

Supplementary documents:

Effect of Polyurethane Structure on Arsenic Adsorption Capacity in Nanofibrous Polymer/Ferrous Sulphate-based Systems

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Comparison of adsorbents:

A number of nanofibre based sorbents have already been tested for the adsorption of arsenic from water, ranging from inorganic nanofibres (mainly carbon fibres, possibly doped with other sorbents) to nanofibres based on organic polymers, mainly polyacrylonitrile or chitosan. Polymer nanofibres are usually also doped with additives, primarily by forming composites with e.g. Fe⁰ nanoparticles or by adding oxides of iron, manganese, titanium, etc. A drawback of the nanofibre based systems tested so far is their brittleness, which leads to an uneasy handling of the adsorption material. In particular, this shortcoming is supposed to reduce the nanofibrous material based on flexible PUs.

Among the synthetic polymers used for the preparation of nanofibrous functionalized sorbents, polyacrylonitrile (PAN), poly(vinyl alcohol) (PVA) respectively poly(vinylidene fluoride) (PVDF) or polyaniline (PANI) are the most common.¹

Functionalized PAN based fibres can be considered as one of the most effective nanofibrous arsenic sorbents. Although the preparation procedure of PAN-CNT/TiO₂-NH₂ nanofibers is quite complex, the maximum adsorption capacities of removing As(III) and As(V) are 251 and 249 mg g⁻¹, respectively (at pH 2). The mentioned composite is prepared by crosslinking of TiO₂ nanoparticles having surface functionalized with amino groups onto the electrospun PAN-carbon nanotubes (CNT) composite substrate.² Another composite structure represent electrospun PAN nanofibers doped with hydrous manganese oxide (HMO) nanoparticles synthesized by oxidation of manganous ions by permanganate. Such a composite is suitable not only for the adsorption of arsenic (95.7 mg g⁻¹) but also lead (194.4 mg g⁻¹).³ A relatively high filtration capacity was also achieved with the composite based on maghemite (γ-Fe₂O₃) and graphene oxide (GO) embedded in a PAN polymer nanofibre matrix (PAN/GO/γ-Fe₂O₃). Also this composite structure was prepared using electrospinning technique.⁴ For the removal of many heavy metals, but also arsenic, another PAN based composite membrane is suitable. This is a membrane prepared by electrospinning from a polymer solution with dispersed α-Fe₂O₃ nanoparticles.⁵

PVA is important biodegradable, non-toxic and biocompatible polymer electrospinnable from aqueous solutions. Insolubility of nanofibers can be achieved with a proper thermal or chemical crosslinking. For example, a nanofibrous material containing Fe^{3+} ions immobilized in PVA nanofibers was prepared. After electrospinning, crosslinking was performed in a desiccator saturated with ammonia vapour. The maximum capacity for arsenic removal was about 67 mg g^{-1} for As(III) and 36 mg g^{-1} for As(V)⁶. In another study PVA nanofibres were prepared for which water stability was achieved by heat treatment in an oven at 190°C . The fibres were doped with superparamagnetic iron oxide nanoparticles (0.14 w/w%) exhibiting tendency towards agglomeration which limits their efficiency. Immobilization in PVA nanofibers overcomes this limitation. However, the prepared adsorption material must undergo a swelling phase prior to the active adsorption phase. Maximum of adsorption capacity is around 52 mg g^{-1} .⁷

As a successful nanofibrous adsorbent is also PVDF membrane doped with nanoparticles based on titanium dioxide halloysite nanotubes. Although this adsorbent containing only 0.5 w/w % of nanoparticulate sorbent was able to remove As(III) down to values below 10 mg l^{-1} (a maximum of arsenic adsorption was 31.2 mg g^{-1}), its preparation was very long and demanding, especially the preparation of the dopant.⁸ Another PVDF nanofibrous structure prepared by electrospinning contained Fe-Mn binary oxide nanoparticles as inorganic arsenic adsorbent. An As(V) adsorption capacity of about 21.32 mg g^{-1} was achieved using 0.5% of Fe-Mn nanoparticles.⁹

In the field of nanofibres based on synthetic polymers, we can also mention polyaniline fibres, which are not prepared by electrospinning. PANI nanofibers can be synthesized via the rapid-mixing chemical oxidative polymerization method at room temperature. Such nanofibrous material can be doped by Fe^0 via reductive deposition of Fe^0 nanoparticles onto the PANI nanofibers matrix at room temperature (FeCl_2 and/or FeCl_3 as the source of nano- Fe^0). Fe^0 nanoparticles embedded onto the PANI matrix have average diameter 6.4 nm. The maximum adsorption capacities for As(III) and As(V) were 232.5 and 227.3 mg g^{-1} , respectively.¹⁰

In connection with the use of polymeric nanofibres for arsenic sorption, a membrane based on polyurethane nanofibres supplemented with an inorganic adsorbent based on iron hydroxide oxide – $\text{FeO}(\text{OH})$ (GEH 102) may also be mentioned.¹¹

In addition to synthetic polymers, natural polymers can also be used as sorbents. The most commonly used of these is chitosan, which is a good sorbent even without further functionalization.

Chitosan-based nanofibrous material is usually prepared from an acidic solution of this polymer in combination with another carrier polymer (usually PEO), which supports the formation of nanofibers in an electrostatic field. Chitosan nanofibers are highly porous and have a large specific surface area. The maximum adsorption capacity was determined to be 30.8 mg g^{-1} . It was indicated, the adsorbed As forms outer-sphere surface complexes with chitosan nanofibers.¹² As for the modified chitosan membranes, a nanofibrous material was prepared by electrospinning a mixture of chitosan, PEO and Fe^{3+} (FeCl_3 as precursor) followed by crosslinking with ammonia vapor. This material exhibited maximum adsorption capacity for As(V) of 11.2 mg g^{-1} (at pH 7.2) and for As(III) 36.1 mg g^{-1} . It was able to remove even trace amounts of arsenic.^{13,14} In another study, nanofibers combining chitosan and PVA doped with Fe^0 were prepared. Not only Fe^0 , but also chitosan and its amine groups act as adsorbent for

arsenic. The nanofibrous sorbent exhibits high sorption capacity of 200 mg g^{-1} for As(V) and 142.9 mg g^{-1} for As(III)¹⁵ Chitosan can be used not only as a polymer for the preparation of nanofibers, but also as a functionalization additive ensuring the adsorption of arsenic, deposited on other polymer nanofibers. Therefore, fibers from a mixture of PLA and sodium alginate (SA) were prepared by electrospinning, which were subsequently modified by spin-coating with a chitosan solution. The maximum As (III) adsorption capacity of that material at neutral pH was really high (540.4 mg g^{-1}).¹⁶

