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Article

Capturing harmful air pollutants using an electrospun mesh embedded with zinc-based nanocrystals

Hansa Doppalapudi, Saunak Badam, Michael Tomlinson
Academy of Science, Academies of Loudoun, Leesburg, Virgina

SUMMARY

Metal-organic frameworks (MOFs) are compounds consisting of metal ions supported by organic ligands and may have the potential to combat the growing issue of air pollution. Zeolithic imidazolate framework-8 (ZIF-8) is a specific MOF that has favorable qualities for use in an air filter including high porosity, high surface area, and a high positive surface charge. ZIF-8 is known to be capable of adsorbing particulate matter. Therefore, the objective of this experiment was to determine the effectiveness of ZIF-8 in adsorbing polar, gaseous air pollutants, specifically nitrogen dioxide and hydrogen sulfide. In order to determine effectiveness, the percent change in concentration for each gas after the application of ZIF-8 crystals was measured via Fourier-transform infrared spectroscopy (FTIR). This is a technique used to obtain high resolution infrared absorption or emission spectra of solids, liquids or gases over a wide spectral range. Both experimental gases, nitrogen dioxide and hydrogen sulfide, were adsorbed by an average of ~32% over just 5 minutes, and the leakage within the capsule was an average of ~3.5%. These results were confirmed with the Kruskal-Wallis tests (*p*-value = 0.05). In the future, ZIF-8 could be embedded into existing air filters or electrospun on its own and tested for its effectiveness in adsorbing other polar pollutants such as carbon monoxide and ammonia. Our work highlights crystals as a potentially promising alternative or addition to current filter materials to reduce atmospheric pollution.

INTRODUCTION

Rapid industrialization and economic growth have caused a massive increase in the amount of harmful air pollution. Polluted air alone causes 3.3 million premature deaths every year worldwide (1). The concentration of photochemical and industrial pollution is visible in the brown and gray curtain looming over city buildings, termed "smog." Smog consists of particulate matter and other harmful gases. Particulate matter (PM) is a form of industrial pollution, composed mostly of organic matter, nitrates, sulfates, ammonium, chloride, and elemental carbon (1). The emissions of millions of cars and factories concentrated in a tiny area contribute to this toxic smog. Smog is not effectively removed by current filters installed in buildings or cars creating a dangerously toxic environment in densely populated areas (1). Activated carbon filters are the most modern forms of filters, but are not effective in these high-smog areas, where the immense amounts of smog render filters unusable after a certain point (2). While efforts are being made to decrease pollution all over the world, a cheap, effective, and reusable way to reduce the toxic chemicals in the air has yet to be found.

Currently, most households and buildings implement activated carbon filters, which are proficient in removing certain toxins from the air (3). However, they cannot remove carbon monoxide, hydrogen sulfides, or certain nitric oxides, among others (3). These filters are also not reusable, as they must be replaced every few months. Although they can form strong chemical bonds with certain chemicals such as odors, noxious fumes, particulate matter, and organic compounds, they function ineffectively in areas where the air pollution contains too many contaminants (2). When pollution is very concentrated, filters that typically last for a long period of time will instead stop functioning in less than half of its lifetime, which is generally about one month (2). An ideal replacement for activated carbon filters should be reusable and adsorb a wide range of pollutants at concentrations at least as high as those commonly found in heavily polluted areas (3).

Metal-organic frameworks (MOFs) may potentially combat issues faced by activated carbon filters. MOFs are compounds consisting of metal ions or clusters of metal ions coordinated by organic linkers. The bond between organic and inorganic molecules yields a crystalline structure with strong bonds. The metal ions and organic linkers constitute the two components that dictate the structure and properties of the compound. MOFs have a much higher surface area and porosity than previously known porous materials, and also possess a generally high chemical and thermal stability. Their surface area ranges from 1,000 to 10,000 m^2/g, and generally, open space accounts for over 50% of the volume. There are over 20,000 types of MOFs to date, each with different properties and uses. The specific metal organic framework that has qualities that would be useful for a filter is a zeolitic imidazolate framework (ZIF-8), a zinc based metal organic framework with high porosity, high surface area, and high surface charge, which has a potential to adsorb certain air pollutants effectively (**Figure 1**). ZIF-8 is also known to be chemically and thermally stable and has been applied

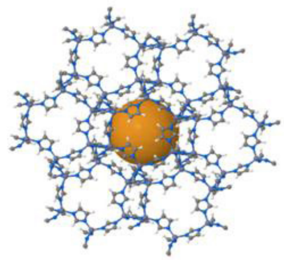

Figure 1. ZIF-8. A zinc-based metal organic framework with high porosity, high surface area, and high surface charge, which has a potential to adsorb certain air pollutants effectively.

in gas separation, catalysis, electronic devices, and drug delivery. Its use in gas separation with its high surface charge shows a high potential of bonding to harmful air pollutants (4). Furukawa et al examined the potential applications of MOFs and showed that MOFs also have a unique capability to selectively adsorb and store certain gases, which makes them useful for decreasing environmental pollution (5).

