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Purification of Gas and Liquid Streams Using Composite Sorbents Embedded in a Polyacrylonitrile Matrix

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1 ABSTRACT

As new sorbents are developed for purifying gases or liquids via physisorption and/or chemisorption processes, the objective is typically to increase the specific surface area (*SSA*) to maximize the available binding sites for capturing various species of interest. One downfall to making a sorbent more porous is that it often leads to a product that is fragile or friable and can be damaged (resulting in unwanted powders), thus imposing process limitations. Techniques can be used to enhance the mechanical integrity of a sorbent, including heat treatments or pelletization with extrusion or granulation processes, but these can result in collapsed, unavailable pore structures within the sorbent, which decreases the diffusivity and eventually reduces the capacities of target species. An alternative approach for improving the mechanical integrity of the sorbent is to bind it (or encapsulate it) within a porous matrix that passively holds the sorbent in place. Typically, this approach leads to a decrease in sorption efficiency on the basis of starting sorbent mass, because the active sorbent is diluted by the binding matrix material and the active surfaces of the sorbent are somewhat obscured by the binding matrix; however, it comes with the advantage that the active sorbent is held in place and better protected from disintegrating during operation. One approach to securing the active sorbent is to embed it in a macroporous, passive polyacrylonitrile (PAN) matrix to create a composite sorbent. When optimized, the PAN matrix is highly porous and allows for gaseous or aqueous media transport through the product, providing adequate binding site access between the active sorbent and the species of interest. Including a polymer in the composite sorbent limits the maximum operating temperature, above which the composite sorbent incurs loss of structural integrity (e.g., decomposes) and/or reduction in *SSA*. Composite sorbents have been demonstrated with sulfide aerogels (SnS-PAN) for capturing I_2(g), hydrogen mordenite (HZ-PAN) and silver-exchanged mordenite (AgZ-PAN) for capturing Kr and Xe, nanoparticle metal oxides (Nano-Composite Arsenic Sorbent, or N-CAS) for removing arsenic from water, ammonium molybdophosphate (AMP-PAN) for removing cesium-137 (^{137}Cs) from aqueous nuclear waste streams, and The Phosphate Sponge (TPS) composite, which is being used to remove inorganic/ortho-phosphates in water treatment processes to mitigate introduction to the environment, which impedes toxic algae bloom formations. This chapter provides details on production of these materials along with options to optimize the synthesis process. It also includes experimental techniques to characterize products and assess their performance.

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2 INTRODUCTION

Sorbents are used for a variety of purposes, including the selective capture and retention of specific target species from gaseous and/or liquid-based process streams. The sorbent of choice for a given application must maintain physical integrity within the active environment, which can pose issues if a particular sorbent is effective for capturing the target species but fragile, in fine particulate form, or otherwise mobile. One way to improve the stability of the sorbent is to embed the active sorbent in a passive and macroporous matrix; polyacrylonitrile [also called PAN or poly(1-acrylonitrile)] is an option for this role. PAN is an organic polymer available in granular or fibrous solid form with the chemical formula of $(C_3H_3N)_n$. PAN exhibits numerous beneficial properties that make it a suitable choice for use as a binding agent, including the following:

1) PAN has fairly high temperature stability (~180–300°C) [1, 2], and thus is naturally suited for gaseous phase capture at elevated temperatures.
2) PAN is soluble in a variety of media including ***organic solvents*** such as dimethyl sulfoxide (C_2H_6OS or DMSO), dimethyl acetamide (C_4H_9NO), dimethyl formamide (C_3H_7NO), ethylene carbonate [$(CH_2O)_2CO$], sulfolane [$(CH_2)_4SO_2$ or tetrahydrothiophene 1,1-dioxide], and N-methylpyrrolidone (C_5H_9NO or *N*-methyl-2-pyrrolidone); ***mineral acids*** such as >5 M phosphoric (H_3PO_4), >5 M sulfuric (H_2SO_4), and >8 M nitric (HNO_3); and ***concentrated inorganic salt solutions*** such as sodium thiocyanate (NaSCN), lithium bromide (LiBr), and zinc chloride ($ZnCl_2$) [3].
3) PAN has a macroporous structure that allows access to the surface area of the active sorbent [4].
4) PAN is chemically stable, or insoluble, in neutral to moderately acidic solutions, making it a good choice as a scaffold for aqueous applications [5].
5) PAN is mechanically robust and particularly stable in radioactive environments [4].

Table 1 provides a summary of some PAN-composite sorbents previously developed that are discussed in the literature. However, only the following composite sorbents will be discussed here in detail: sulfide aerogels (SnS-PAN) [6] for capturing $I_2(g)$ [7], hydrogen mordenite (HZ) [8, 9] and silver mordenite (AgZ) [10, 9] (i.e., HZ-PAN and AgZ-PAN, respectively) for capturing Kr and Xe from used nuclear fuel reprocessing streams [7], Nano-Composite Arsenic Sorbent (N-CAS) for removing toxic metals from drinking water (e.g., As, Se, Sb) [11, 3, 12-14], The Phosphate Sponge (TPS) for removing inorganic/ortho-phosphates from water to remediate toxic algae blooms [15], and ammonium molybdophosphate (AMP-PAN) for removing ^{137}Cs from highly acidic aqueous nuclear waste streams [16, 17].

