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Evaluation of a robust, diimide-based, porous organic polymer (POP) as a high-capacity sorbent for representative chemical threats

Gregory W. Peterson · Omar K. Farha · Bryan Schindler · Paulette Jones · John Mahle · Joseph T. Hupp

Abstract A previously described porous organic polymer (NU-POP-1) was evaluated against four representative chemical threats: ammonia, cyanogen chloride, sulfur dioxide, and octane. Ammonia, cyanogen chloride, and sulfur dioxide are examples of toxic industrial chemicals (TICs) spanning the range from highly basic to strong-acid forming substances, while octane is used to assess physical adsorption capacity. Experiments were carried out using a microbreakthrough test apparatus, which measures the adsorption capacity at saturation and gives an indication of the strength of adsorption. The NU-POP-1 material exhibited substantial removal capabilities against the majority of the toxic chemicals, with capacities as high as or better than an activated, impregnated carbon. The ability to remove the highly volatile toxic chemicals ammonia and cyanogen chloride was intriguing, as these chemicals typically require reactive moieities for removal. The present work presents a benchmark for toxic chemical removal, and future work will focus on incorporating functional groups targeting the toxic chemicals of interest.

Keywords Porous organic polymer · Adsorption · Toxic industrial chemical · TIC · Breakthrough studies

G. W. Peterson (✉) · J. Mahle
Edgewood Chemical Biological Center, 5183 Blackhawk Road, Aberdeen Proving Ground, MD 21010, USA
e-mail: gregory.w.peterson@us.army.mil

O. K. Farha (✉) · J. T. Hupp
Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA
e-mail: o-farha@northwestern.edu

B. Schindler · P. Jones
SAIC, PO Box 68, Gunpowder, MD 21010, USA

1 Introduction

Low-density microporous solids [1–7] have garnered considerable recent scientific and popular attention due to their potential for applications in catalysis [8], gas storage [9–11], and gas and chemical separations [12, 13], as well as chemical protection [14–17]. In addition to traditional materials such as zeolites and high-area carbons, a number of newer classes of microporous materials have been described, including metal–organic frameworks (MOFs) [18], covalent-organic frameworks (COFs) [1, 16], (micro)porous organic polymers (POPs) [12, 13, 19, 20], and others [21, 22]. MOFs have been the most widely studied of these newer materials due to their well-defined crystalline structure. However, many MOFs lack the chemical stability required for the removal of acidic or basic chemicals. Therefore, the synthesis of all-organic porous materials featuring exceptionally robust connectivity (e.g. covalent carbon–carbon and/or carbon–nitrogen bonds) is an attractive alternative strategy.

Here we report on the potential chemical protective behavior (sorption behavior) of a previously synthesized POP material (NU-POP-1 (NU = Northwestern University) [12], This material is characterized by pores ranging in width from 3.5 to 8 angstroms and a total surface area of ca. 950 m^2/g (i.e. comparable to most zeolites, but ca. four-fold lower than the very highest area carbon materials [23]). Scheme 1 illustrates its synthesis and the resulting connectivity. The scheme is idealized, in the sense that: (a) the material is clearly amorphous rather than crystalline when evaluated with X-ray diffraction, and (b) additional polymeric material likely is threaded through the pores, making the available pore widths smaller than suggested by the illustration.

We have examined the behavior of NU-POP-1 with respect to challenges by four representative chemical

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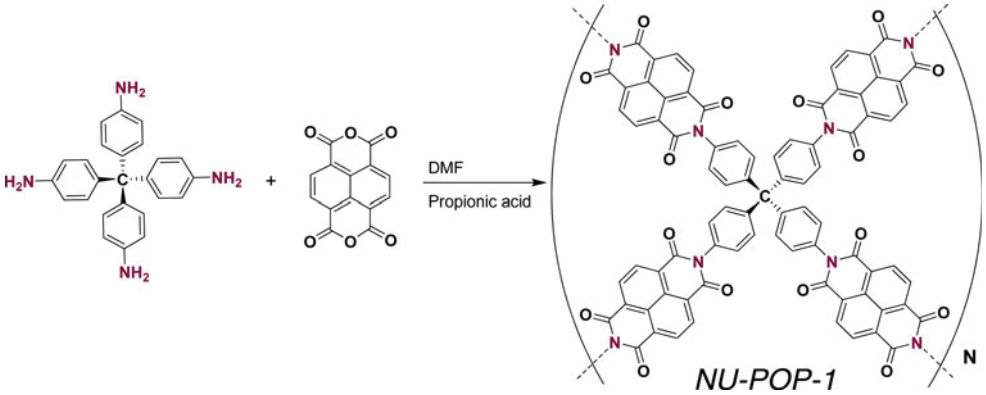

