Journal of Water Process Engineering 35 (2020) 101194

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

3D printed solid-phase extraction sorbents for removal of volatile organic compounds from water

Luke A. Lagalante, Ayden J. Lagalante, Anthony F. Lagalante*

Villanova University, Department of Chemistry, 800 Lancaster Avenue, Villanova, PA 19085-1699, United States

ARTICLE INFO

Keywords:
Fused deposition modeling
3D printing
Activated carbon
Volatile organic compounds
Water purification

ABSTRACT

A carbon black modified polylactic acid (PLA) sorbent was 3D printed from a commercially available conductive PLA filament on a personal 3D printer. The internal porosity of the sorbent was controlled through software-controlled infill print densities from 15 to 50%. The 3D printed sorbent was evaluated for its ability to remove model VOC contaminants (benzene, toluene, and ethyl benzene) from water where the pseudo-second order rate constants for VOC sorption were found to increase with a decrease of internal pore size of the sorbent infill density. The ability to 3D print carbon-based sorbents for on-demand, point-of-use water purification presents a potentially useful mechanism for in-home or emergency purification situations where consumption of clean water is not possible.

1. Introduction

Fused deposition modeling (FDM) is type of additive manufacturing (AM) that has moved into the home consumer marketplace over the past 10 years with the advent of low-cost, desktop 3D printers. In FDM, a molten thermoplastic filament is passed through a heated, moveable extruder at a temperature slightly above the melting point of the thermoplastic to render a 3D object on a substrate through a layer-by-layer deposition process. Recently, commercial modifications of polylactic acid (PLA) filaments have been developed to include metals, wood fibers, magnetic particulates, and conductive carbon-based materials. Within the conductive carbon filaments, PLA-carbon black and PLA-graphene are commercially available filaments sold by Proto-pasta Inc. and Graphene 3D Labs Inc., respectively.

The use of 3D printed materials for the realization of porous filtration, sorbents, and chromatographic separation columns has also been the subject of several recent publications [1–3]. The ability to control the size, shape, position, and orientation of a sorbent in a porous bed is attractive because control of the design space is greatly enhanced in comparison to conventional packed bed sorbents using spherical particles to dictate mass transfer. Though a printed sorbent is similar to a porous monolith, an organized mesostructure for the printed bed can be engineered using CAD programs while the microstructures in a monolith are dictated by random polymerization processes. A CAD approach offers not only the ability to better understand and model porous flow, but also to potentially revolutionize chromatographic column production and enhance resolution [4].

The following communication details the 3D printing of a sorbent from an unmodified, commercially available carbon black conductive PLA filament on a personal 3D printer and its ability to remove VOC contaminants from water. Activated carbon (AC) is currently the most widely used sorbent for point-of-use (POU) water cleanup [5]. The ability to 3D print AC sorbents for on-demand, POU water purification presents a potentially useful mechanism for in-home or emergency purification situations where consumption of clean water is not possible.

2. Materials and methods

2.1. Chemicals and 3D printing filament

Benzene (> 99.0 %, Sigma-Aldrich), toluene (> 99.7 %, Pharmco), and ethyl benzene (> 99.0 %, Sigma-Aldrich) were used as received. All aqueous solutions were prepared using > 18 MΩ cm distilled-deionized water from a Millipore Direct-Q water purification system (Billerica, MA). 1.75 mm o.d. Proto-pasta CDP11705 Composite Conductive PLA (1.75 mm o.d., 500 g) and nonconductive 3D Hero PLA (1.75 mm o.d., 2 kg) were used as received.