Table 1. PAN-composite sorbents from the literature along with the active sorbent, whether the sorbent can be regenerated ("Reg."), the applications where each composite sorbent has been demonstrated with moderate-to-high selectivities for specific contaminants, and corresponding references. An overview of several composites from this list is provided elsewhere [4, 18-24] and the reader is referred to additional references for more composites not listed here (some with unspecified applications) [4, 25]. *Y = yes, N = no, U = unknown

Sorbent name	**Active sorbent**	**Reg.***	**Application(s)**	**Reference(s)**
AgZ-PAN	Silver mordenite	Y	Xe, Kr	[10, 9]
AMP-PAN	Ammonium molybdophosphate	Y	Cs, Sr, Ln, Am	[16, 17, 19, 23]
Ba(Ca)SO_4-PAN	Barium/calcium sulfate	U	Sr, Ce, Y	[19, 23]
CLIN-PAN	Natural clinoptilolite	U	Sr	[26]
CSbA-PAN	Crystalline antimonic acid	U	Sr	[20, 23]
CuFC-PAN	Copper ferrocyanide	U	Cs	[25, 27]
HZ-PAN	Hydrogen mordenite	Y	Xe, Kr	[8, 9]
KCoFC-PAN	Potassium cobalt ferrocyanide	U	Cs	[28]
KCuHCF-PAN	Potassium copper ferrocyanide	U	Cs	[29]
KNiFC-PAN	Potassium nickel ferrocyanide	U	Cs	[30]
KZnHCF-PAN	Potassium zinc ferrocyanide	U	Cs	[29]
M315-PAN	Synthetic mordenite M315	U	Cs, Sr, Ce	[19, 23]
MgO-PAN	Magnesium oxide	U	Sr, Am, Y	[19, 23]
MnO-PAN	Manganese dioxide	U	Pu, Ce, Am, Sr, Y	[19, 23]
N-CAS	Metal oxides, hydroxides, oxyhydroxides, or salts	U	As, Se, Sb	[11, 3, 12-14]
Na-Y-PAN	Synthetic Na-Y zeolite	U	Pu	[19]
NaTiO-PAN	Sodium titanate	Y	U, Sr, Am	[19, 23]
NiFC-PAN	Nickel hexacyanoferrate	N	Cs, Sr, Am, Y	[31, 19, 23]
NM-PAN	Manganese dioxide and nickel ferrocyanide	U	Sr	[23]
SnS-PAN	Sn_2S_3 aerogel	N	I	[7]
SnSbA-PAN	Tin(IV) antimonate	U	Sr	[23]
TiO-PAN	Titanium oxide	Y	Sr, U, Am	[19, 23]
TiP-PAN	Titanium phosphate	U	Sr, U	[23]
TiSbA-PAN	Titanium(IV) antimonate	U	Sr	[23]
TPS	Proprietary (unspecified)	Y	PO_4^{3-}	[15]
ZrO-PAN, ZrP-PAN, and ZrOP-PAN	Zirconium oxide and/or phosphate	U	Sr, Ce, Am	[23]

3 GENERAL PROCEDURE FOR SYNTHESIZING COMPOSITE SORBENTS

Figure 1 shows the general process for generating a composite sorbent using PAN, DMSO, and a sulfide-based aerogel (chalcogel) sorbent. In this general process, the steps are as follows:

1) The active sorbent is added at a known concentration (i.e., mass of sorbent per unit volume of solvent) to a solvent (e.g., DMSO) in vessel-1 and is properly suspended in the solvent using agitation (e.g., magnetic stirring, vortexing).
2) Then, the PAN is added to the solvent-sorbent mixture in vessel-1, typically as a granular or fibrous material; gentle heating at ~40–80°C can be used to accelerate dissolution of PAN into the solvent.
3) Once the PAN dissolves, the mixture (i.e., PAN + solvent + sorbent) is removed from vessel-1 using a pipette and added dropwise into vessel-2, which contains water or another fluid in which the PAN is insoluble, thus creating a granular composite product.
4) The product is rinsed in water and the granular composite product is dried in an oven (e.g., ~50°C) and/or under vacuum.

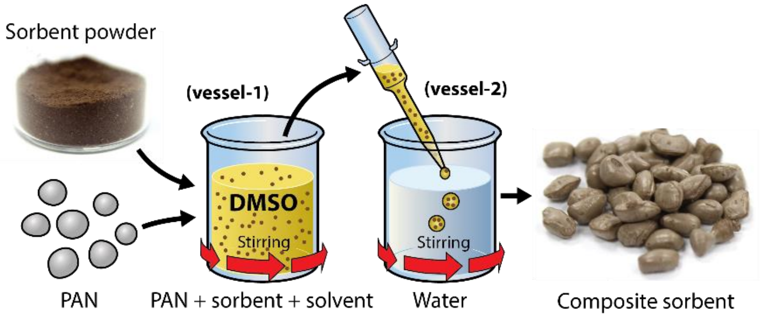

Figure 1. Conceptual design of PAN-composite sorbent synthesis. This figure was modified from the original by Riley et al. [6] and reprinted with permission from the American Chemical Society.

Note that many modifications can be made to this process, including (a) the order of steps (1) and (2) can be reversed [6]; (b) instead of adding drops of the mixture into a second solvent as described in Step-3 above, different shapes could be made using molds, and then these could be immersed in water (or other liquid), where the product can float out of the mold; (c) these could be made in a more continuous process in which the mixture in Step-2 is poured into water; (d) the water could be replaced with acidic or basic solutions (0.1–8 M NaOH); or (e) alternative polymers with high specific surface areas (i.e., *SSA*, typically in $m^2\ g^{-1}$) can be used in place of PAN as the passive matrix.