Scheme 1 Synthesis and connectivity of NU-POP-1

threats: ammonia, cyanogen chloride, sulfur dioxide, and octane. These four are examples of toxic industrial chemicals (TICs) spanning the range from highly basic (NH_3) to strong-acid forming substances (CNCl and SO_2). The challenges were carried out via micro-breakthrough measurements. Besides yielding relative retention times, the breakthrough measurements report on the maximum capacity (i.e. saturation loading) of the sorbent material for each of the chemicals of interest.

As adsorbed water can often alter the effectiveness of a sorbent, the performance of NU-POP-1 was evaluated under dry conditions and under conditions of 80% relative humidity, both using air as the carrier. For comparison, the behavior of a porous carbon material, BPL (Calgon Carbon Corporation), was examined. The carbon material was doped with both ZnO and triethylenediamine. These additives are known to facilitate (either catalytically or stoichiometrically) the hydrolytic decomposition of selected adsorbates—in particular, acid-forming gases such as CNCl and SO_2 [24, 25].

2 Experimental section

2.1 Materials preparation

NU-POP-1 was synthesized and activated as previously described [12]. BPL carbon, a bituminous coal-based activated carbon, impregnated with zinc oxide (Zn/BPL, approximately 5% zinc by weight) was acquired from Calgon Carbon Corporation. To a vial containing Zn/BPL, 3% triethylenediamine (TEDA, Aldrich Chemical Company) by weight was added. The vial was put on a rotating mixer and allowed to equilibrate for two days, impregnating the material with TEDA through sublimation. Previous efforts have shown this to be an efficient method for TEDA impregnation [25, 26]. The resulting material is denoted as Zn/BPL/TEDA.

2.2 Characterization methods

Water sorption data were collected as a function of relative humidity (RH) referenced to 25 °C. Water was delivered from a saturator cell to the sorbents on a temperature-controlled microbalance. The water vapor content was systematically increased by changing the temperature of the saturator cell, and the sorbent was weighed to calculate the moisture loading at each RH.

Materials were evaluated for toxic chemical and simulant performance in a microbreakthrough test apparatus, as described elsewhere [14, 25]. Briefly, materials were placed in a nominal 4-mm ID fritted-glass tube, which was then submerged into a temperature-controlled water bath. For ammonia, cyanogen chloride, and sulfur dioxide, a known amount of compound was injected into a stainless steel ballast, which was then charged with dry air to a predetermined pressure. The ballast contents were discharged through a mass-flow controller and mixed with a dilution stream to achieve the required concentration, as summarized in Table 1. In the case of octane, a saturator-cell containing octane was used for the challenge ballast. Air was flowed across the saturator cell and then mixed with a dilution stream to achieve the required concentration. Once the challenge was established, the stream was pushed through the packed sorbent bed under the conditions summarized in Table 2.

Table 1 Challenge concentrations

Chemical	Challenge concentration (mg/m^3)
Ammonia	1,000
Cyanogen chloride	4,000
Sulfur dioxide	1,000
Octane	4,000

Table 2 Microbreakthrough operating conditions

Operating parameter	Value
Sorbent mass	20–50 mg
Sorbent volume	55 mm^3
Flow rate	20 mL/min
Temperature	20 °C
Relative humidity	0% (−40 °C T_{dp}), 80% (pre-equilibrated)

Four chemicals were used to evaluate the performance of the two media. For octane and cyanogen chloride, a flame-ionization detector was used to monitor the effluent concentration. Ammonia elution was monitored with a photoionization detector equipped with a 10.6 eV lamp. Sulfur dioxide elution was measured using a flame photometric detector.

