combination of the wound filter with PU918 nanofibers on PU MB with the addition of FeO(OH) (0.5 g) at the top of the roll. The flow rates tested for filtration were set to approximately 4 mL/min.

Determination of arsenic capture
The arsenic concentration of adsorptive solution (discontinuous test) and permeate (continuous test) was measured by atomic absorption spectroscopy (AAS). The spectrometer Zeeman Graphite Furnace AA (GFAA) systems (AAS DUO 240FS/240Z/UltrAA, Agilent technologies, USA) was used. Due to the instability exhibited by arsenic in water, it was important to apply an optimized method of AAS, adding 10 μL of palladium modifier to each sample (1 g/L Pd$_2$(NO$_3$)2/20% HCl + 1% ascorbic acid, Merck, Germany). The methodology required nine stages of increase in atomic temperature (0–2600°C). The amount of arsenic was determined at the wavelength of 193.7 nm, and the calibration curve was derived by employing 100 μg/L of bulk concentration of a standard (storage from 1000 mg/L, Agilent technologies, USA). Each sample was analysed three times in two parallel measurements. Relative standard deviation values (RSD) were seen to lay in the quantifying limit for determining arsenic by AAS. The RSD values were always less than 4%. We also evaluated the quantities of some other elements (in mg/L; Fe, K, Na, Mg and Ca) in the mineral water by AAS on a spectrometer utilizing a flame.

The percentage of arsenic capture on nanostructured material was calculated using equation 1.

$$R \ (\%) = 100 \cdot (1 - \frac{c_p}{c_0}), \qquad\qquad (1)$$

where R is the capture of arsenic (%), and c_p and c_0 are the concentrations of arsenic in the permeate and feed contaminated water, respectively (μg/L).

The elemental microanalysis of used nanostructured surfaces was performed via NovaNanoSEM 450 microscope (FEI company, Netherlands) provide by the Octane SSD (area of 30 mm^2) EDX (energy-dispersive X-ray) detector (AMETEK, USA). Microscopic images were taken using an ETD (topographic contrast) and CBS (material contrast) detector at accelerating voltages of 5 kV and 15 kV, respectively. The analysed surface was covered by alloy of gold and palladium layer using a sputtering equipment for 30 seconds.

Results and Discussion

Selection of suitable polymeric sorbent
In the first step of this work nanofibers from eight various polymers were prepared and their capability for sorption of arsenic from water was assessed. The eligible nanofibrous sorbent material was selected according to the main criterion of the maximum sorption of arsenic after one hour of the adsorption process. A highly efficient commercial inorganic sorbent FeO(OH) was also used for comparison. The result of the comparative adsorption test is evident from the graph in Fig. 2.
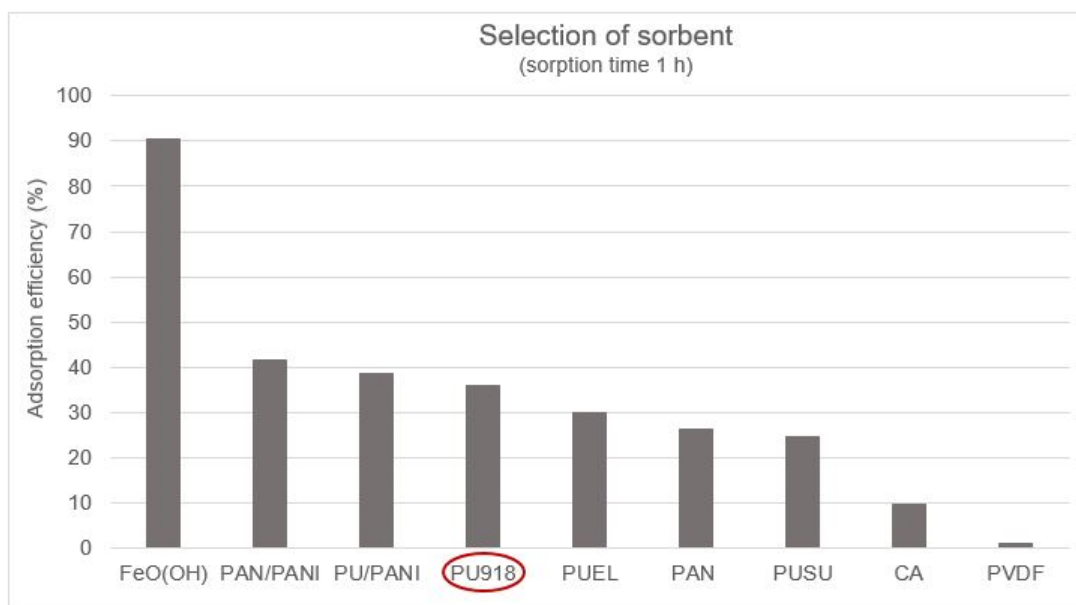
Fig. 2 Arsenic sorption on different polymeric nanofibers and FeO(OH), arsenic contaminated distilled water (CW) with c_{As}=150 µg/L, pH=6.5 and T=23°C was used for sorption process

Nanofibers made from cellulose acetate (CA) and polyvinylidene fluoride (PVDF) showed very little sorption capacity. On the other hand, the positive results were achieved with polymers that contain a nitrogen atom in their chains (PAN/PANI, PU/PANI). However, because polyaniline (PANI) cannot create a sufficiently homogeneous nanostructures and polyacrylonitrile-based nanofibers (PAN) are very brittle, the research has further focused on polyurethanes (PU). Both commercially available polyurethanes (PUSU and PUEL) exhibited interesting sorption properties. It was an impulse to synthesize a polyurethane with a maximum content of nitrogen in its chains and good workability in an electrostatic field. The aromatic polyurethane of ester type PU918 was prepared, which had an arsenic adsorption capacity higher than commercial types of polyurethanes. Figure 2 presents the comparison of adsorption efficiencies after one hour of sorption. Nevertheless, the sorption test continued for another 1, 2 and 7 days. It can be stated that the results of analyses performed during the longer tests corresponded well with those for one hour.