4 SORBENT CHARACTERIZATIONS

Once a composite sorbent is synthesized, it can be characterized with a variety of analytical techniques that can be broadly categorized into (1) physical/structural analyses,

(2) chemical analyses, and (3) performance analyses. Analytical characterization techniques to consider for a given sorbent are listed below:

- ***Physical/structural analyses***
    - Mechanical strength testing to determine the crush resistance and attrition/abrasion resistance of sorbents to validate their use in process applications.
    - Microscopy to look at changes in pore structure as a function of active sorbent loading in the PAN matrix, e.g., scanning and/or transmission electron microscopies (i.e., SEM, STEM, TEM), optical microscopy.
    - Crystallographic analysis to assess crystalline phase changes in the active sorbent after capture, e.g., X-ray diffraction, selected area diffraction.
    - Specific surface area, pore volume, and pore size distribution analyses using adsorption/desorption isotherms, e.g., Brunauer-Emmett-Teller method [32], Barret-Joyner-Halenda method [33].
- ***Chemical analyses***
    - Assessment of actual versus targeted composition using surface techniques, e.g., energy-dispersive spectroscopy, electron energy loss spectroscopy.
    - Assessment of actual versus targeted composition using bulk techniques, e.g., sample dissolution followed by analysis of liquid product with inductively coupled plasma mass spectroscopy, ion chromatography, and/or ion selective electrodes.
- ***Performance analyses***
    - Determination of maximum capacity for target species without known competing species present [e.g., I_2(g) capture without Cl_2(g) present] using batch or continuous-stream processes.
    - Determination of the influence of sorption competition with other species present that may or may not interfere with the capture of the target species. Analytically evaluated with gas chromatography.
    - Breakthrough experiments where the active sorbent performance is evaluated under various test conditions, e.g., bed temperature, gas/liquid flow rate, target species concentration, bed interaction time (residence time of sorbent bed in contact with the target species).

5 CAPTURE OF GASEOUS IODINE WITH SULFIDE AEROGEL COMPOSITES

Capturing iodine gas [I_2(g)] is one of the greatest concerns associated with reprocessing of used nuclear fuels because one of the most prominent iodine isotopes, ^{129}I, has a very long half-life ($t_{½}$) of 1.6×10^7 y (ß-emitter) and because it can incorporate into the human metabolic process through the thyroid, potentially causing cancer in affected individuals [34-36]. Methods for the capture and immobilization of gaseous iodine have been investigated for decades and generally include alkaline scrubbing options (e.g., hydroxides) and solid sorbents; a more comprehensive review is provided elsewhere [37].

The most promising technologies are porous sorbents that use a metal getter to chemisorb the $I_2(g)$ into a metal-iodide complex. Typical metals used for gettering $I_2(g)$ include Ag, Cd, Cu, Hg, Mn, Pb, Pd, and Tl [38-43]. Some of the more common sorbents evaluated to date include silver-loaded ceramics (e.g., AgZ [44], silver faujasite (AgX) [45]), silver-loaded aerogels (e.g., Ag^0-functionalized silica aerogel [46], silver-loaded aluminosilicate aerogels [47]).

In work done by Riley et al. [6], sulfide-based aerogels (or chalcogels) were used to capture $I_2(g)$. The specific chalcogel composition used for this study was Sn_2S_3, but several others have been demonstrated to capture $I_2(g)$ and could be used to make composite sorbents as well including $PtGe_2S_5$ [48, 49], $(CoNi)MoS_4$ [49], $NiMoS_4$ [50], $CoMoS_4$ [50], $Sb_4Sn_3S_{12}$ [50], $Zn_2Sn_2S_6$ [50], and $K_{0.16}CoS_x$ (x = 4−5) [50]. For this particular study, three different composites (i.e., SnS_{33}, SnS_{50}, and SnS_{70}) were synthesized with the chalcogel masses (m_{Cg}), PAN masses (m_{PAN}), and DMSO volumes (V_{DMSO}) listed in Table 2. The general process used is shown in Figure 1 and was described previously.

Table 2. Recipes for making PAN-chalcogel composite sorbents. "m", "m%", "V", "Total", and "Cg" denote mass, mass%, volume, chalcogel+PAN, and chalcogel, respectively.

Sample	m_{Cg} (g)	m_{PAN} (g)	m_{Total} (g)	$m\%_{Cg}$ (mass%)	m_{Cg}: m_{PAN}	V_{DMSO} (mL)
SnS_{33}	0.20	0.40	0.60	33	0.33	6.00
SnS_{50}	0.13	0.13	0.26	50	0.50	2.50
SnS_{70}	0.19	0.08	0.27	70	0.70	1.20

Since PAN is a lightly colored polymer, it was found that the easiest method for visualizing the porosity of these materials was through analysis of cross-sectional views of the granular product with SEM. The PAN matrix is generally soft, so the granular product can be easily cut in half for cross-sectional polishing. Prior to SEM analysis, the granular products were mounted in resin and polished. The general pore structure of the three composite sorbents along with a pure PAN granule are shown in Figure 2. Through the contrast of backscattered electrons, the active sorbent shows up much brighter than the PAN matrix, and the increased concentrations of chalcogel can be easily observed through the increases in brightness as $SnS_{33} < SnS_{50} < SnS_{70}$. Also, it is apparent from Figure 2 that the pore structure does collapse (fewer open pores) as the active sorbent concentration within the composite increases, in the order of $SnS_{70} < SnS_{50} < SnS_{33}$. Figure 2 also provides visual comparisons between the as-made and iodine-loaded composites; since the SnS_{70} composite was not iodine loaded using the same approach as the others, it was not shown in the comparison collage. The as-made PAN granules were white. The as-made SnS_{33}, SnS_{50}, and SnS_{70} were light tan, medium gray, and dark gray, respectively. For the iodine-loaded sorbents, the PAN+I, SnS_{33}+I, and SnS_{50}+I were light yellow, light brown, and dark purple, respectively.