3 Results and discussion

As we were interested in understanding the behavior of NU-POP-1 as a chemical sorbent under both dry and humid conditions, we first examined the material's propensity for sorption of water by recording ambient-temperature isotherms (Fig. 1). Under conditions of low relative humidity, both Zn/BPL/TEDA and NU-POP-1 sorb relatively little water. In the mid-RH region, NU-POP-1 clearly has a higher affinity for water than does Zn/BPL/TEDA, likely due to the presence of both oxygen and nitrogen sites within the pores, as well as due to smaller pore sizes. In other words, the structure of NU-POP-1 is more hydrophilic than the hydrophobic carbon substrate. At an RH of just over 60%, the isotherms cross, and the carbon material achieves significantly higher water loading as saturation is approached. The higher overall loading of carbon is attributed to its greater pore volume, i.e. ~0.5 versus ~0.32 cc/g for NU-POP-1.

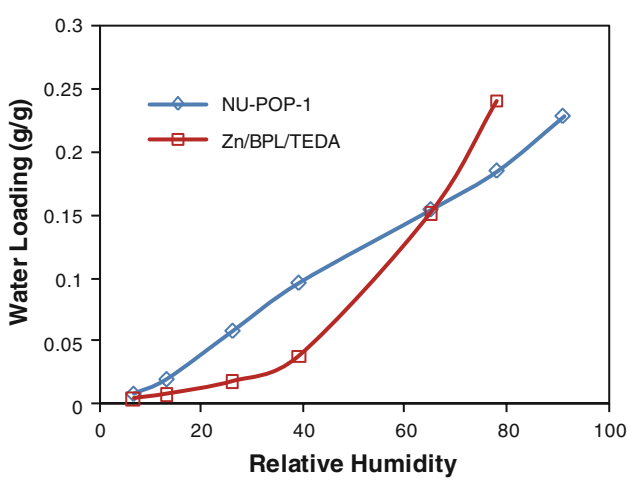

Fig. 1 Ambient-temperature water adsorption isotherms for NU-POP-1 and Zn/BPL/TEDA

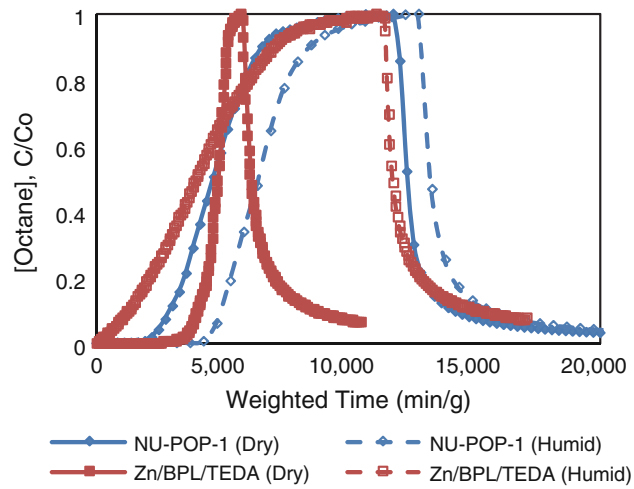

Fig. 2 Octane micro-breakthrough curves for NU-POP-1 and Zn/BPL/TEDA

Figure 2 illustrates the breakthrough behavior of octane with Zn/BPL/TEDA and NU-POP-1 as sorbents. Under dry conditions, both materials exhibit extensive uptake, indicating substantial capability for *physical* adsorption—behavior attributable to high microporosities in both materials. It is clear that Zn/BPL/TEDA exhibits better internal mass transport as evidenced by the steep slope of the breakthrough curve. This is not surprising as the sorbent is structurally heterogeneous, containing hierarchically interconnected macro-, meso-, and microporous domains known to facilitate rapid mass transfer. NU-POP-1 is characterized by less rapid transport kinetics, likely due to the absence of a meso/macro feeder pore structure. Indeed, we have found evidence previously only for microporosity [12]. For both sorbents, it is clear that while some octane continues to elute during purging, significant

Table 3 Saturation loadings of sorbents

Chemical	RH	Saturation loading (mol/kg)	
		NU-POP-1	Zn/BPL/TEDA
Octane	AR/0	3.19	3.30
	80/80	4.64	2.88
Ammonia	AR/0	5.56	0.69
	80/80	6.17	0.45
CNCl	AR/0	1.79	1.22
	80/80	2.20	2.14
SO2	AR/0	0.19	0.30
	80/80	0.05	0.82