Characterization of PU918 polyurethane and PU918 nanostructure

Polyurethane PU918 was synthesized in solution by the per partes method of polyaddition reaction. Fig. 3 depicts the FTIR spectrum of electrospun nanofibers prepared of PU918. The spectrum shows an absorbing peak appearing at 3332 cm^{-1} that is caused by stretching vibration of N–H stretching of the amino group in carbamate. Strong peaks occur between 1700 cm^{-1} and 1736 cm^{-1} corresponding to mono or disubstituted compounds. It gives rise to the peak of 1732 cm^{-1}, which is attributed to the C=O stretching of amido ester. The peak at 1531 cm^{-1} displays N–H bending and C–N stretching for the amide group. Then, a peak at 1227 cm^{-1} is due to the C–N stretching for the other amide group. As a result of stretching vibration of the C=C bond in the benzene ring's skeleton, the peaks appear at 1417 cm^{-1} and 1596 cm^{-1}. According to the figure, an adsorption peak appeared in the band of 1076 cm^{-1} due to the characteristic bands of alkyl ether causing asymmetric flexing vibration of C–O–C bonds.
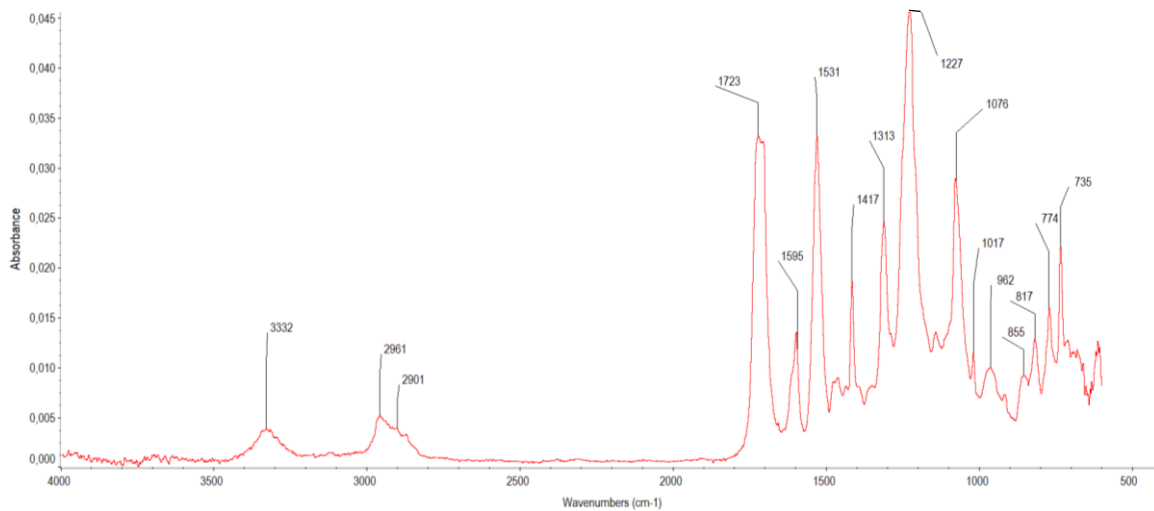
Fig. 3 FTIR spectrum of polyurethane PU918

The nanofiber materials were prepared from the PU918 solution. The SEM micrographs of nanofibers PU918 layered on three different supports are presented in Fig. 4. The nanofiber diameters were in range from 150 to 250 nm, depending on the solution and support textile properties and the parameters of electrospinning process. To prepare smooth fibers without defects, the spinning voltage had to be adjusted differently for each substrate. For PU MB with higher basis weight (50 g/m^2) the adjusted voltage was around 65 kV, while for PU MB with 30 g/m^2 the used voltage was 70 kV and for PP SB 75 kV.


a   b   c
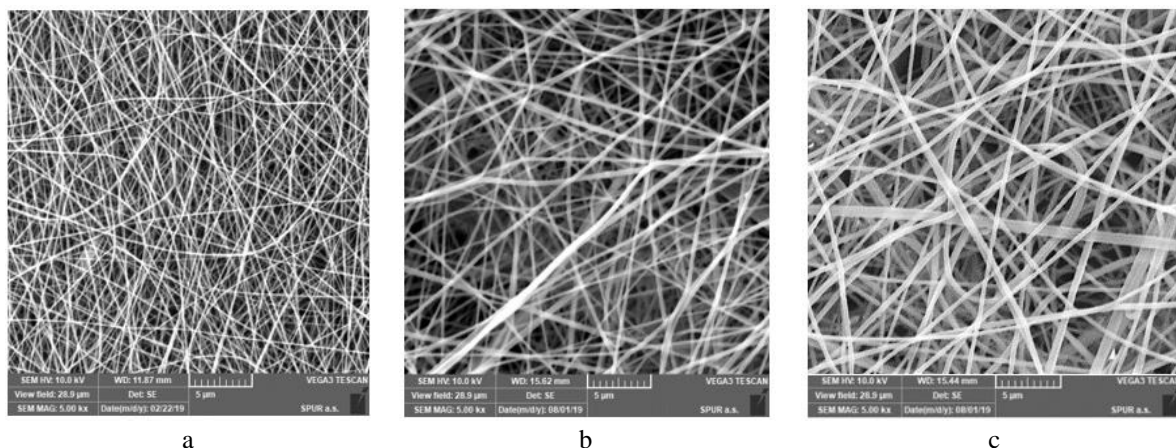
Fig. 4 SEM images of PU918 nanofibers on (a) PP SB, 30 g/m^2, (b) PU MB, 30 g/m^2, (c) PU MB, 50 g/m^2 (magnification 5000)

The prepared nanostructured material's hydrophobicity was determined using contact angle measurement. The PU918 nanostructure can be considered hydrophilic, because the measured contact angle for water was about 27.3°, as can be seen in Fig. 5.