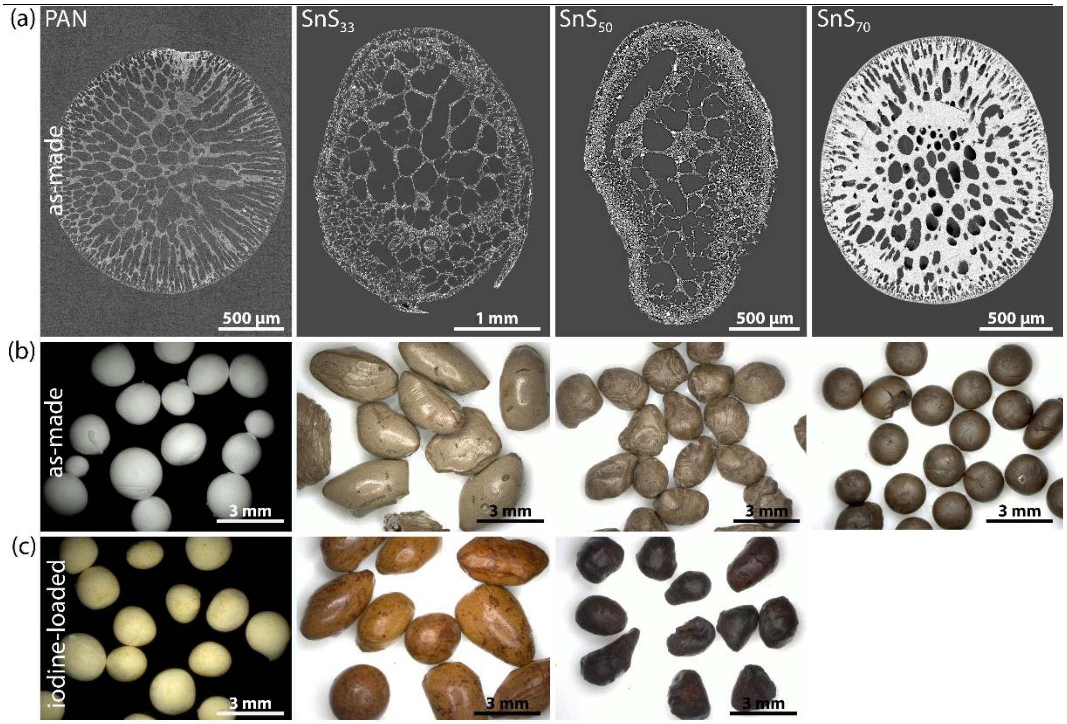

Figure 2. (a) Scanning electron micrographs of pure PAN form ("PAN") along with Sn_2S_3-loaded PAN (SnS-PAN) at 33 mass% Sn_2S_3 (i.e., SnS_{33}), 50 mass% Sn_2S_3 (i.e., SnS_{50}), and 70 mass% Sn_2S_3 (i.e., SnS_{70}) in cross-sectional view. Photographs of (b) as-made and (c) iodine-loaded composites in full form view.

The maximum iodine uptake was determined under static conditions by placing granules of the different samples into pre-tared glass vials, putting a known mass of iodine (99.9999%) into a separate pre-tared glass vial, putting these vials (along with a blank vial) into a vacuum desiccator, evacuating the desiccator, and periodically breaking vacuum to weigh all of the vials. The instantaneous iodine mass uptake (i.e., m_I) of the *i*-th sampling interval (i.e., $m_{I,i}$) was monitored as the difference between the mass after sitting in the desiccator in the presence of iodine (i.e., m_{Cg+I}) and the starting sample mass (i.e., m_{Cg}) using Equation (1) (all accounting for the tare mass of each vial). The cumulative iodine uptake (i.e., m_I) is defined as the difference between the final sample mass containing iodine after the experiment (i.e., m_{Cg+I}) and m_{Cg}, as shown in Equation (2). Additionally, the mass% of iodine in the final iodine-loaded specimen can be calculated either incrementally at different intervals using Equation (3) as $m_{\%I,i}$ for the *i*-th interval, or at the end of the experiment using Equation (4) as $m_{\%I}$.

$$m_{I,i} = m_{Cg+I,i} - m_{Cg} \tag{1}$$

$$m_I = m_{Cg+I} - m_{Cg} \tag{2}$$

$$m_{\%I,i} = 100 \times (m_{I,i} - m_{Cg}) / m_{I,i} \tag{3}$$

$$m_{\%I} = 100 \times (m_I - m_{Cg}) / m_I \tag{4}$$

Figure 3 provides some comparisons of the iodine uptake in the different chalcogel-PAN composite sorbents. Equation (3) was used to calculate the incremental mass uptake as a function of time for the PAN, SnS_{33}, SnS_{50}, and SnS_p (PAN-free) sorbents, and these data are plotted in Figure 3a with the final maximum iodine concentrations, which were calculated with Equation (4), presented as the numbers shown in the boxes to the right of each dataset. Figure 3b shows the utilization of the sorbent in terms of iodine loading (i.e., mass or moles) as a function of Sn_2S_3 mass and moles of Sn in the composite. Figure 3c shows the iodine concentration in the final composite after maximum iodine uptake as a function of PAN concentration in the composite; in the comparison are the pure chalcogel powder (SnS_p+I) and the PAN granules without chalcogel (PAN+I). Figure 3d shows the mass of iodine uptake as a function of chalcogel mass in the starting sorbent. Here, it can be seen from the 1:1 and 2:1 loading trend lines that the iodine loading is closer to 2:1 (by mass) of iodine per mass of Sn_2S_3 that is present within the composite.