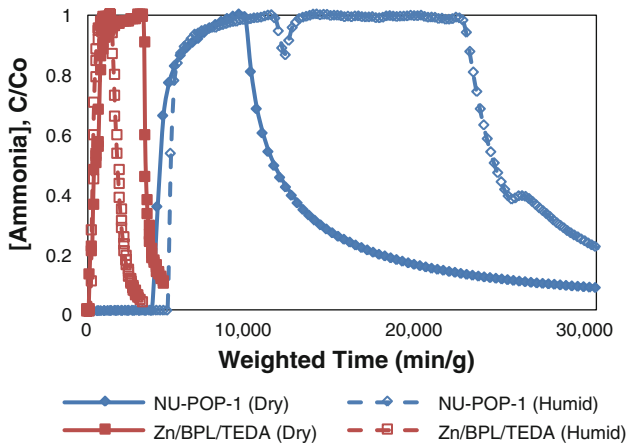

Fig. 3 Ammonia micro-breakthrough curves for NU-POP-1 and Zn/BPL/TEDA

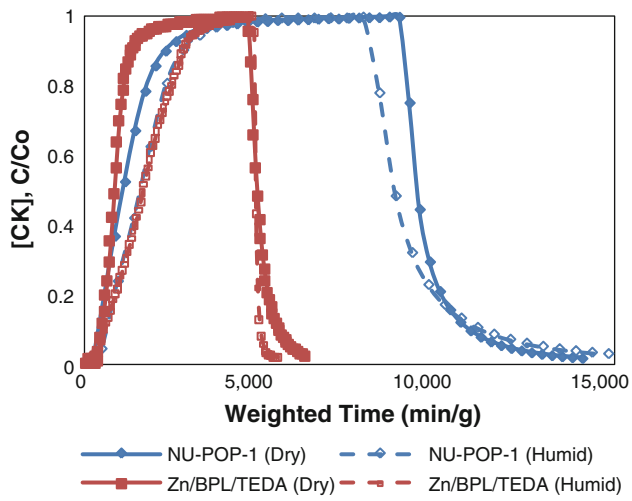

Fig. 4 CNCl micro-breakthrough curves for NU-POP-1 and Zn/BPL/TEDA

quantities of octane remain strongly adsorbed, eluting only after long purge times.

Under humid conditions, both materials yield elongated curves, likely due to competitive adsorption of octane and water. Curiously, however, NU-POP-1 actually provides better octane removal under humid versus dry conditions; see Table 3. This finding is counterintuitive and a plausible explanation is still lacking.

We next examined the breakthrough behavior of ammonia (Fig. 3). Under both dry and humid conditions, NU-POP-1 significantly outperforms Zn/BPL/TEDA. The high capacity of NU-POP-1 for ammonia, as summarized in Table 1, may be attributed to the available nitrogen and/or oxygen groups. Previous studies have indicated that oxygen groups can function well as sites for ammonia adsorption [27]. The highly microporous nature of the POP also likely plays an important role in ammonia adsorption. Whereas the heterogeneous activated carbon substrate provides some initial ammonia uptake, the tighter pore structure of NU-POP-1 provides preferential ammonia adsorption. Previous pore size analysis (N_2) yielded micropores of diameter 3.5, 5.2, and 8.2 Å.

The ammonia uptake by NU-POP-1 is similar under dry versus humid conditions, indicating that NH_3 is capable of penetrating the pore structure even in the presence of water, although it may be aided by solubility effects. In any event, the ammonia removal capabilities of both materials are purely through physical adsorption, as evidenced by the desorption curves. Almost all of the ammonia that is initially adsorbed elutes after the feed is terminated, as shown by the long tail after saturation.

Breakthrough curves for cyanogen chloride are shown in Fig. 4. The elongated curve shapes indicate that both materials provide substantial removal capabilities. In fact, the materials exhibit similar initial CNCl uptake to each other under both dry and humid conditions, respectively. In the case of Zn/BPL/TEDA, in addition to adsorption, under humid conditions the occurrence of reaction chemistry is well established. Wagner and co-workers [24] have shown CNCl is initially hydrolyzed through interaction with hydroxyl radicals facilitated by the TEDA impregnant, forming HCl and other byproducts. HCl then reacts with the zinc oxide, allowing the TEDA to continue to promote CNCl hydrolysis. Once the ZnO impregnant is used up, through the formation of zinc chloride, saturation occurs. That the hydrolysis chemistry is irreversible, is evidenced by the sharp decline in the micro-breakthrough curve after feed termination, and is enhanced under humid conditions due to faster hydrolysis rates. (To a limited extent, hydrolysis conceivably may also be occurring under nominally dry conditions if residual water is present.