The last group of nanofibres consists of inorganic fibres. The preparation of this type of nanofibers is usually accompanied by post-process calcination, which complicates the preparation process. In the literature we can find e.g. adsorbent based on CuO–ZnO nanofibres fabricated via electrospinning technique (PVA as carrier polymer) with post-calcination at 500°C for 4 hours in the presence of air. The maximum adsorption capacity of this adsorbent was 27.7 mg g^{-1} in a wide range of pH.¹⁷ The maximum adsorption capacity of 117.72 mg g^{-1} of As(III) and 60.19 mg g^{-1} of As(V) exhibit nanofibers based on manganese dioxide and its specific crystalline phases. The $\alpha\text{-MnO}_2$ nanofibers were prepared by a hydrothermal synthesis procedure.¹⁸

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Distribution of nanofibres diameters:

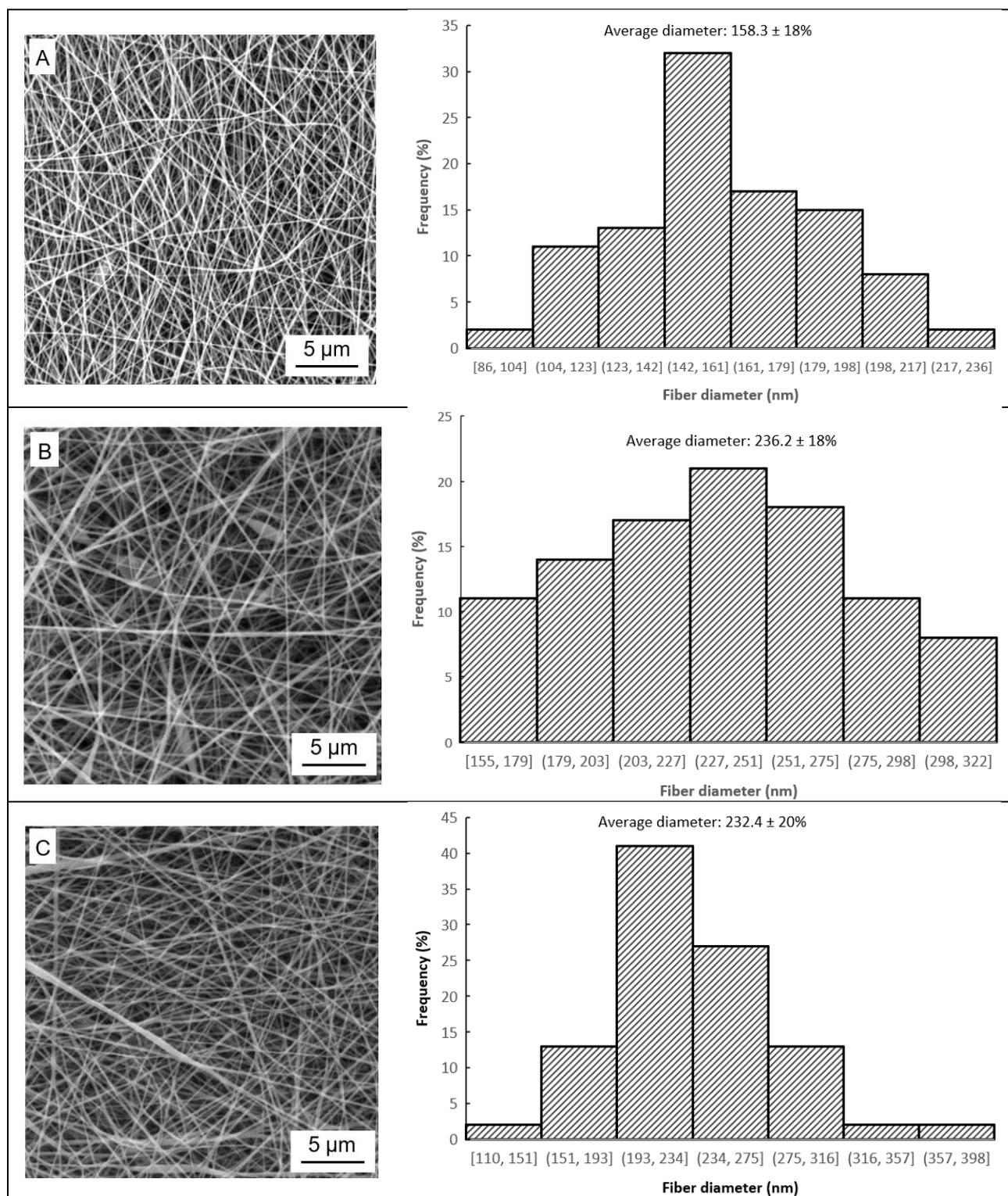


Fig. S1. SEM images for nanofibres of (A) PU918, (B) PUSU and (C) PUEL (5000 times magnification) and corresponding histograms of nanofibre diameter distributions