Previous research by Zhang et al, tested the effects of different MOFs electrospun into a filter on PM in the air (6). In this study, four different MOFs were spun via an electrospinner with one of two different polymers: polyacrylonitrile (PAN) and polystyrene (PS), creating a total of eight different filters. The different MOFs were: ZIF-8 (**Figure 1**), UIO-66-NH2, MOF-199, and Mg-MOF-74. Each metal organic framework was chosen for a different specific quality that would theoretically enable it to adsorb toxins from the air. The pollutants can be adsorbed by the MOF through chemisorption, a chemical reaction in which two substances react together, and the resultant chemical is trapped on the filter material (3). The researchers highlighted ZIF-8 as the most efficient MOF because of its large surface area, which enables it to be exposed to more air pollutants and its high surface charge, which is the primary reason it was the most efficient MOF. The ZIF-8 filter spun with a PAN polymer exhibited the highest removal efficiency for PM of various sizes. The polarity of the PM enhanced the adhesion with the unbalanced metal ions on the surface of the MOF, whereas the net positive charge of the filter attracted the partial negative charges of the polar molecules. After the test, the structure of the MOF remained intact, suggesting some degree of reusability, but the extent of this reusability remains unknown (6). These results could be explored in a different experiment, by testing a similar MOF for different pollutants. Nonpolar gases in the future have also been found to be able to be adsorbed with the use of various types of ZIF crystals such as ZIF-95 and ZIF-100. (7)

Other studies have also shown promise for the reusability of ZIF-8 filters, such as a study done by Chen et al in Beijing, where the ZIF-8 filter showed > 90% particulate matter capture even after 30 days of continual use and exposure to pollutants (8). It can also be reused after washing with water and ethanol. The ZIF-8 is able to adsorb molecules due to the structural deformation of “gate-like” openings which is induced by characteristics of the gas, such as polarity and molecular shape (9).

ZIF-8 can be nanospun as a filter on its own or eventually fabricated onto a variety of substances. As shown in this study, spinning onto plastic meshes yielded the best results in terms of the performance of the filter, rather than metal filters (8). The electrospinning process with metal organic frameworks allows the dispersion of the structures onto a surface. When a high enough voltage is applied to the solvent solution with the ZIF-8, the body of the liquid becomes charged, and electrostatic repulsion between the surface charges counteracts the surface tension, creating a cone. This forces the ejection of a liquid jet from the nozzle, which undergoes a stretching and whipping process, causing the creation of a long, thin thread. Once the electrospinning process is complete, the substrate should only have the polymer and the additive (ZIF-8) on it, as the solvent does not get electrospun (10).

Over the past year, research has shown that ZIF-8 crystals in pure powder form are able to selectively adsorb polar air molecules; the strong positive charge of the zinc ions in ZIF-8 created strong electrostatic interactions with the partial negative side of polar air molecules. Previous research has indicated that these polar molecules will be further attracted to the active sites of the ZIF-8 crystals, when electrospun, because these active sites will be further exposed through the fiber creation process (11). This research showed that nitrogen dioxide and hydrogen sulfide were significantly adsorbed by the crystals. In this study we were electrospinning these ZIF-8 crystals into a filter to test if the properties of binding air pollutant crystals still remain after electrospinning. Building on this knowledge, in this study we tested whether the properties of ZIF-8 remained after electrospinning into an air filter. The filter was made with polyethylene oxide (PEO) as the polymer and ethanol as the solvent. Previous research has shown that PEO is a polymer which works well with electrospinning ZIF-8, but this combination has yet to be tested in the context of gases (12).