Fig. 5 Contact angle measurement for PU918 (water drop)

The nanostructured material was further characterized by porometry. The medium diameter of pores in nanostructure was 0.32 µm, maximum pore diameter was 0.4 µm and assessed permeability of nanostructure for the dry air was 51 L/cm^2. min. bar. In the Fig. 6 is showed the pore size distribution for mentioned material.
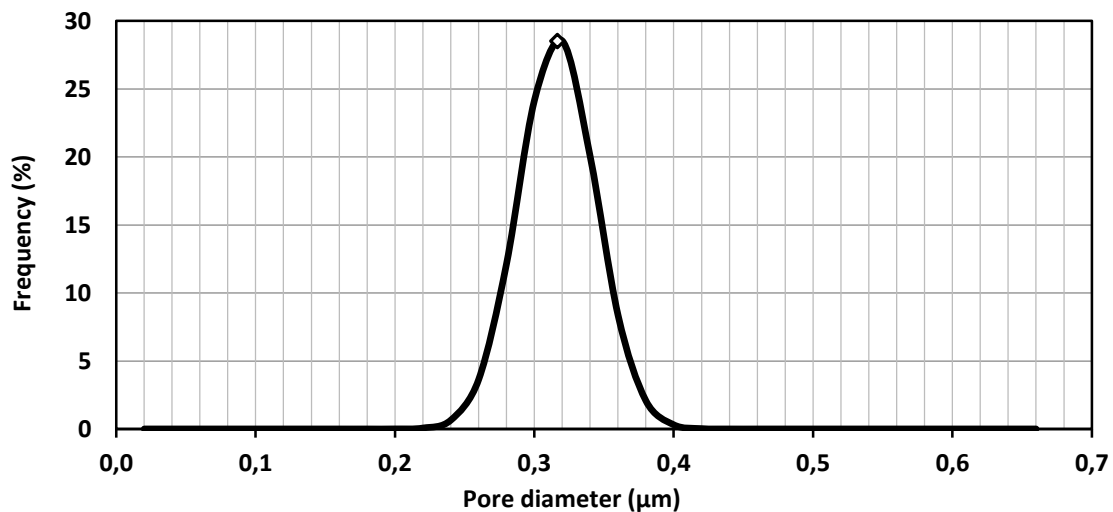

Fig. 6 Distribution of pore sizes for PU918 nanofibers on PP SB, 30 g/m^2

Arsenic sorption during the discontinuous process

In order to better understand the adsorption processes taking place on the selected nanofibrous sorbent the discontinuous adsorption tests were carried out. These tests were realized on nanofibrous nonwoven textile or granulated iron hydroxide oxide in an amount of 0.1 - 2.0 g that were immersed into 100 mL of model contaminated water (CW). The concentration of arsenic in the contaminated distilled water was 150 µg/L, pH of CW was 6.5. The tests were carried out for 5 days with repeated replacing of fresh CW every 24 hours. The tests were carried out at room temperature.

During these five-day tests the content of adsorbed arsenic (µg/L) was evaluated and recalculated to sorption efficiency (%). In Fig. 7 and 8 the relations between sorption efficiency and utilized volume of contaminated water and dosage of adsorbent respectively are presented. As anticipated, the FeO(OH) powder demonstrates great capacity for the sorption of arsenic, while adsorption on nanofibers is significantly lower.
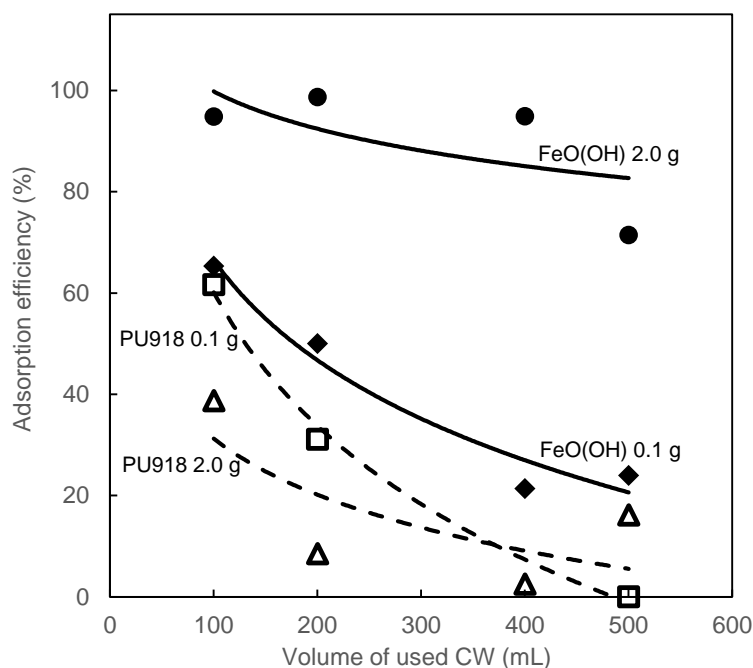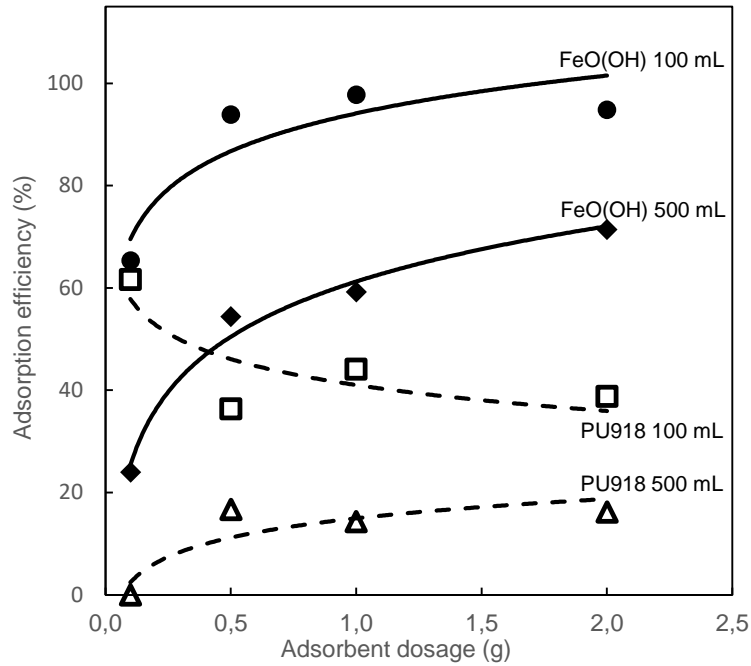
Fig. 7 Arsenic sorption in the model contaminated distilled water in relation to utilized volume of CW for different amounts of iron hydroxide oxide and the polyurethane PU918 nanofibers (c_{As}=150 µg/L, pH=6.5, T=23°C)