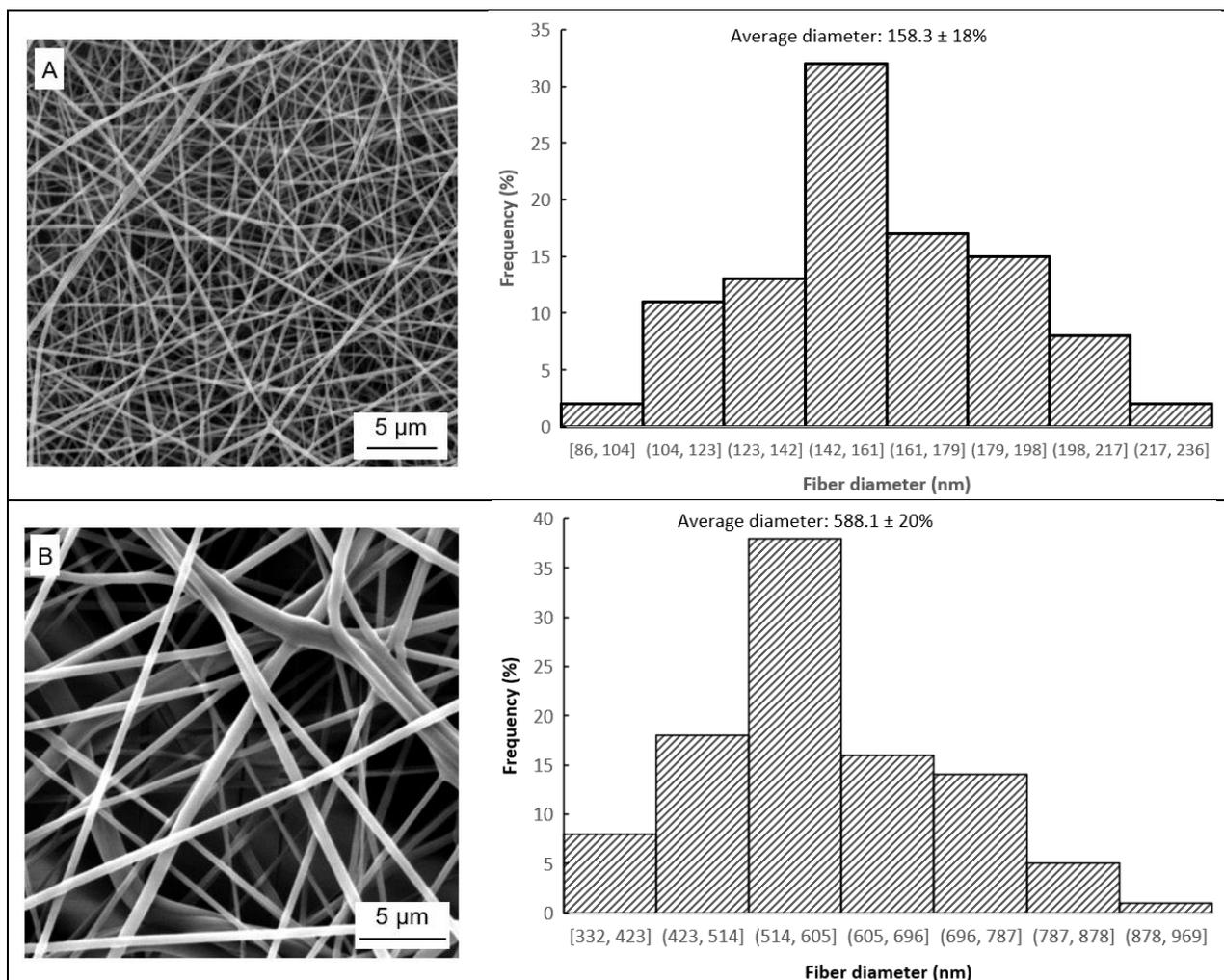
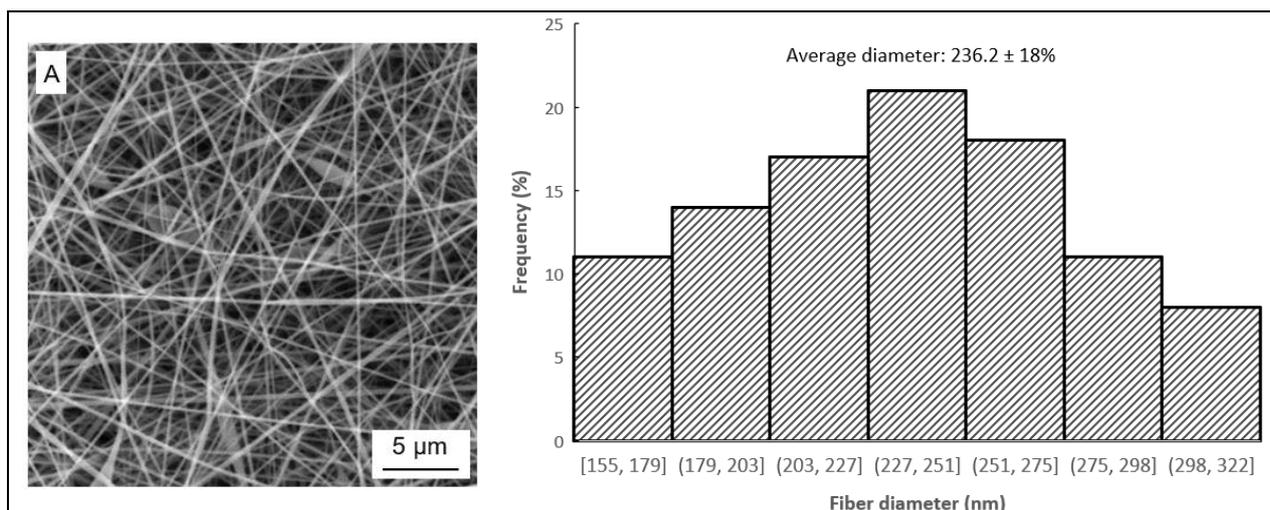


Fig. S2. SEM images of nanofibers of PU918 (A) without the adsorption additive and (B) with FeSO_4 as the adsorption additive (5000 times magnification) and corresponding histograms of nanofiber diameter distributions