RESULTS

We hypothesized that zeolitic imidazolate framework-8 (ZIF-8) will adsorb polar air pollutants, more efficiently than current heating, ventilation, and air conditioning (HVAC) filters. Current HVAC filters are presently the best suited for preventing particulate matter from entering the human airway. Some of these current filters even have activated carbon, known as a universal adsorbent and have been proven to be effective in eliminating the chemical pollution found in HVAC systems. However, these carbon-activated filters still lack in required characteristics for an ideal filter (7).

To test whether ZIF-8 filters could adsorb polar gases, we electrospun ZIF-8 crystals into a filter and then measured the absorbance efficiency of two gases : nitrogen dioxide and hydrogen sulfide. ZIF-8 loading was done for the experimental group, and its gas adsorption of nitrogen dioxide and hydrogen sulfide was measured against the control group, which would

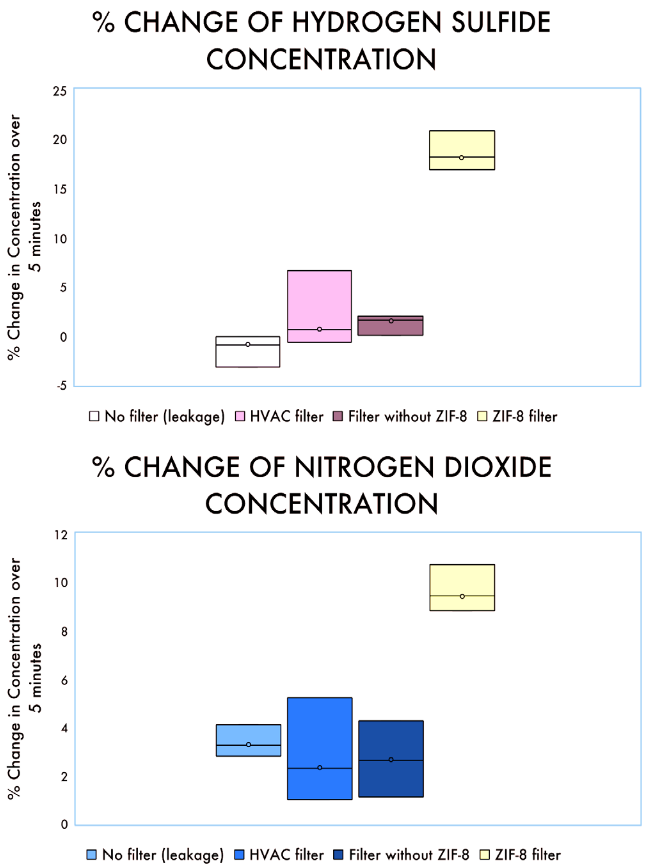

Figure 2. Percentage change in concentration of Hydrogen Sulfide during ZIF-8 filter usage. The change from the ZIF-8 filter was more than any other experimental filter tested. (Non ZIF-8 filter : 5.33% change; ZIF-8 filter : 22.58% change). $p = 0.05$. Similarly the percentage change in concentration of Nitrogen dioxide was greater when ZIF-8 filter was used, more than any other experimental filter tested. (Non ZIF-8 filter : 1.73% change; ZIF-8 filter : 33.20% change). $p = 0.05$. Each filter was tested three times.

be just the electrospun filter without ZIF-8 loading. All of the data were compiled into two tables and tested for significant differences using a Kruskal Wallis test. The percentage change in concentration of Nitrogen dioxide was greater when ZIF-8 filter was used, more than any other experimental filter tested. (Non ZIF-8 filter : 1.73% change; ZIF-8 filter 33.20% change). $p = 0.05$. Similarly, the percentage change in concentration of Hydrogen Sulfide was greater when ZIF-8 filter was used, more than any other experimental filter tested. (Non ZIF-8 filter : 5.33% change; ZIF-8 filter 32.58% change). $p = 0.05$ (**Figure 2**). That could be believed to be one of the lowest possible p-values for that size data set because both had the same values indicating that the change caused by ZIF-8 could be significant. By testing the efficiency of ZIF-8, a reusable filter was devised that can adsorb harmful air pollutants, which cannot be effectively adsorbed by current filters such as toxic carbon monoxide and volatile organic compounds. Removing harmful pollutants from the air is crucial, especially as this becomes an increasingly larger problem as the state of air quality around the world worsens.