As depicts Fig. 7, the dependence of arsenic adsorption on the utilized volume of CW, the adsorption efficiency rises with increasing amount of FeO(OH) used. Unfortunately, the nanostructures based on PU918 did not follow this trend. During the discontinuous adsorption process in 100 mL of contaminated water in a glass flask, the PU nanostructures in the amount of 0.1 g formed an open veil-like membrane, the entire surface of which was easily accessible to the sorption process. In stark contrast to these airy open structures are wrapped flocks of nanostructures formed when using a dose of 2 g. These bundles are much less accessible to the sorption process, which is reflected in lower values of adsorption efficiency. It was found that even smaller amounts of nanofibers demonstrated better sorption efficiency than a larger quantity of chopped nanofibers, although it is true that the adsorption curve for smaller amount of nanofibers decreases significantly faster and reaches zero at the end of the test. However, this specific property must be taken into account when designing adsorptive filters.

Fig. 8 shows the dependence of the adsorption efficiency on the dose of adsorbent used after the first day of the adsorption experiment (100 mL) and the fifth day of the sorption test (500 mL). The results obtained were in good agreement with theoretical assumptions [31, 45 – 47]. The sorption process proved to be more effective for the first 100 mL volume of CW and less during the five changes of CW (500 mL), when the active centres were partially exhausted. Increasing amount of FeO(OH) boosted the level of sorption, especially in the shorter test, i.e. using a smaller volume of CW (100 mL). In the case of using PU nanostructure as a sorbent, a rise in the adsorption efficiency with an increase in the amount of sorbent will only become apparent after the use of higher volume of CW (500 mL). If the experiment is shorter (100 mL of CW used), the dependence curve of the sorption efficiency on the amount of adsorbent decreases. These results are associated with the possible availability of adsorption centres in nanostructured material and, of course, with amount of the sorption centres. It is essential that the entire surface of the nanostructured material is in direct contact with arsenic contaminated water.

Fig. 8 Effect of dosage of adsorbent on the adsorption of arsenic in the model contaminated water for granulated FeO(OH) and polyurethane PU918 nanofibers (c_{As}=150 μg/L, pH=6.5, T=23°C)

It can be assumed that removing arsenic from the water by FeO(OH) would require an adsorption mechanism, which produces ferric arsenate or ferric arsenite [32]. This mechanism can be described by simplified equations:

Arsenate sorption: $\qquad OFeOH + H_3AsO_4 \rightarrow OFeH_2AsO_4 + H_2O$

Arsenite sorption: $\qquad OFeOH + H_3AsO_3 \rightarrow OFeH_2AsO_3 + H_2O$

For the adsorption mechanisms on the polymeric chains can be supposed that complexation would occur, utilizing a free electron pair of a nitrogen atom. The proven adsorption of arsenic ions on the nitrogen atoms of the polypyrrole polymer is written e.g. by Mahmud et al. [48].

When using a combination of a polymeric nanostructured sorbent and an inorganic FeO(OH) adsorbent, the explanation of the adsorption mechanism can be even more difficult because the chemical interaction can be complicated by morphological and surface effects in the heterogeneous system. Nevertheless, the kinetics of the adsorption process were studied on this combination. The adsorption test to determine the kinetics was carried out on a samples of nanofibrous structure based on PU918 with FeO(OH) caught on the nanostructured layer by pressing between two layers of nanofibers. The sorption test was performed by immersing the sorbent in 250 ml of arsenic contaminated water (CW) with an arsenic concentration of 150 μg/L and pH 6.5 at room temperature of 23°C. The conical flasks with immersed samples were shaken at 175 rpm, the total time of the test was 8 h. The weight of the combined sample used was 0.166 g, the sample containing 0.077 g of nanofibers and 0.089 g of FeO(OH). This weight ratio between nanostructure and inorganic sorbent was optimal in terms of incorporation of inorganic powder into the nanostructure.

To interpret the kinetic mechanism that controls the adsorption process, pseudo-first order and pseudo-second order kinetic models were investigated [49-51]. The pseudo-second order kinetic equation, based on the adsorption capacity of the solid phase, proved to be more appropriate for the investigated system (regression coefficient of linearized equation was R^2=0.9994). The pseudo-second order rate equation is represented by:

$$q_t = q_e^2 \cdot k \cdot t / (1 + q_e \cdot k \cdot t) \qquad (2)$$

The linear form of pseudo-second order rate is presented by equation:

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

In equations (2) and (3) q_e and q_t are quantity of contaminant adsorbed at equilibrium and at any time t, respectively (µg/g), t is time of adsorption (min), k is pseudo second order rate constant (1/min).

The adsorption capacity of PU nanofibers doped by FeO(OH) is depicted in figure 9. As can be seen, the experimental data and the course of sorption capacity versus time curve, calculated by means of pseudo-second order model, are in very good compliance. The removal of arsenic by adsorption on tested material increased with time reaching equilibrium after about 480 min. The adsorption rate is very fast in the beginning, till time of 40 min. After 90 min the adsorption rate is gradually decreasing to assuming plateau at 480 min. Almost all arsenic has been adsorbed during first hour of test. Fig. 10 based on linearized pseudo-second order model equation confirms agreement between experimental and calculated values ($R^2=0,9994$). According to the linearized equation describing the graph in Fig. 10, the value of the equilibrium concentration adsorbed by the sorption material was $q_e=120,5$ µg/g and the magnitude of the rate constant k reached 0,001403 1/min.