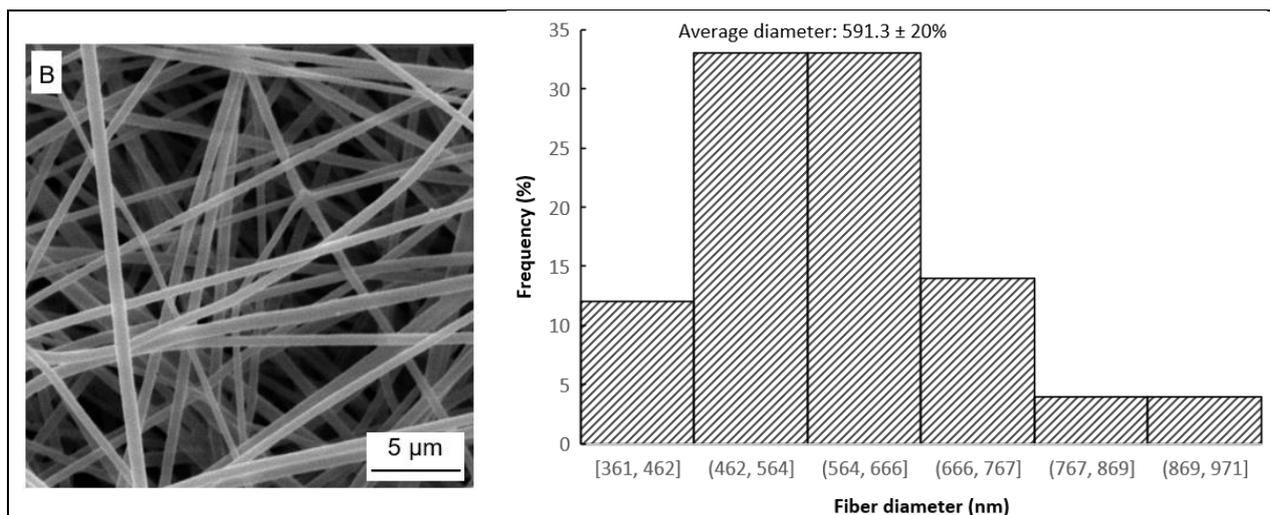
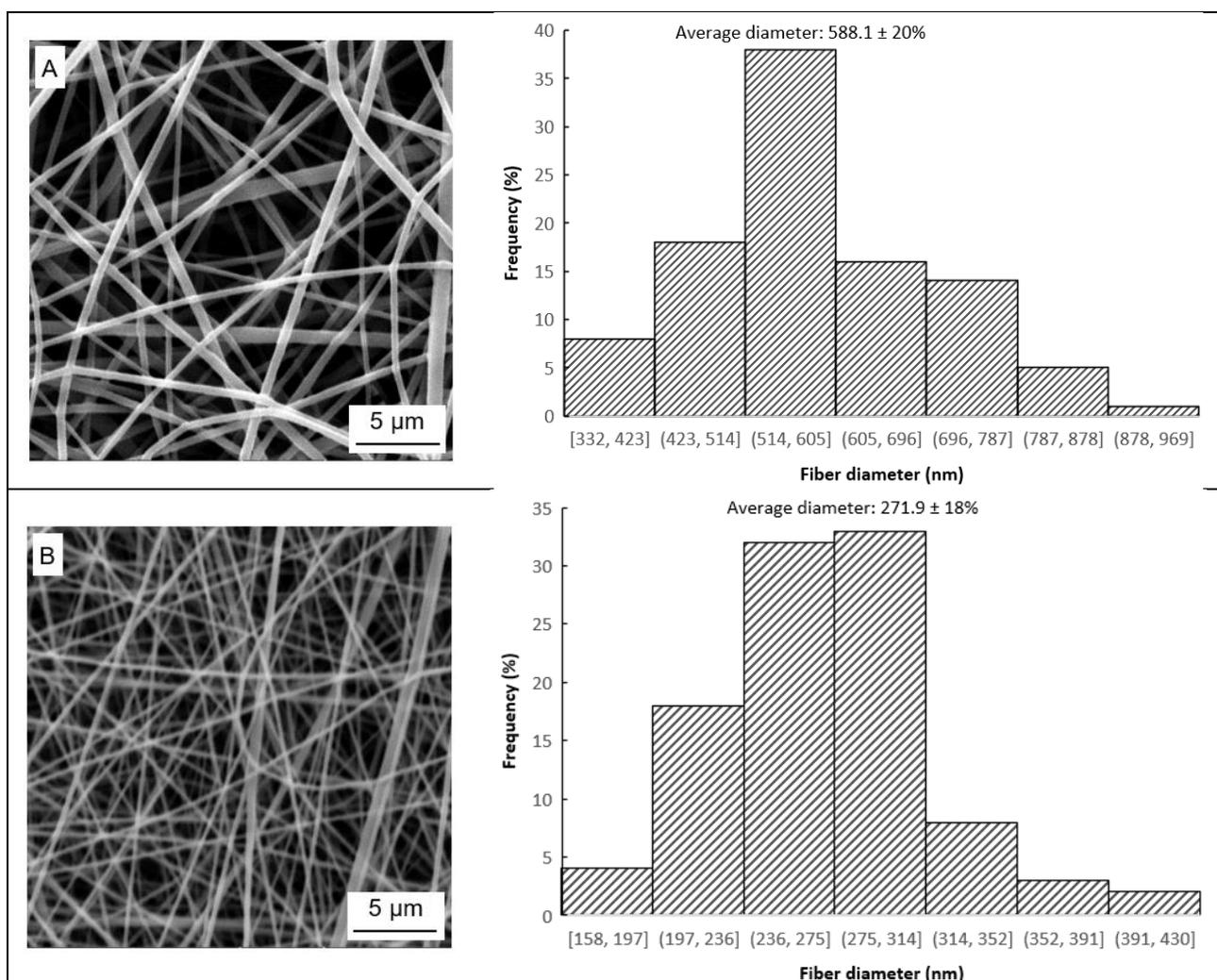


Fig. S3. SEM images of nanofibers of PUSU (A) without the adsorption additive and (B) with FeSO₄ as the adsorption additive (5000 times magnification) and corresponding histograms of nanofiber diameter distributions



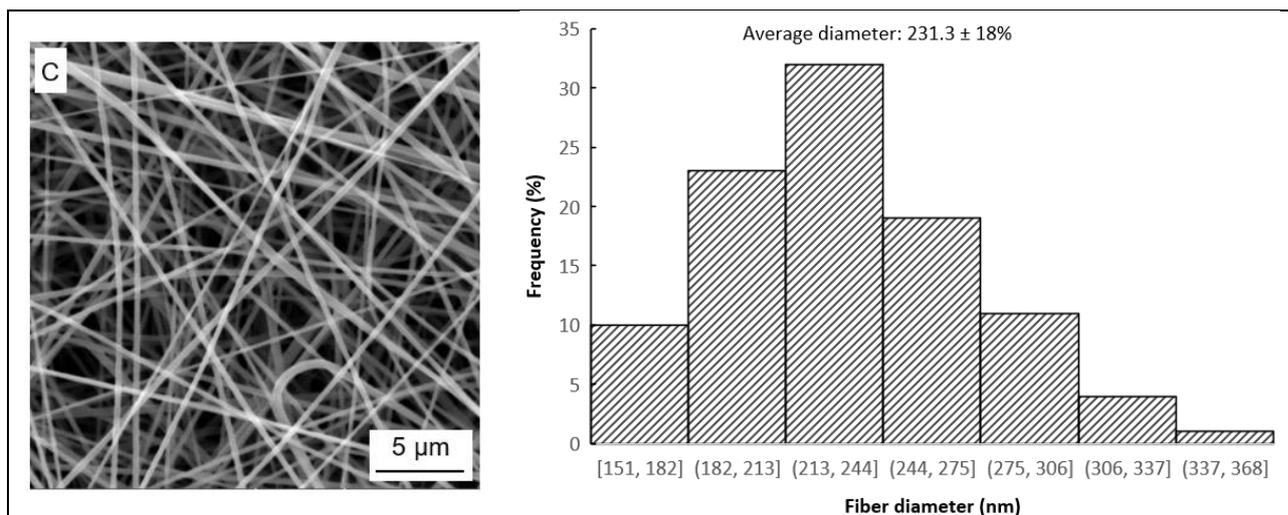


Fig. S4. SEM images of nanofibres of PU918 with FeSO_4 as the adsorption additive prepared from solutions where conductivity had been increased by (A) no additive, (B) a combination of sodium tetraborate decahydrate and citric acid (BC) and (C) quaternary ammonium salt (QAS) (5000 times magnification) and corresponding histograms of nanofibre diameter distributions

Water contact angle analysis: Surface Energy Evaluation (SEE) method

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 5 samples was tested by water drop of 3 μL in volume. The testing liquid was distilled water. The angle was measured approximately 1 second after release of droplet from micropipette. An average of fifth measurements was reported. Table S1 shows the contact angles of individual polyurethane nanostructures (PU918, PUSU, PUEL) without FeSO_4 adsorption additive and the contact angles of PU918 and PUSU structures doped with FeSO_4 . The contact angles are accompanied by illustrative images of the microdroplets of water used for their determination.