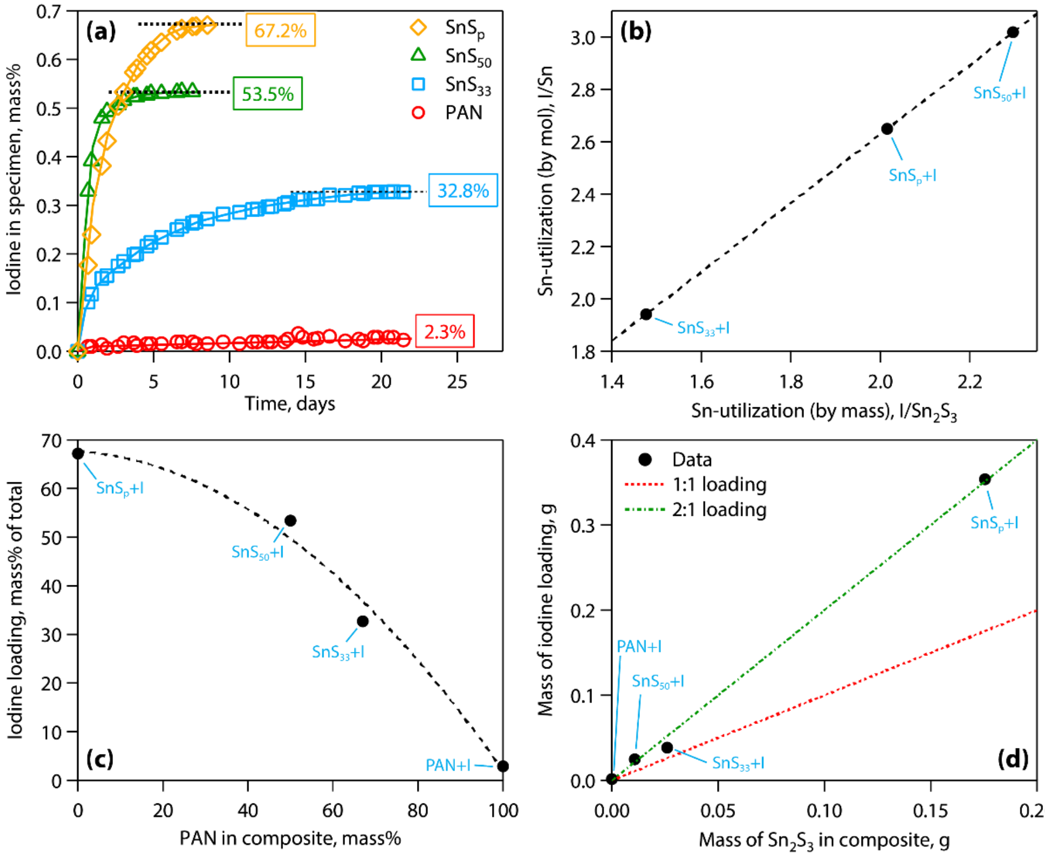

Figure 3. (a) Summary of maximum iodine uptake experiments in a vacuum desiccator using powdered chalcogel (i.e., SnS_p; see powder in Figure 1), two PAN-chalcogel composites (i.e., SnS_{33} and SnS_{50}), and pure PAN (i.e., PAN) granules for comparison. Values are shown as the mass% of iodine in the final form. (b) Comparison of Sn utilization including I/Sn_2S_3 (by mass) and I/Sn (by mole). (c) Summary of iodine uptake (in mass% of total mass after capture) as a function of PAN content in the sorbent (the PAN-free sorbent, SnS_p, and pure PAN are included for comparison). (d) Summary of iodine mass loading as a function of Sn_2S_3 mass in the composite along with 1:1 and 2:1 loading lines (mass basis) for comparison of sorbent utilization.

6 CAPTURE OF XENON AND KRYPTON

The capture of Xe and Kr present in nuclear fuel reprocessing off-gas streams is necessary to mitigate the release of radioactive materials to the environment. Some of the more common technologies historically used include cryogenic distillation [51-55] and solid sorbents such as activated carbon (or charcoal) [56], metal-organic frameworks

(MOFs) [57-59], metal-impregnated zeolites [60], and chalcogels [61]. In recent work by Garn, Greenhalgh, and Law, selective volatile noble gas (i.e., Xe and Kr) capture was demonstrated with both HZ-PAN [8] and AgZ-PAN [10]; these are described in more detail below.

Xenon exhibits characteristics useful to numerous commercial applications [62]. If Xe can be selectively partitioned and purified, an economic supply to the commercial sector is anticipated. Examples of industry uses for xenon include (1) lamp manufacturing, which consumes 60–80% of the available quantities, (2) computerized tomography, (3) anesthesiology, (4) lasers, and (5) the space industry.

6.1 HZ-PAN for Krypton Capture

An HZ-PAN sorbent was fabricated by mixing 10 g CBV90A hydrogen mordenite (Zeolyst International) and 2 g 3.3 dtex semi-dull PAN fibers (Dralon GmbH) in 30 mL DMSO at 80°C. Spherical droplets were formed using a glass apparatus fitted with an air-assisted nozzle design. The homogeneous mixture was poured into the apparatus and gravity fed to the air-assisted nozzle, where droplets were formed and dropped into an agitated nanopure water bath, which removed the water-soluble solvent to form spherical granules. The granules were dried in a vacuum oven overnight at 60°C. While the *SSA* of the starting HZ sorbent was 493 $m^2\ g^{-1}$, that of the final HZ-PAN sorbent was 336 $m^2\ g^{-1}$. Considering the additional mass of PAN added, minimal loss of *SSA* was reported during the HZ-PAN sorbent preparation.