Since the reaction kinetics is in good agreement with the pseudo-second order model, it can be assumed that the adsorption mechanism of the combined adsorption material based on PU918 nanostructure and FeO(OH) sorbent may include valence forces by electron sharing between adsorbent and arsenic.
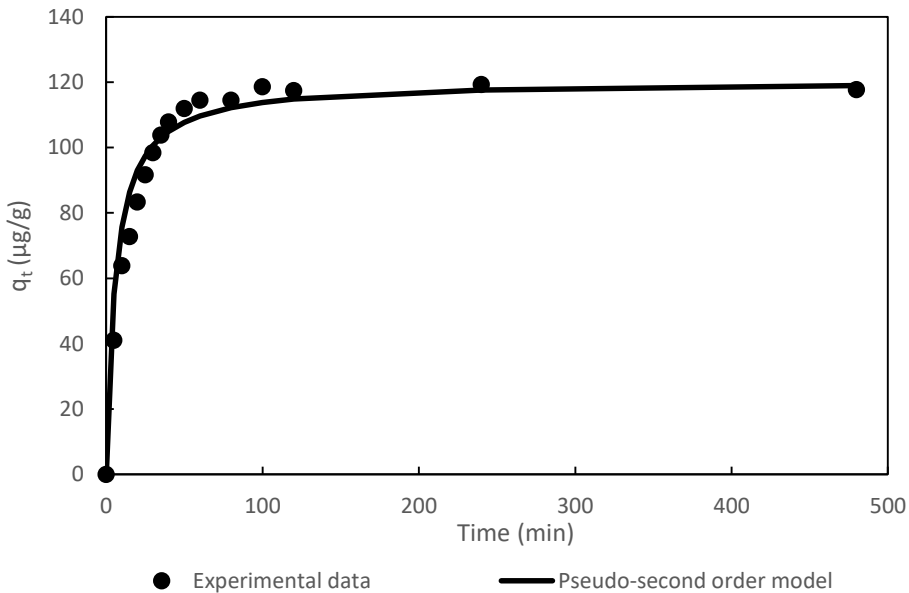
Fig. 9 Dependence of adsorption capacity on contact time for the combined sorbent based on PU918 nanostructure and FeO(OH) – pseudo-second-order model (CW: $c_{As}=150$ µg/L, pH=6.5, T=23°C)
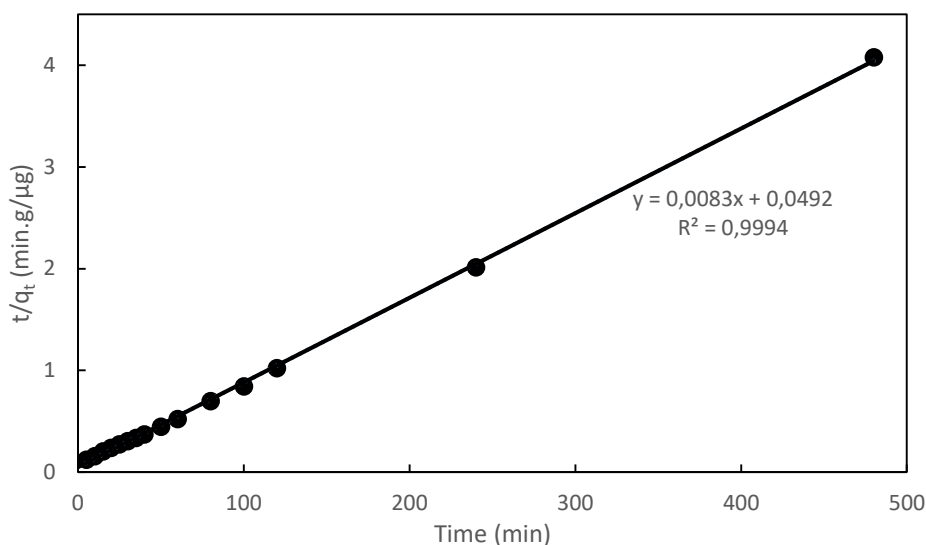
Fig. 10 Adsorption kinetic plot for the combined sorbent based on PU918 nanostructure and FeO(OH) – linearized pseudo-second-order model

In conclusion to the discontinuous sorption experiments can be stated that the sorption tests with 2.0 g of nanostructures revealed the extent to which access to the active surfaces of the nanofibers was reduced, thereby inhibiting the sorption process. As mentioned above, the wrapped flocks of nanofibers were inaccessible due to the limited contact between their entire surfaces and the CW, therefore the PU nanofibers showed restricted capacity for sorption. For this reason, a wound filter arrangement was chosen to provide the continuous filtration-sorption experiments. In the wound filters, the layers of the PU918 nanofibers were separated from each other by microfibrous layers of hydrophobic or hydrophilic nonwoven textiles, either spunbond or meltblown. During filtration through a polyurethane nanostructured sorption filter, it is necessary to ensure maximum contact between the nanofibers and the filtered medium, otherwise the liquid will flow along the way representing minimal drag flow.

Arsenic sorption during the continuous filtration-sorption process

The nanostructured adsorptive filters were prepared by electrospinning process. A layer of PU918 nanofibers was applied on a nonwoven substrate. Two types of substrate were used, namely a hydrophobic polypropylene spunbond (PP SB) and hydrophilic polyurethane meltblown (PU MB). The prepared belts of such two-layer materials were wound into compact cylinders used as adsorptive filter. The wound filter based on PU nanofibers on a PP SB substrate had a total area of 0.307 m^2. The total weight of nanofibers in this area was 0.5 g, which corresponds to an active sorption area of the nanostructure of about 11.6 m^2. In the case of the filter with the hydrophilic PU MB support, the total filter area was 0.480 m^2. The total weight of nanofibers in this area was 0.8 g. Because the diameter of the nanofibers on PU MB was slightly larger than on hydrophobic PP SB (250 nm on PU MB and 150 nm on PP SB) the corresponding active sorption area of nanostructure was slightly smaller, approximately 10.5 m^2.