Table S1: Contact angles for used PU structures

PUEL nanostructure	$113.1^\circ \pm 8.4^\circ$	
PU918 nanostructure	27.3 ± 4.3	
PU918 + FeSO ₄ nanostructure	130.4 ± 5.7	
PUSU nanostructure	122.8 ± 4.3	
PUSU + FeSO ₄ nanostructure	128.6 ± 3.7	

EDX-XRF analysis:

The content of arsenic and iron elements in the samples (PU918 and PUSU doped with FeSO₄) were determined by EDX-XRF (Energy ray dispersion spectroscopy - X ray fluorescence), which is based on the emission of a specimen characteristic X-rays. The X-rays are generated according to the characteristics and nature of the elements present in the sample. The method is suitable for determination of elemental concentration in matrices in powder, liquid and solid form; it is a non-destructive method. The amount of element analyzed is evaluated in weight percent (% w/w). EDX method is the only orientation method suitable for evaluation of element under 5%. Elemental concentrations below 0.05% are assessed as indeterminate. The limit of quantification (LOQ) of the element content is around 1% and the limit of detection (LOD) around 0,5%.

The content of the elements was determined using an Energy Dispersive X-ray Spectrometer (Thermo Scientific, ARL Quant X). The samples were analyzed in a special selected method: Any sample Helium in Quant program. Each sample was analysed 3 times (RDS: $\pm 0,01289 - 0,00112\%$). The averaged values from three parallel measurements of the individual samples are shown in the table S2.

Tab.S2 EDX-XRF analyse of adsorption polyurethane material

Sample	CHON (%)	Sx (%)	Fe (%)	As (%)
PU918 + FeSO ₄	96.5	0.98	0.56	/
PU918 + FeSO ₄ +As	96.4	0.91	0.58	/
PUSU + FeSO ₄	96.5	0.98	0.56	/
PUSU + FeSO ₄ +As	96.3	0.91	0.58	/

CHON – basic polymer matrix

Sx – sulphur oxides

Arsenic was not identified in any of the samples subjected to the adsorption test. The amount of arsenic adsorbed is probably below the detection limit due to the low concentration of arsenic in the contaminated water used (150 µg/l). The EDX method is not suitable for the detection of As in this case.

Approximately 96.5% of the elements detected are carbon, nitrogen, oxygen and hydrogen representing the hydrocarbon basis of the polymer chain. There were detected also trace amounts of calcium, chlorine and potassium. Low quantities of iron (0.5%) and sulphur oxides (0.9%) were detected, which corresponds to the fact that tested material contains about 1% FeSO₄.

Point of zero charge:

Point of zero charge (pH_{pzc}) of adsorption materials were determined by salt addition method. A 0.1 M sodium chloride aqueous solution was used as the electrolyte. Point of zero charge (fig. S5) was determined from the dependence of the pH differences of initial and final pH ($\Delta pH = pH_i - pH_f$) on the initial pH_i (point when $\Delta pH = 0$).

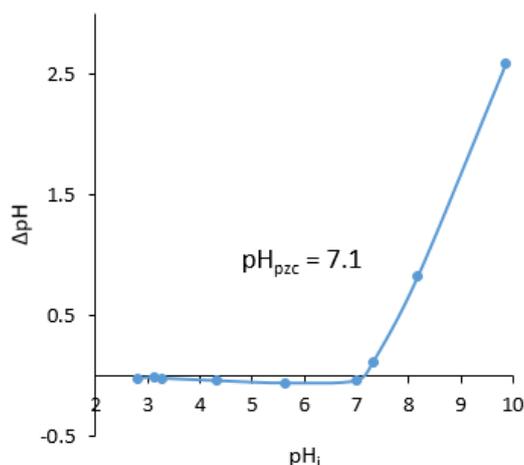


Fig. S5. Point of zero charge for nanostructure based on PU918 doped with 1% of FeSO₄

BET analysis:

There were analysed samples of polyurethane adsorption materials: PU918 + FeSO₄ and commercial PUSU + FeSO₄.

Nitrogen adsorption/desorption isotherms were recorded by a volumetric gas adsorption analyser (BELsorp Mini II, BEL, Japan) at 77 K. Prior to the measurements, the samples were degassed in the sample cells at 90 °C for 5 hours. The specific surface area (SSA) was determined by multipoint Brunauer-Emmett-Teller (BET) analysis using at least five data points in the range of relative pressure range (p/p₀) from 0.05 to 0.20 (Data Analysis Software, version 6.3.0.0).

Results of BET specific surface areas are:

PU918+FeSO₄ - 8.09 m²/g

PUSU+FeSO₄ - 9.95 m²/g

Adsorption/desorption isotherms are identified as Type II which suggest the nanofibers are practically nonporous (Fig. S6, Fig. S7).

Pore size and distribution of the nanostructured materials were 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 and maximum pore diameter. A pore size distribution was counted as well.