The Kr capacity of the HZ-PAN was then evaluated using a cryostat system for thermal-swing adsorption operations. Prior to sorbent capacity measurements, the HZ-PAN was activated at 150°C using a He flow of 50 standard $cm^3\ min^{-1}$ (sccm) for 12 h to remove any entrained water. Then, the column containing the HZ-PAN sorbent was cooled to −82°C while flowing He across the bed. A feed gas of 150 µL Kr L^{-1} (in He balance) was introduced at 50 sccm, using a mass flow controller to obtain the desired Kr concentration ranging from 75–2544 µL L^{-1}. Using a Langmuir equilibrium isotherm fit for the experimental dataset, the model had the following form:

$$q = \frac{q_{\mathrm{max}} K_{\mathrm{eq}} C}{1 + K_{\mathrm{eq}} C} \tag{5}$$

where q is the sorbent capacity at equilibrium with feed concentration (C), K_{eq} is the Langmuir adsorption equilibrium constant, and q_{max} is the predicted maximum capacity of the sorbent at the specified temperature. Figure 4 shows a Kr adsorption isotherm. The Kr capacity was determined for a series of 24 breakthrough tests, between which the sorbent was thermally cycled up to 100°C for desorption, with capacity values ranging from 100–112 mmol kg^{-1} (baseline conditions). The Langmuir parameters, K_{eq} and q_{max}, were determined to be 23.4 $m^3\ mol^{-1}$ and 0.94 mol kg^{-1}, respectively.

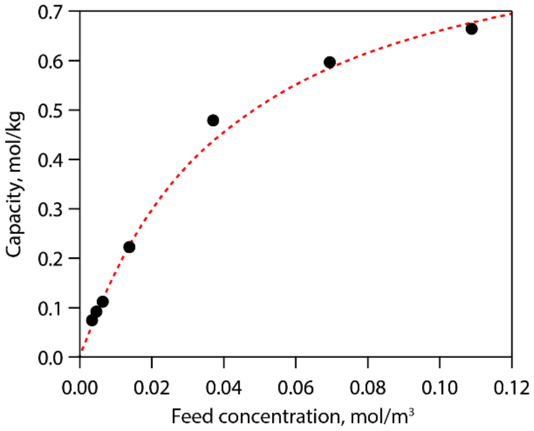

Figure 4. Kr adsorption isotherm showing Kr capacity as a function of feed concentration for HZ-PAN composite (circles) along with the Langmuir prediction (dotted line) [8].

In addition to capacity evaluations, thermal cycling effects were also evaluated to determine the robustness of the sorbent and, more importantly, the ability of the PAN to withstand aggressive temperature conditions. The consistent baseline condition capacity measurements obtained throughout the course of the evaluation gave strong indication the HZ-PAN composite was unaffected by thermal cycling. SEM micrographs showing the porosity of the exterior and interior of the HZ-PAN composites are shown in Figure 5.

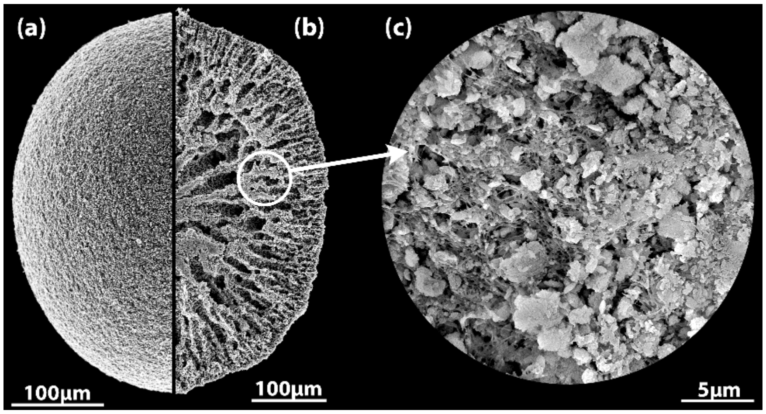

Figure 5. SEM micrographs HZ-PAN granules depicting (a) an exterior view of a whole granule, (b) a cross-sectional view of a granule, and (c) a higher-magnification view of the cross section.

6.2 AgZ-PAN for Xenon Capture

Research findings for silver-exchanged zeolite materials suggest a strong adsorptive property, presumably due to a strong interaction between silver and Xe [63], which is possible because the large Xe atoms are polarizable. The Xe polarization, along with highly porous structures found within zeolites, can improve Xe capture, reducing the need for wide-range thermal-swing operations. The AgZ-PAN composite sorbent provides the highly porous structure, allowing for strong Ag-Xe interactions, even at temperatures approaching ambient.

The AgZ-PAN sorbents were made following procedures similar to those described previously for the HZ-PAN. For the AgZ-PAN sorbent, some synthesis parameters were varied in an attempt to produce a composite sorbent with high *SSA*; these included converting the sodium mordenite (NaZ) to AgZ before making the PAN composite with (a) DMSO, (b) dimethylacetamide, and (c) 1-methyl-2-pyrrolidinone as the solvents; and (d) making the composite with NaZ followed by exchanging the Na for Ag within the composite by soaking the NaZ-PAN composite in 0.1 M silver nitrate ($AgNO_3$) solution for 24 h at 90°C under mild agitation to obtain AgZ-PAN. The final synthesis method resulted in an acceptable high-*SSA* material with a ~10 mass% Ag loading.