Filtration tests were carried out for almost 60 hours, during which more than 14 L of filter medium were filtered through the filter used. The flow rate through the filter column was set at 4 mL/min at a pressure of 0.75 m water column (7.35 kPa). The filtered medium was distilled water contaminated with arsenic (CW). The concentration of arsenic in CW was 150 μg/L, the pH of the filtered medium was 6.5 and the temperature was 23°C. The wound filters are formed not only by the nanofiber structure itself, but also by the substrate on which they are applied. For this reason, the value of the adsorption efficiency of these substrates was determined by discontinuous adsorption tests. The average value of arsenic removal efficiency for hydrophilic PU MB was 7.9%, for hydrophobic PP SB 1.4% (the base weight of both substrates was 30 g/m^2).

A comparison of the arsenic removal efficiency for both of the above mentioned filters is plotted in Fig. 11. It can be clearly seen from the graph that the PU918 nanostructure filter on the PU MB substrate showed higher arsenic removal than the filter on the PP SB substrate, even though the active area of the nanostructure on PU SB was slightly smaller. The sorption-filtration properties of the nanostructured filter are greatly impacted by the structure

and affinity to water of all the materials in it. This is especially true for wound filters, where filter layers and flow direction are arranged in parallel and affinity for water is crucial. This aspect is demonstrated here by comparison of the values recorded for arsenic removal by the wound PU918 nanostructured filters on the hydrophobic and hydrophilic supports. Higher arsenic removal efficiency was identified for wound filter based on PU918 nanofibers on hydrophilic PU MB support material. The structures of PP SB, PU MB (magnification 500× only) and PU918 nanostructure (magnification 5000×) are presented as SEM images in Fig. 12.
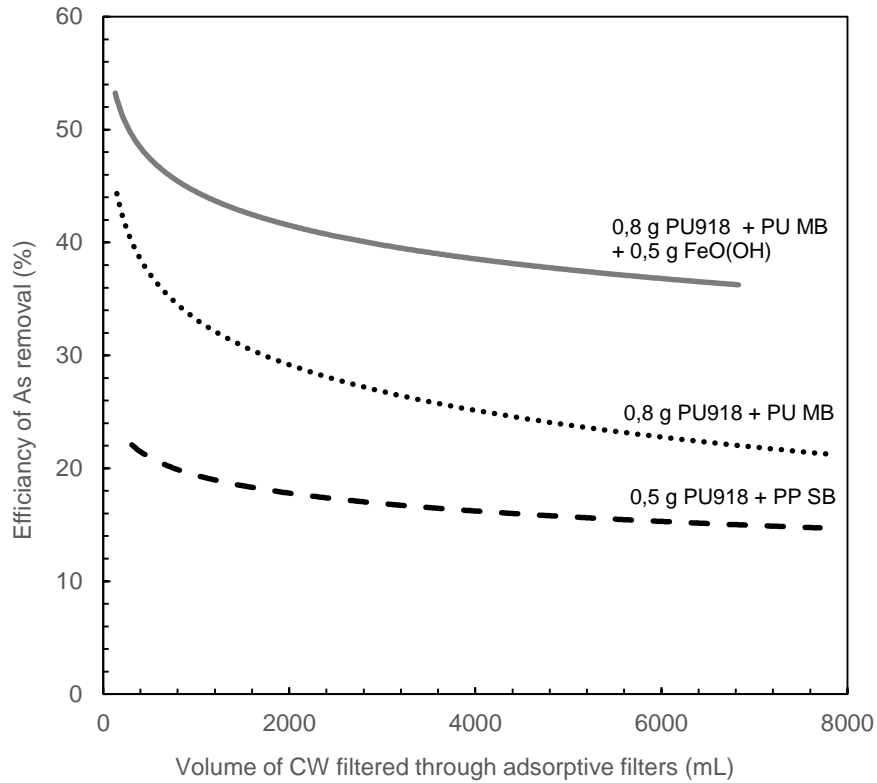

Fig. 11 Comparison of arsenic sorption on the wound PU nanostructured filters on PP and PU supports and of the filter modified with FeO(OH), parameters of filtered medium CW: c_{As}=150 µg/L, pH=6.5, T=23°C, parameters of filtration process: flow rate v_f=4 mL/min, p=7.35 kPa
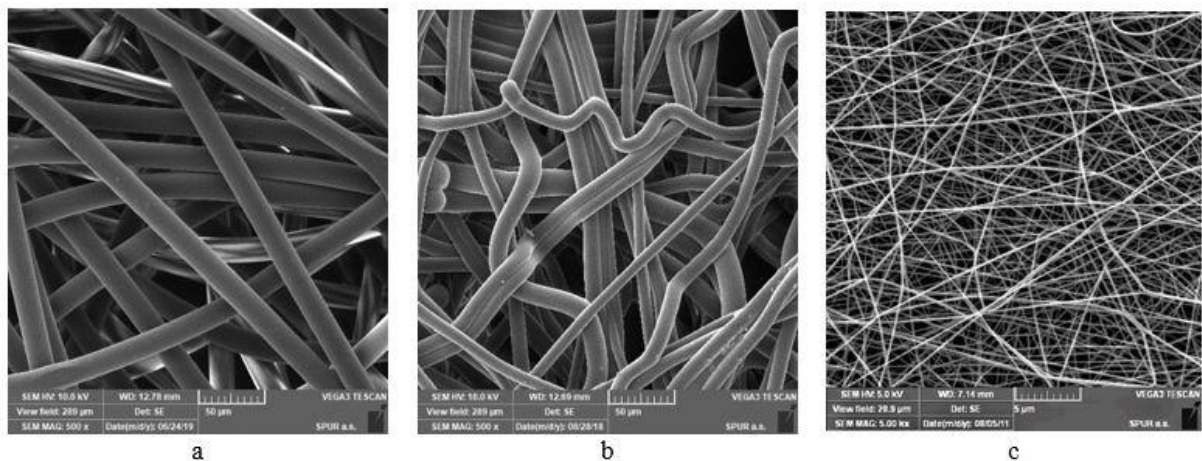
Fig. 12 SEM images of PP SB (a) and PU MB (b) at 500× magnification and the PU918 nanostructure (c) at 5000× magnification