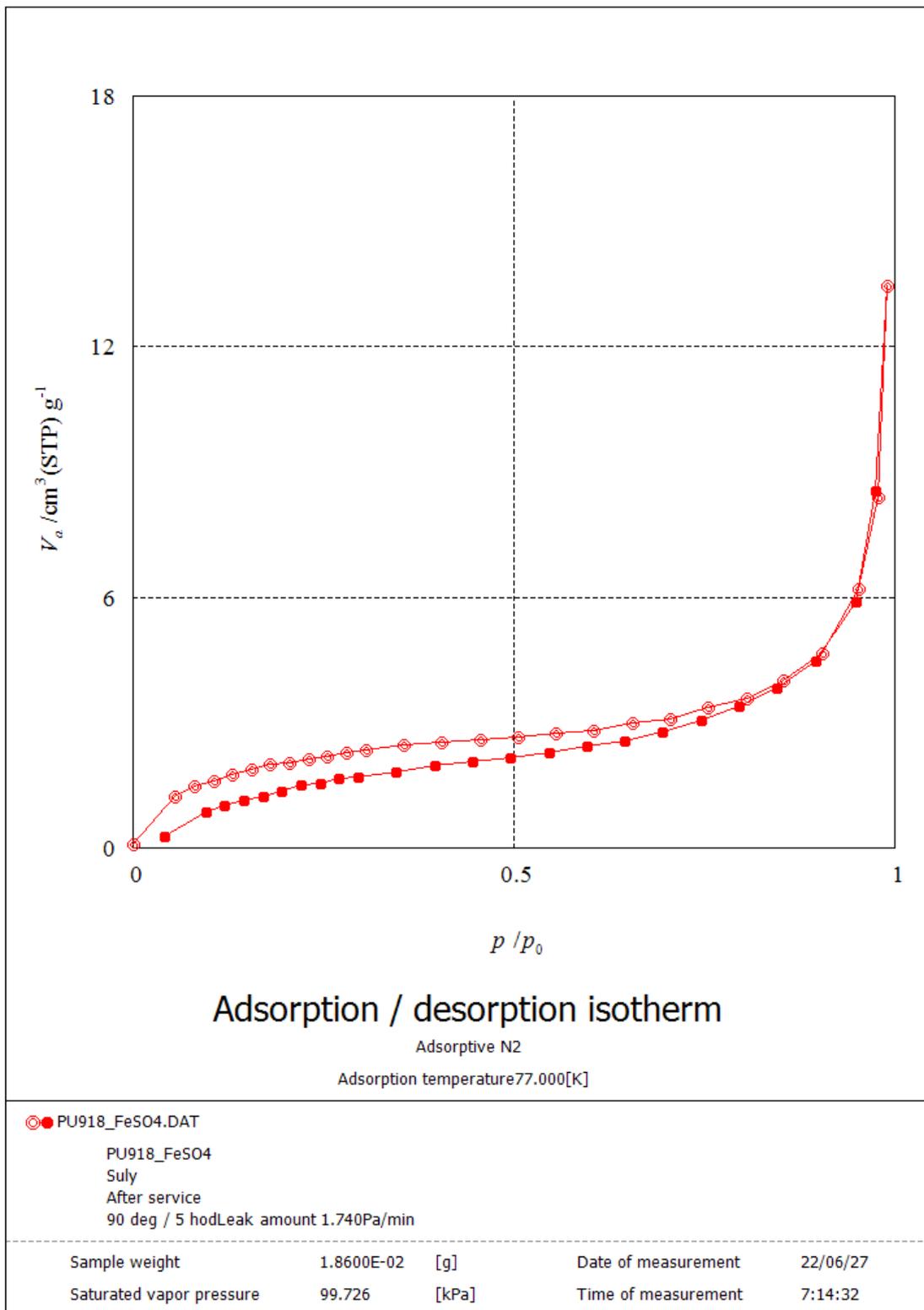


Fig. S6. Adsorption/desorption isotherm of PU918 + 1% FeSO₄ (QAS enhanced conductivity)

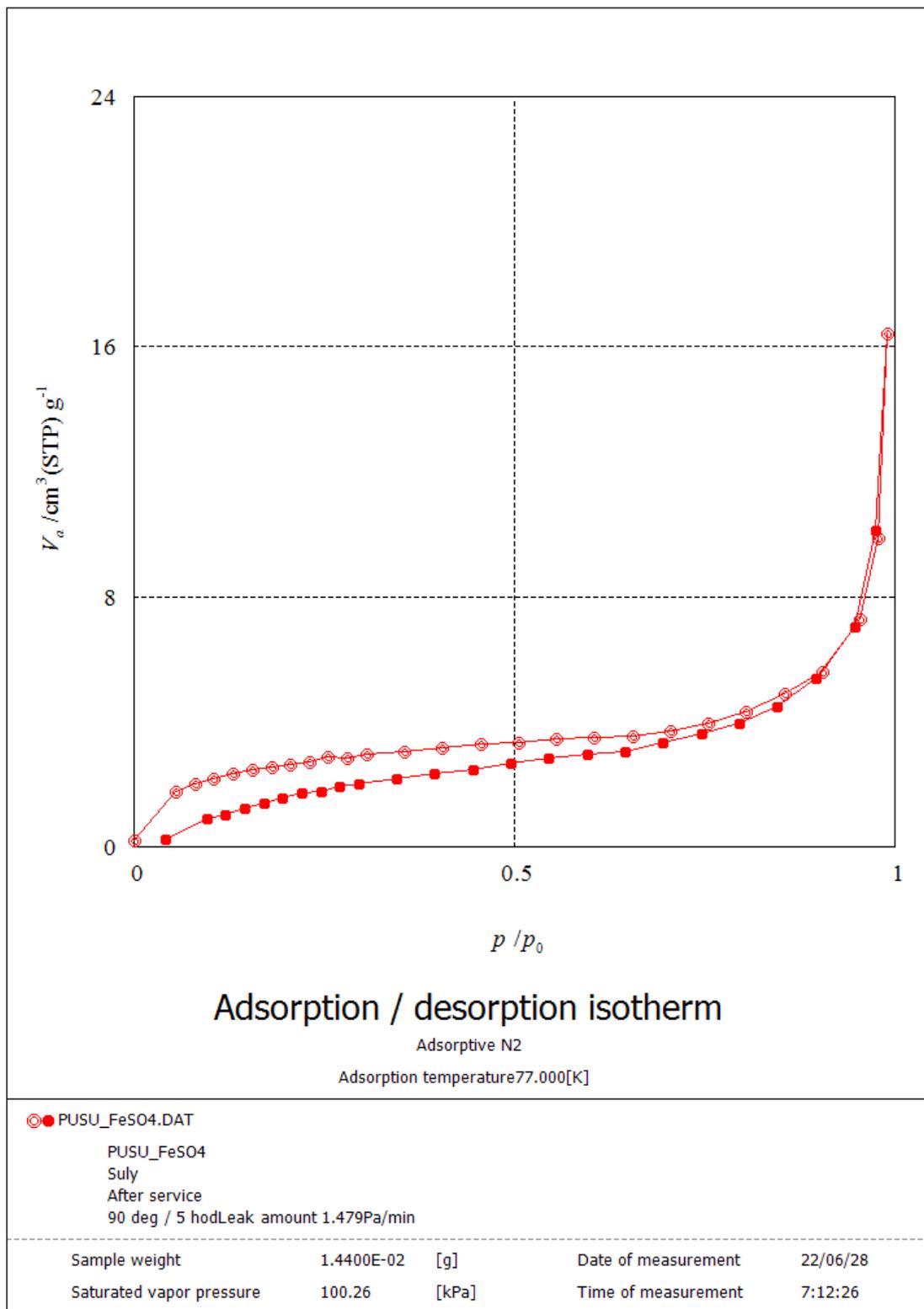


Fig. S7. Adsorption/desorption isotherm of PUSU + 1% FeSO₄

The nanostructured materials based on PU918 and PUSU doped with 1% of FeSO₄ were characterized by porometry. The medium diameter of pores in nanostructure for PU918 material was 0.31 μm ± 9% and maximum pore diameter was 0.4 μm ± 7%. In the Fig. S8 is showed the