DISCUSSION

We originally hypothesized that the zeolitic imidazolate framework-8 (ZIF-8) crystals would adsorb polar pollutants better than current filters. We used FTIR (Fourier-transform infrared spectroscopy), a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. The hypothesis was tested by comparing absorption of nitrogen dioxide and hydrogen sulfide between electrospun filters embedded with ZIF-8 crystals, electrospun filters without ZIF-8 crystals and store-bought grade 2 HVAC filters. The data gathered in this investigation supports the claim that ZIF-8 crystals are able to effectively and selectively remove polar air pollutants from the air. The filter with ZIF-8 crystals in it decreased the concentration of the pollutant in the capsule, and much more so than any of the control groups (**Figure 2**). The tests themselves were also done over only five minutes, so it is possible that over a longer period of time, even more gas would be adsorbed. Additionally, the way the experiment was designed, the air had no way of actually flowing through the filter, it was only on top of it. This suggests that electrospun meshes embedded with ZIF-8 crystals not only can adsorb these harmful air molecules, but selectively attract them down to its surface and trap them. This increases the likelihood of ZIF-8 preventing air pollution, because the air only has to be in contact with, not flowing through it.

This experiment also paves the way for the possibility of ZIF-8 being able to adsorb many other polar gases. For example, carbon monoxide is a polar gas, that is very dangerous causing thousands of deaths each year. Due to carbon monoxide's strong polar bonds and partial charges, ZIF-8 has the potential to adsorb carbon monoxide, in addition to certain volatile organic compounds (VOCs). Both of these gases currently have no viable filtration method and are very to the environment and public health. In the future, its thermal stability could be tested to determine the level of its reusability. Due to ZIF-8's propensity to adsorb polar molecules, there are numerous possible applications. ZIF-8 can be used as its own filter and used as a substitute for traditional filters currently used in air vents as it will be able to prevent a greater number of dangerous gases to go through. It can also be used in conjunction with catalytic converters in automobiles to adsorb dangerous pollutants that are not able to be catalyzed. Metal-organic frameworks could be the future of gas absorption, as ZIF-8 shows the possibility of a working, cost-effective method of adsorption that may be reusable.

MATERIALS AND METHODS

We originally hypothesized that the ZIF-8 crystals would adsorb polar pollutants better than current filters. The hypothesis was tested by comparing absorption of nitrogen dioxide and hydrogen sulfide between electrospun filters embedded with ZIF-8 crystals, electrospun filters without ZIF-

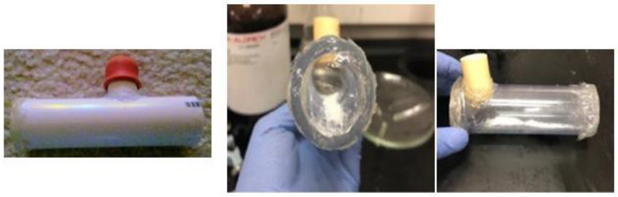

Figure 3. Fabrication of a gas capsule using a PVC pipe. A PVC pipe of 18 cm length and 2.5 cm bore was acquired by cutting from a longer PVC pipe. A smaller PVC pipe of 2 cm length and 1 cm bore was also acquired. A hole of about 1.3 cm diameter was cut into the side of the former PVC pipe using a drill press. The latter PVC pipe was glued into the hole using hot glue. Then saran wrap was hot glued onto the ends of the larger PVC pipe to ensure gas could not escape through the sides. Finally, a septum stopper was placed on the open end of the smaller PVC pipe to create an airtight seal. Gases would be injected via hypodermic needle through the septum stopper.

8 crystals and store-bought grade 2 HVAC filters.

To complete this research, nitrogen dioxide and hydrogen sulfide had to be synthesized. Fourier-transform infrared spectroscopy (FTIR) was used to determine concentration changes, and a gas capsule was made to put into the FTIR. The percent change in concentration of each gas was then recorded on the FTIR machine, calculated as the area under the IR spectra curve at five minutes as a percentage of the area under the IR spectra at zero minutes.

Gas capsule creation

A set up consisting of PVC, saran wrap and a septum stopper was used (**Figure 3**). Gases were injected via hypodermic needle through the septum stopper.

Synthesis of gases

Nitrogen dioxide

Nitrogen dioxide was synthesized using the reaction that occurs between tin and nitric oxide. 0.2 g of tin was placed in a small Erlenmeyer flask and a septum stopper was placed on top of it (**Figure 4**). Then, with a syringe and a hypodermic needle, 5 mL of nitric acid was inserted into the flask. Nitric acid was used in excess. An open needle was placed into the septum stopper to prevent extreme pressure buildup. The reaction was allowed to occur until the expulsion of heat was easily detected. Then, a second hypodermic needle was used to intake the desired volume of gas and then place into the gas capsule. The concentration of the gas in the capsule was determined through stoichiometric calculations, with an assumption of 100% yield.