The interception of arsenic using adsorption filters is a combination of a sorption process associated with complexation on the nitrogen atoms in the polymer chains and capture on the nanofibrous surface of the filter. The

capture of arsenic on the filter surface was studied by SEM-EDX. Fig. 13 presents a SEM image of the filter surface after 48 hours of filtration of arsenic contaminated water (As concentration 150 µg/L, pH 6.5, RT) and EDX spectra reflecting the elemental analysis performed on an area of 0.084 mm^2. The presence of arsenic on the surface of the nanostructured filter in an amount of 0.22 weight percent was identified by EDAX.
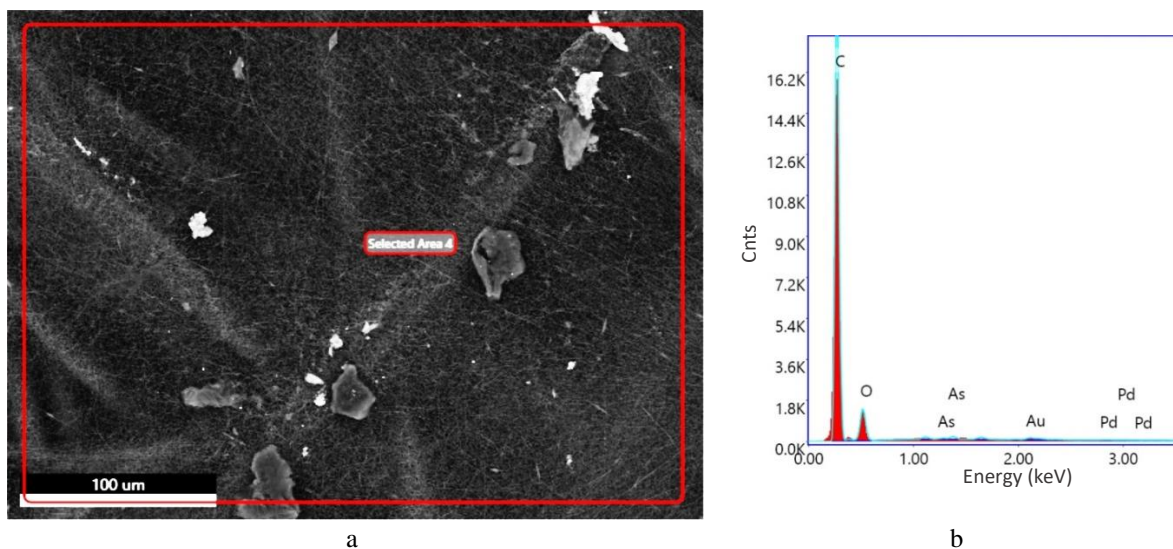
**Fig. 13** (a) SEM image of nanofibrous filter surface after 48 hours of filtration (CW: c_{As}=150 µg/L, pH=6.5, T=23°C), (b) EDAX of area from SEM image (a)

Since the efficiency of the PU-based adsorptive filters for arsenic removal from water was rather limited (Fig. 11), particularly after an extended period of filtration (greater filtered volumes), it was decided to improve it by adding another sorbent. Therefore, the sorption efficiency of the wound filter was increased by adding 0.5 g of FeO(OH) on the top of wound filter based on PU918 nanostructure on hydrophilic PU MB substrate. Although the amount of additive was very small, a significant increase in arsenic sorption was observed.

Rinsing test on nanostructured filters

The stability of the arsenic anchorage on the surface of the adsorption nanostructured filter was assessed using a rinsing test. The purpose of the test was to determine how much arsenic can be released from the surface of the filter when the filter column is rinsed with distilled water after a longer filtration process. The column was rinsed with 3 L of water. The last sample taken from the rinsing water did not contain arsenic in either case. However, for the purpose of evaluating the rinsing test, the value of the arsenic concentration from the sample obtained immediately after opening the valve of the filter column after filling it with distilled water was used.

The graph in Fig. 14 presents the results of the rinsing test for the three filters. The first two are wound filters based on PU918 nanofibers, with different support for PU nanofibers (PP SB and PU MB). Filtration through these filters took place at a pressure of 75 cm water column and the flow rate was regulated to a value of about 4 mL/min. The filtered medium was model contaminated water (c_{As}=150 µg/L, pH=6.5, T=23°C). The third filter was prepared from chopped nanofibrous nonwoven textile (nNT). The filter cartridge consisted of 8 g of chopped polyurethane nanofibers (without support). Filtration was performed at a pressure of 75 cm water column and the flow rate was regulated to 10 mL/min. The filtered medium was mineral water naturally contaminated with arsenic (NCMW: c_{As}=64 µg/L, pH=6.9, T=23°C). The filters were also rinsed with distilled water at a pressure of 75 cm water column and a flow rate of 4 and 10 mL/min respectively. These results reveal a surprisingly strong anchorage of arsenic on the surface of the nanostructured PU filter, resistant to rinsing with distilled water. This feature can be an advantage when disposing of a used filter.
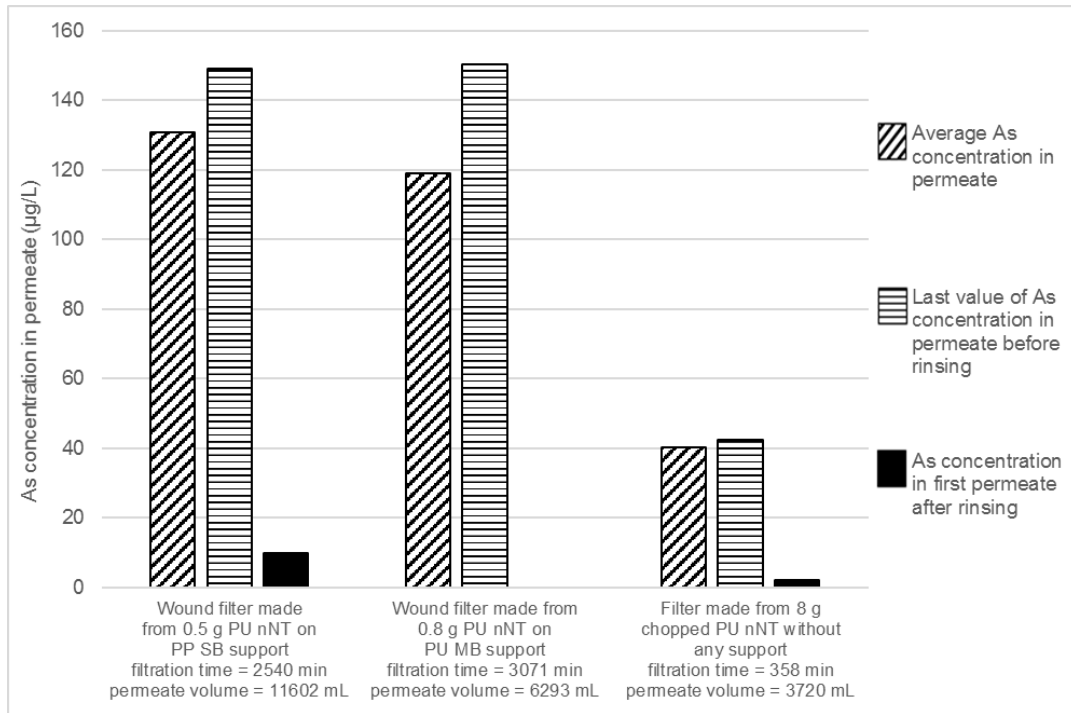
Fig. 14 Arsenic concentration in the permeate after rinsing the filters with distilled water