In contrast, CNCl continues to elute from NU-POP-1 after feed termination. This is not surprising as there is no buffer for uptake of CNCl byproducts, if in fact hydrolysis occurs at all; CNCl is not easily hydrolyzed at neutral pH. That being said, the initial uptake is comparatively high, likely owing again to the high microporosity of the polymer. Although a mechanism for reactive cyanogen chloride removal is not postulated here, it is noteworthy that NU-POP-1 performs better under conditions of high relative humidity. CNCl is somewhat soluble in water (approximately 7% at 68°F, NIOSH Pocket Guide [28]); nevertheless, at 80% RH we expected that the polymer would competitively and preferentially adsorb water over CNCl. That competitive adsorption effects are not seen is evidence for specific chemical interactions between CNCl and NU-POP-1. Identification of the nature of these interactions, however, will have to await the results of computational modeling studies.

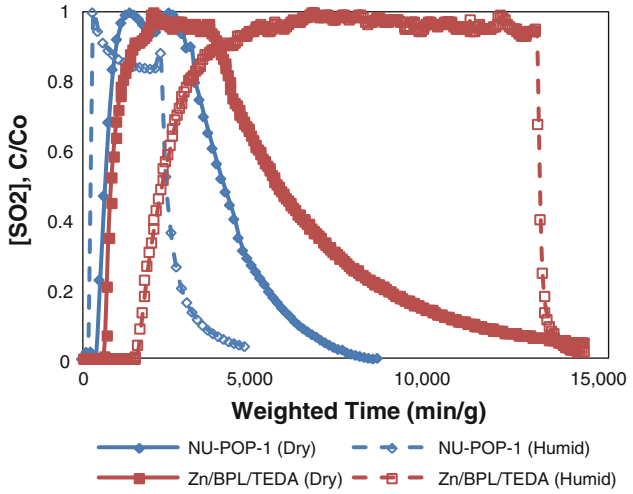

Fig. 5 SO_2 micro-breakthrough curves for NU-POP-1 and Zn/BPL/TEDA

Figure 5 shows breakthrough curves for sulfur dioxide. Under dry conditions, neither Zn/BPL/TEDA nor NU-POP-1 shows substantial SO_2 removal capability. This is unsurprising, since a typical removal mechanism of SO_2 on metal oxide-impregnated carbons is hydrolysis followed by air oxidation, the products of which react with metal oxide impregnants to form the corresponding sulfate [29]. Because of the lack of moisture, and perhaps the lack of oxidation mechanisms, SO_2 breakthrough occurs rapidly. Under humid conditions, the Zn/BPL/TEDA provides significant sulfur dioxide removal via the mechanism described above. In contrast, SO_2 breaks through NU-POP-1 almost immediately, indicating very little sorption capacity and no chemical reactivity.

4 Conclusions

In summary, we have investigated a microporous organic polymer, NU-POP-1, prepared from inexpensive precursors via amine/anhydride condensation reaction. This material is characterized by a reasonable capacity for purely physical sorption of octane under both dry and humid conditions, a surprisingly high capacity for ammonia under both dry and humid conditions, a fair capacity for cyanogen chloride (albeit, with no propensity for decomposition of the adsorbate), and a low capacity for the potentially acid-forming gas, sulfur dioxide. Octane and ammonia results indicate superior removal capabilities to the impregnated, activated carbon studied, while cyanogen chloride capacities were similar. Sulfur dioxide results indicate that functional groups must be incorporated to remove this chemical, as the NU-POP-1 material provides significantly less removal than the Zn/BPL/TEDA material.

Initial results show significant promise for POP materials in the areas of separations and sorption of toxic chemicals as possible alternatives for activated carbons. With these benchmark results in hand, our goals going forward are to design, synthesize, and functionally characterize new microporous organic polymers featuring: (a) higher surface areas, (b) greater micropore volumes, and c) sites capable of targeting the sorption (and perhaps destruction) of specific chemical threats or classes of chemical threats.

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