Figure 4. N**itrogen dioxide synthesis by reacting tin and nitric oxide.** 0.2 g of tin was obtained, placed in a small Erlenmeyer flask and a septum stopper was placed on top of it.

Hydrogen sulfide

Hydrogen sulfide was synthesized with the reaction that occurs between sodium sulfide and hydrochloric acid. 3.0 mL of 2.0 M sodium sulfide was placed in a small Erlenmeyer flask, and a septum stopper was placed on top of it. With a syringe and a hypodermic needle, 6.0 mL of 3.0 M hydrochloric acid was inserted into the flask. An open needle was placed into the septum stopper to prevent extreme pressure buildup. The reaction was allowed to complete, and transferred to the gas capsule in a manner similar to previously described for nitrogen dioxide.

Electrospinning

The electrospinning parameters remained constant for all of the filters. The voltage was 15 kV, the flow rate was 1.2 mL/hr, the spinneret diameter was 21 gauge, and the distance of the needle to the plate was 15 cm. Two types of filters were made: -ZIF-8 and +ZIF-8. For both types of filters, polyethylene oxide (PEO) was used as the polymer and ethanol as the solvent. 0.200 g of PEO and 10 mL ethanol were used in both filter types.

The +ZIF-8 filter also had 0.1 g of ZIF-8 crystal dissolved in the ethanol via sonication. Polymer solutions were made by mixing PEO and ethanol solutions for three hours. The solutions were spun with the electrospinning parameters aforementioned onto an aluminum foil substrate about 3 cm by 3 cm.

Testing ZIF-8

For the no filter control trials, 6.0 mL of the gas was inserted into the gas capsule, and the initial area under the IR spectra was recorded. For the ZIF-8 control trials, a 1.5 cm by 7 cm strip of ZIF-8 filter was placed in the capsule. 6.0 mL of the gas was inserted into the gas capsule, and the initial area under the IR spectra was recorded. Finally, for the HVAC control trials, a MERV level 2 HVAC filter was bought for this experiment. A 1.5 cm by 7 cm strip of HVAC filter was placed in the capsule. 6.0 mL of the gas was inserted into the gas capsule, and the initial area under the IR spectra was recorded. For each of these experiments, the area was recorded again after five minutes, and the change in area was used to determine the percentage change in concentration of the gas due to leakage. This was done three times for both gases, for a total of six HVAC control trials.

Experimental trials

A 1.5 cm by 7 cm strip of +ZIF-8 filter was placed in the capsule. 6.0 mL of the gas was inserted into the gas capsule, and the initial area under the IR spectra was recorded. After five minutes, the area was recorded again, and the change in area was used to determine the percentage change in concentration of the gas due to leakage. This was done three times for both gases, for a total of six experimental trials. A 100% yield could be assumed because there is a density difference between nitrogen dioxide, hydrogen sulfide and normal air; nitrogen dioxide and hydrogen sulfide are both denser than air, and thus are at the bottom of the flask. When the syringe was used to pull out the gas, the syringe was put at the bottom, to make sure that it was only picking up the synthesized gas.

The expulsion of heat was measured relatively compared to the original temperature of the glassware. Because it was done by the same person every time, the expulsion of heat was mostly a way to make sure the gas itself was created and that the reaction was complete.

Statistical Analysis

To test the significance of ZIF-8 on absorbance of just polar molecules, nonparametric Kruskal-Wallis tests were performed on control trials without ZIF-8 and experimental trials with ZIF-8. Gas absorption between without ZIF-8 and with ZIF-8 filters was tested.

A nonparametric, Kruskal-Wallis test was run to determine the effect of the filter on each of the gases. This was done to see if a significant amount of gas was removed by the filter with ZIF-8, by comparing it to one without ZIF-8. The Kruskal-Wallis test was used as the primary test rather than its corresponding parametric test, an ANOVA test, due to the limited sample size. The Kruskal-Wallis compared the data without a comparison to a normal curve, and with the use of medians and ranks rather than with the use of means. Nonparametric tests are less affected by any outliers or skewed data, and work best for data with small sample sizes which may not necessarily fall under a normal curve. For these reasons, a Kruskal-Wallis was the primary statistical test for this experiment.

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