Test of selectivity of arsenic adsorption

The nanostructured polyurethane adsorptive filter was originally intended also for the removal of arsenic from mineral water. In such a case, it is necessary that the sorbent is significantly selective with respect to arsenic and that the other substances contained in the mineral water remain practically intact by the sorption-filtration process [52]. For this reason, a selectivity test of the PU adsorptive filter was performed in comparison with the use of an FeO(OH) based filter. Iron hydroxy oxide is considered a selective arsenic sorbent [53], so this comparison is possible.

A chopped filter was used for the selectivity test. The filter cartridge consisted of 8 g of chopped PU nanofibrous nonwoven textile (without support). The cartridge of comparative filter consisted of 8 g of granulated FeO(OH). In both cases, the filtration process was carried out at a flow rate of 10 mL/min and a pressure of 75 cm water column. The filtered medium was mineral water naturally contaminated with arsenic (NCMW). The concentration of arsenic in NCMW was 64 μg/L and the pH value was 6.9, at temperature of 23°C. The test lasted for almost 6 hours, filtering about 3.7 L of NCMW.

In addition to the change in the concentration of arsenic in the permeate, the change in the total concentrations of iron (in μg/L) and potassium, sodium, magnesium and calcium (all in mg/L) were also monitored in the case of the selectivity test, as is presented in Table 1. FeO(OH) showed excellent ability to arsenic sorption (100% elimination). However, its use also significantly reduced the potassium concentration by more than 68%. Iron capture was also considerable. Its concentration decreased by 63%. On the other hand, the concentration of iron in mineral water is relatively low (in units of μg/L), so its considerable elimination does not mean too significant change in the composition of mineral water. The decrease of concentration of other substances present in the mineral water is between 10% and 15%.

Table 1 Quantity of elements determined after filtration-sorption treatment of arsenic contaminated mineral water (from natural source)

Content of elements	As [μg/L]	Fe [μg/L]	K [mg/L]	Na [mg/L]	Mg [mg/L]	Ca [mg/L]
NCMW default	64.20	3.51	12.12	92.80	21.80	78.25
NCMW filtrated through PU nNT	24.24	1.93	11.09	91.88	20.84	76.25
NCMW filtrated through FeO(OH)	0.00	1.29	3.83	78.21	19.52	67.51

In the case of PU nanostructured chopped filter, only arsenic and iron were significantly eliminated. The decrease in the concentration of other monitored substances ranged from 8.5% for *K* to 1% for *Na*. The iron concentration in the permeate was 45% lower, compared to the original NCMW. Although this is a significant decrease, it is again true that the original *Fe* concentration in NCMW is relatively low, so even this considerable decrease in concentration does not mean a significant change in the composition of the mineral water. However, the elimination of arsenic using a chopped PU sorption filter was the most significant. It reached 62%. Although this efficiency is somewhat lower compared to the 100% efficiency of FeO(OH), it is high enough to use a selective nanostructured PU-based filter supplemented with another inorganic adsorbent to eliminate arsenic from water to concentrations below the recommended limits for drinking water.

Conclusions

The nanostructured materials were prepared from polyurethane materials by nanofiber forming process in an electrostatic field. These materials were then employed to eliminate arsenic from water via a method combining filtration and sorption. The polyurethanes determined as the most favourable were selected from a set of polymers from which nanostructures were created by electrospinning. Decisive factors in this respect were the simple and efficient preparation afforded by electrospinning and the high degree of selectivity to the sorption of arsenic. During the filtration-sorption procedure, sorption activity was measured for samples of model contaminated water and real contaminated mineral water by atomic absorption spectroscopy. The reproducibility of adsorption efficiency was evidenced by the discontinuous and continuous filtration tests. The results measured for the sorption activities of the model contaminated water were in good accordance with those for the naturally sourced sample. The findings presented in this article highlight the great extent to which the active surfaces of the nanostructures have to be accessible to filtration and sorption processes. In particular, it was necessary to arrange the surfaces of the nanofibers so as to ensure maximum contact with water when applying nanostructured materials to sorption filters. Rinsing tests performed on PU nanostructures have shown a high resistance to wash out of trapped arsenic with distilled water. Although polyurethane nanostructures have been found to be effective as relatively selective arsenic adsorbents, it is desirable to add them with another inorganic sorbent, which will further increase the adsorption efficiency. However, it is possible to take advantage of the ease of preparation and simple application of microfiltration membranes.

Acknowledgments

Conflict of Interest statement

The authors declare that they have no conflict of interest.

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