pore size distribution for mentioned material. The medium diameter of pores in nanostructure for PUSU material was $0.91 \mu\text{m} \pm 13\%$ and maximum pore diameter was $1,22 \mu\text{m} \pm 10\%$. In the Fig. S9 is showed the pore size distribution for mentioned material.

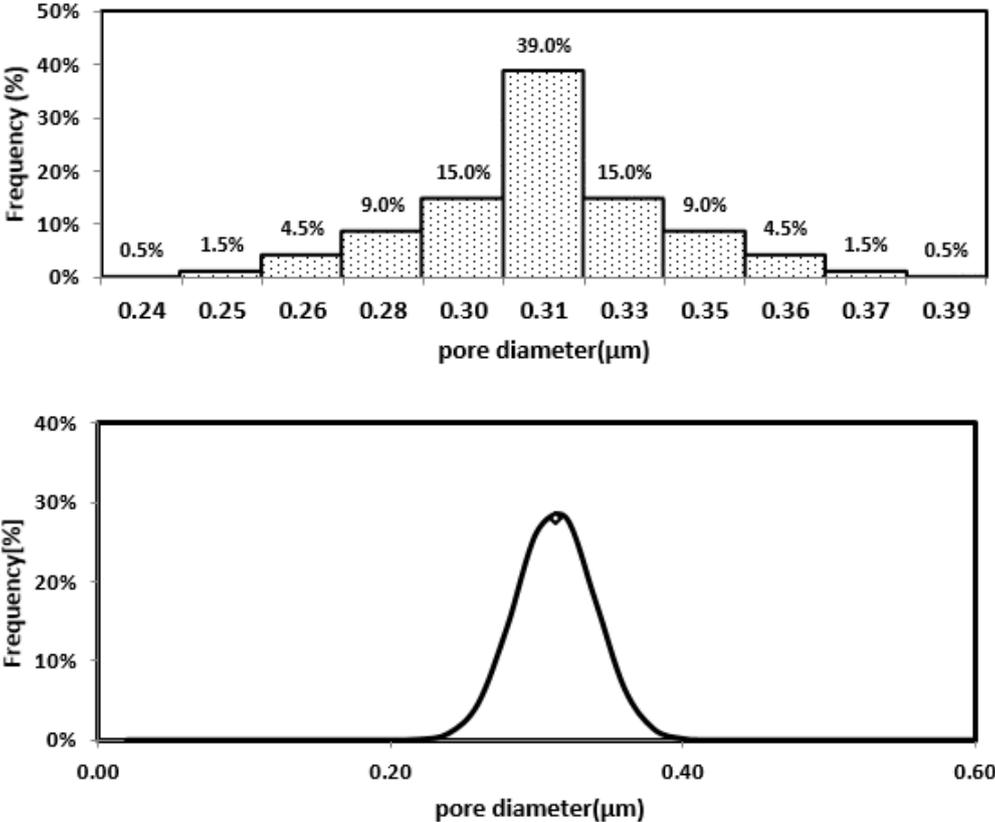
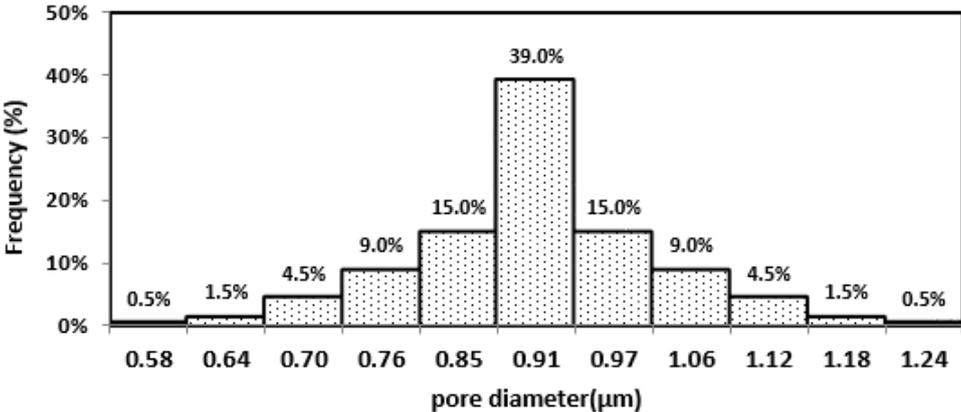


Fig. S8. Histogram and distribution curve of pore size in PU918 +FeSO4



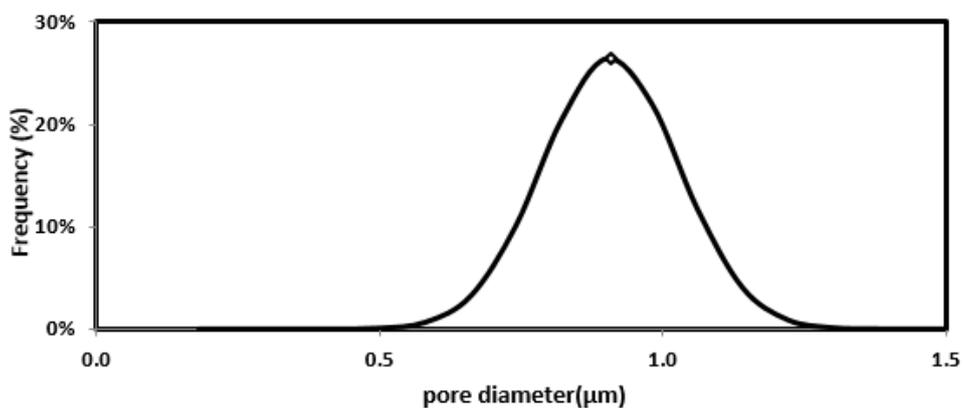


Fig. S9. Histogram and distribution curve of pore size in PUSU +FeSO₄

FeSO₄ adsorption efficiency increases by adding CaCO₃

Informed by the literature, an experiment was designed to further improve adsorption efficiency and its duration. It is known that the adsorption efficiency of FeSO₄ increases when ferrous sulfate is combined with calcium carbonate (CaCO₃) at a molar ratio of Ca to Fe of 1.5:1. As a consequence, samples of nanostructures based on PU918 doped with FeSO₄ were prepared, where CaCO₃ was also incorporated directly in the fibres. Thus, calcium carbonate was added directly to the polymer solution for electrospinning, maintaining the recommended Ca to Fe ratio of 1.5:1. The subsequent nanostructured material was subjected to an adsorption test.