The AgZ-PAN demonstrated a selectivity for Xe > Kr over a temperature range of ambient to 240°C. Selectivities (S) were calculated using Equation (6), where X_{Xe} and X_{Kr} are molar fractions of Xe and Kr in the adsorbed phase (capacities), and Y_{Xe} and Y_{Kr} are molar fractions of Xe and Kr in the bulk phase (feed gas concentrations 1020 ppm Xe and 150 ppm Kr, by volume; ppm = parts per million), respectively. Using the capacity values from Table 3, the selectivities at ambient conditions for Xe over Kr were 7.8 in the He balance gas and 6.9 in the air balance test gas using the minimum determinable krypton capacities.

$$S_{\mathrm{Xe,Kr}} = \frac{X_{\mathrm{Xe}}/Y_{\mathrm{Xe}}}{X_{\mathrm{Kr}}/Y_{\mathrm{Kr}}} \tag{6}$$

Table 3. Experimental results from AgZ-PAN sorption in different Xe-Kr feed gas mixtures under a 50 sccm flow rate. "*" denotes minimum determinable capacity; "N/A" denotes not applicable.

Feed gas composition	T (±1 K)	Xe capacity (mmol kg^{-1})	Kr capacity (mmol kg^{-1})
Xe-Kr-Air	296	27.8	0.6*
Xe-Kr-He	295	31.6	0.6*
Xe-He	296	31.5	N/A

Thermal cycling effects were also evaluated for the AgZ-PAN composite similar to those for HZ-PAN. After numerous thermal cycles with intermittent baseline testing, the composites experienced no decline in *SSA* or capacities throughout the testing. The results from the HZ-PAN and AgZ-PAN testing indicates that the PAN-composite structures experience no deleterious effects from extensive thermal cycle capacity tests.

7 REMOVAL OF CONTAMINANTS FROM WATER

The purification of water supplies (i.e., drinking water or industrial streams) from toxins generated from industrial activities including agriculture, mining, semiconductors, batteries, and petroleum production is a major concern throughout the world. The following sections discuss heavy metal removal (e.g., As, Se, Sb) and radionuclide removal (i.e., cesium-137) from aqueous streams using PAN-based composites.

7.1 Arsenic Removal from Aqueous Streams

Removing heavy metals from aqueous streams will be increasingly important as populations across the world continue to grow. This topic has been a focus in the scientific community for decades. Sorbents for heavy metal capture from aqueous streams include iron compounds [64-66], manganese oxides [67], and chelating polymers [68]. The Nano-Composite Arsenic Sorbent, or N-CAS, is a composite that uses metal oxides (e.g., Fe_2O_3, Fe_3O_4), metal oxyhydroxides [e.g., FeO(OH)], hydrated metal oxides or hydroxides (e.g., $5Fe_2O_3 \bullet 9H_2O$, $Fe_5HO_8 \bullet 4H_2O$), or metal salts (e.g., chlorides, oxychlorides, sulfates, nitrates, acetates) embedded in a PAN polymer matrix for removing toxins such as As, Se, and Sb from aqueous streams [11, 3, 12-14]. This product is also referred to as a PAN-HIO composite (HIO = hydrated iron oxide) [3]. The primary sorbent is 10–85 mass% of ferrihydrite (i.e., $\mathrm{Fe_2^{3+}O_2 \bullet 0.5H_2O}$ or Fe(III) hydrous oxide), the active binding material, with the balance being PAN; this can be adjusted based on the application.

This material is produced as follows: (1) a metal compound is dissolved in a solvent to create a metal solution, (2) PAN is then dissolved into the metal solution, and (3) the mixture is placed into a quenching bath. Depending on the type of metal being used, the quenching bath in Step 3 contains an alkaline pH achieved with 0.1–8 M NaOH (the optimal conditions for ferrihydrite are in the range of 0.5–6 M NaOH, with 1 M being a good starting concentration). During quenching, depending on how the process is conducted, the morphology produced can be a granule-type (i.e., bead-type) shape or a filter can be impregnated with the mixture, where the active sorbent is homogeneously distributed throughout the composite. For reference, the *SSA* of the 85 mass% ferrihydrite composite is 275–350 m^2 g^{-1}.

The lifetime estimate for this material is that 1 L of the composite sorbent could likely be used to purify 350,000–400,000 L of contaminated water. When this composite was patented, it was also estimated that, at the cost of $1.00 US, over 37,000 L of water could be treated, demonstrating the cost effectiveness of this sorbent. A demonstration of the arsenic loadings as a function of active sorbent concentration in the composite sorbents is summarized in Figure 6. The sorbent can be regenerated multiple times by soaking it in dilute caustic solution, without significant reduction in the arsenic loading capacities [3].

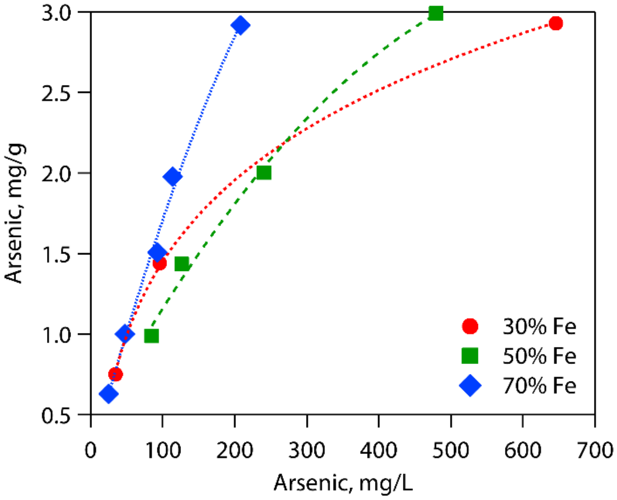

Figure 6. Equilibrium arsenic-loading isotherms for N-CAS sorbent at different ferrihydrite concentrations in the composite sorbent [11].

7.2 Phosphate Removal for Remediating Toxic Algae Blooms

If not controlled, an increase in nitrogen and phosphate levels in waterways can accelerate algae growth. Significant algae increases will reduce oxygen levels, which can kill fish and other aquatic marine life. If these algae growths become very large, they can be referred to as algae blooms. These blooms are harmful to humans due to the increased toxins and bacterial growth present in polluted waters. Contact of these blooms with humans, including activities such as swimming, drinking contaminated water, or consuming tainted fish, result in sickness. A Kansas State University research effort in November 2008 came to the conclusion that pollution caused by the overabundance of nitrogen and phosphate in water costs the US $4.3B annually [69]. Toxic algae blooms are problematic throughout the world. From large population fish mortality in Chile and Texas to the large blooms found in Lake Erie and Lake Okeechobee, these environmental challenges post direct threats to human health and high cost restoration to government agencies.

Global Phosphate Solutions is a company formed to combat the algae problem [15]. They have developed a composite sorbent that has been shown to remove inorganic/ortho-phosphates from water. The composite known as TPS consists of a proprietary adsorbent material, which is bound in a PAN matrix. The PAN provides a stable engineering form that prevents the loss of the active adsorbent. This material has been installed in water treatment facilities and has demonstrated effluent water phosphate levels below 10 ppb.

The captured phosphate can be eluted from the sorbent and resold to commercial markets such as the fertilizer industry. After elution, the material can be reused with no reduced capacity.

7.3 Cesium and Strontium Removal from Aqueous Nuclear Waste Streams

Cesium-137 is one of the high-activity radionuclides that is released from fission of isotopes found in both nuclear reactors and weapons. It is of high concern for several reasons, the most prevalent being that it has a very high activity due to its $t_{½}$ of 30.2 yr, primarily by ß decay, and the high mobility of Cs^+ throughout the environment. Different technologies have been evaluated for removing Cs from aqueous solutions, including ion-exchange resins (e.g., resorcinol-formaldehyde or $C_7H_8O_3$, SuperLig® 644) [70, 71] and metal-based sorbents (e.g., Fe-, Ni-, and/or Cu-based materials) [72-74].

An alternative sorbent option is a PAN-based composite that uses an active sorbent of ammonium molybdophosphate [i.e., $(NH_4)_3P(Mo_3O_{10})_4•3H_2O$, or AMP] [17, 75, 76, 16]; this composite sorbent is referred to as AMP-PAN and was developed at the Czech Technical University in Prague (Czech Republic) [16]. The application discussed here is the use of AMP-PAN for removing $^{137}Cs^+$ from acidic nuclear waste streams. The AMP-PAN sorbent is ideal for acidic nuclear waste streams because it meets the following criteria:

1) The sorbent should be stable in acidic conditions.
2) The sorbent should be stable in oxidizing conditions.
3) The sorbent should have a high capacity for Cs^+ in the presence of other waste constituents (e.g., Na^+, K^+, Al^{3+}, Fe^{3+}) and in acidic conditions, because the concentration of Cs is low in the waste streams.

4) The sorbent should be radiation tolerant (i.e., resistant to radiolytic damage).
5) The sorbent should be temperature tolerant (i.e., heat from radionuclide decay).

The AMP-PAN composite uses an ion-exchange mechanism to remove Cs^+ from aqueous solutions: Cs^+ ions are exchanged for NH_4^+ and H^+ ions from within the hollow sphere formed by $(PMo_{12}O_{40})^{3-}$ in the AMP crystal structure [77, 78] (see Figure 7), resulting in the release of NH_4^+ and H^+ into the solution [79]. In acidic solutions, AMP can also be used to ion exchange other species including K^+, Rb^+, and Tl^+, where some NH_4^+ ions always remain no matter what type of exchange is conducted [79, 78].

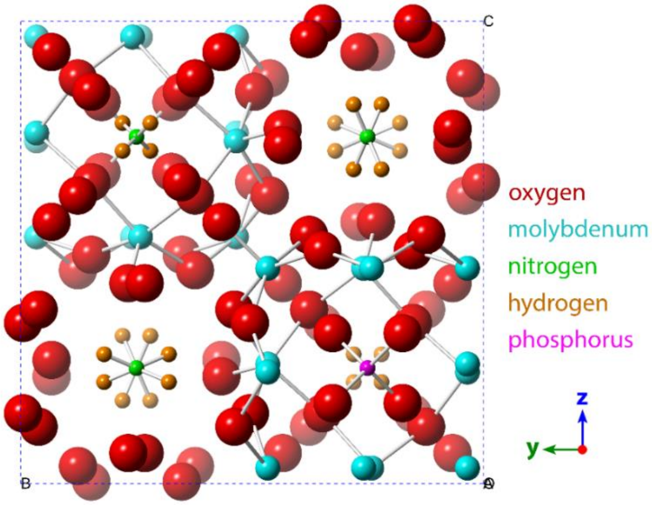

Figure 7. Crystal structure of AMP according to Boeyens et al. [78] shown on N(100) so that the cages can be seen. This is Inorganic Crystal Structure Database entry number 212 with the chemical formula of $(NH_4)_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$ of cubic space group $Pn\bar{3}mz$ (224).

Additional work through a collaboration with US-based Department of Energy national laboratories demonstrated that the AMP-PAN sorbent worked well at removing Cs from acidic solutions as well as basic solution, but Cs was co-adsorbed with lanthanides and/or actinides [19].

8 CONCLUSION

A wide variety of polyacrylonitrile-based composite sorbents have been produced (or envisioned) over the past few decades and are reported throughout the literature. The compositions described here are only a small reflection of the wide variety of sorbent types that can be produced using this basic process, which can support a diverse range of applications for purification of gaseous and/or liquid-based process streams. Polyacrylonitrile is a highly resilient material that is porous, stable in a wide range of pH values, and radiolytically stable, making it a great scaffold material for an assortment of composite sorbents for use in numerous process applications.

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