Fig. S10 contains a graph that details the adsorption efficiencies of nanostructures supplemented with the FeSO₄ and CaCO₃ combined adsorption additive, compared to those of nanostructures enriched with FeSO₄ only. It is clear that adding CaCO₃ diminished capacity for arsenic adsorption. The cause may have been incorrect timing of the reaction between FeSO₄ and CaCO₃, which cannot be controlled when both components are incorporated in the mass of the nanofibres.

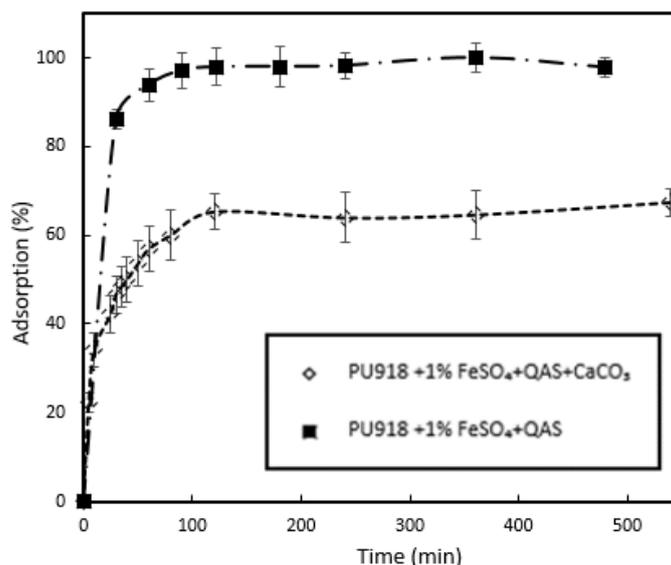


Fig. S10. Removal of arsenic over time for PU918 doped with FeSO₄ and a combination of FeSO₄ and CaCO₃ (1.5:1) in contaminated water CW ($c_{As}=150 \mu\text{g L}^{-1}$, pH=6.5, T=23°C; RSD of AAS: $1.9 \pm 0.03\%$)

Adsorption efficiency change after adding support textile

As mentioned above, the prepared nanostructured sorption materials should be subsequently applied in the filtration-adsorption process. In order to prepare a filtration membrane from the nanofibre based structure, the nanofibre layer must be disposed on a support. A polyethylene terephthalate (PET) nonwoven textile with a basis weight of 60 g m^{-2} was chosen as a suitable substrate material on which the nanofibrous layer can be well fixed and which provides the membrane with good mechanical properties and easy manipulability. For this reason, it was decided to perform the adsorption test also with materials that simulate a filter membrane, i.e. a bilayer material composed of a support textile (PET) and a nanofibrous structure PU918+FeSO₄ (conductivity of the polymer solution enhanced by QAS) and also PET and nanofibrous structure PUSU+FeSO₄ (conductivity enhanced by QAS).

A comparison of the values for adsorption efficiency of the filtration membranes with the PET support and for nanostructures without such a support is given in Fig. S11. In both cases (PU918 and PUSU), adding a substrate meant a loss of adsorption efficiency, by about 10% for PU918+FeSO₄ and over 25% for PUSU+FeSO₄. The curves for the membranes with the support showed the initial part, prior to reaching the plateau of equilibrium, were noticeably gentler in angle than for the nanofibres without the support, indicating a decrease in the adsorption rate had occurred. This came about through the area of direct contact between the nanofibres and the test medium being reduced by the fixing of the nanofibres on the support.

The loss in efficiency is low, especially for the PU918 nanostructure with FeSO_4 and PET, a material that means the material can be applied in the form of an adsorption-filtration membrane. This experiment and others showed that the most effective sorbent for the removal of arsenic in aqueous media was the nanofibrous material based on PU918 doped with 1% FeSO_4 , with QAS as a conductivity enhancing additive.

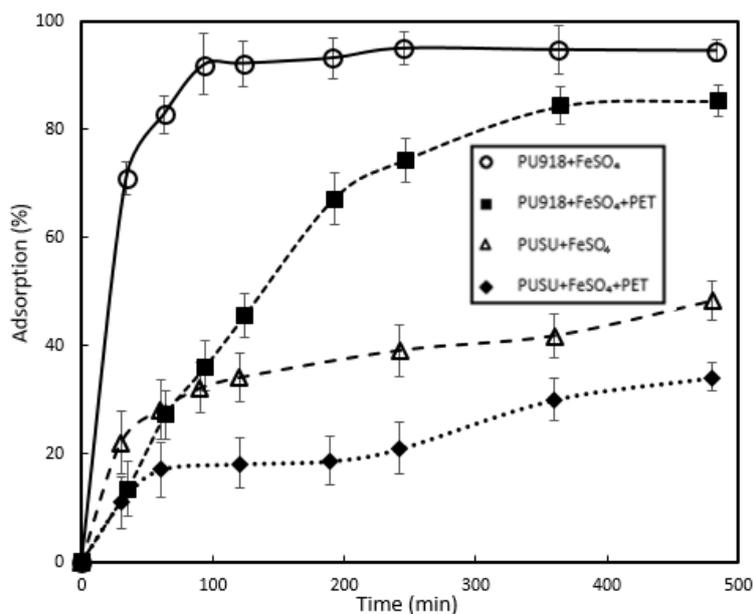


Fig. S11. Adsorption of arsenic over time for nanostructures based on PU918 and PUSU doped with 1% of FeSO_4 with and without PET support (CW: $c_{\text{As}}=150 \mu\text{g L}^{-1}$, $\text{pH}=6.5$, $T=23^\circ\text{C}$; RSD of AAS: $2.1 \pm 0.03\%$)