2.2. Preparation of 3D printed sorbents

Cylindrical sorbents were designed with Autodesk 2019 to fit into 60 mL vials (Fig. 1) and printed on a Monoprice Mini Pro controlled by Ultimaker Cura version 15.04.6 at a layer resolution of 0.15 mm through a 0.4 mm nozzle heated to 215 °C. A grid pattern fill density

* Corresponding author.
E-mail address: anthony.lagalante@villanova.edu (A.F. Lagalante).

https://doi.org/10.1016/j.jwpe.2020.101194
Received 27 October 2019; Received in revised form 12 February 2020; Accepted 14 February 2020
Available online 26 February 2020

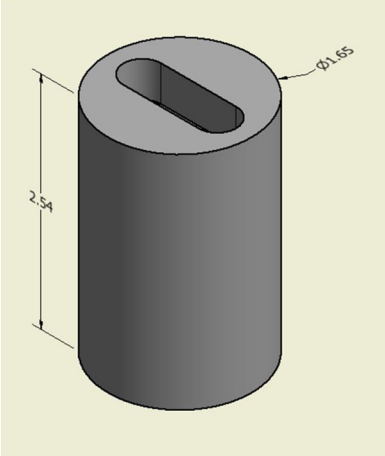

Fig. 1. Engineering drawing of cylindrical sorbent. All dimensions are in cm. The PTFE stir bar is placed into the cavity at the top. The cylindrical sorbent pictured is inverted in the 60 mL vial so that the stir bar rests on the bottom of the vial.

was used to print individual sorbents at 15, 20, 25, 30, 40, and 50 % infill densities that resulted in sorbents of masses 1.75, 1.90, 2.10, 2.25, 2.60, and 2.90 g, respectively. The top and bottom layer fill densities were set identical to the infill density when printing to ensure a uniform porosity throughout the sorbent. A PTFE-coated stirbar (12.5 × 4.5 mm) was press fit into the bottom cavity of the sorbent cylinder. Additionally, a cylindrical sorbent was printed at 30 % fill density using nonconductive PLA to serve as a control. A STL file of the cylindrical sorbent (Autodesk 2019) is included in the supplemental material.

2.3. Extraction of VOCs from water

An aqueous solution of model VOCs was prepared by pipetting 60 µL of benzene, toluene, and ethyl benzene into 500 mL of distilled, deionized water. The resulting aqueous solution of 105 ppm benzene, 104 ppm toluene, and 103 ppm ethyl benzene is below the aqueous solubility limit for each VOC. The 3D printed cylindrical sorbents were placed in individual 60 mL EPA PTFE/silicone-lined screwcap vials (Kimble Chase) and 50 mL aliquots of the aqueous VOC solution were added to each vial. All sorbent experiments were done at ambient temperatures between 19.0 ± 0.5 °C. For each vial, an initial 300 µL sample (time zero) was taken using a 1 mL Hamilton glass syringe through the PTFE/silicone-lined septum and magnetic stirring was initiated. Each sampled aliquot was dispensed into a glass autosampler vial insert contained within a 2 mL autosampler vial (Thermo Scientific) and capped with a PTFE/silicone-lined septum. Subsequent 300 µL samples were taken every 30 min through the PTFE/silicone-lined septum of each vial over the course of 5 h.

2.4. HPLC analysis of VOCs

Benzene, toluene, and ethyl benzene were analyzed on a HPLC system consisting of binary Varian Prostar 310 high-pressure pumps, a Varian Prostar 410 autosampler with heated column oven, and a Varian 325 dual-wavelength, UV–vis detector operating under Varian Galaxie v.1.8 software control (Walnut Creek, CA). An isocratic gradient of water:methanol (20 %:80 %) at 1.0 mL min^{-1} produced baseline separation of benzene, toluene, and ethyl benzene in under 5 min on an Agilent Rapid Resolution XDB-C18 column (100 mm × 4.6 mm, 3 µm particle) heated to 50 °C. Peak areas monitored at 210 nm were used for quantitation and the percent remaining in solution was expressed relative to time zero sampling.

3. Results and discussion

3.1. 3D printed sorbents

According to data from the manufacturer's website, safety data sheet [6], and Daniel et al. [7], Proto-pasta PLA-carbon black fiber contains < 21.83 % carbon black, the volume resistivity of molded resin before 3D printing is 15 Ω cm, and resistance of a 10 cm length of 1.75 mm diameter filament is 2–3 kΩ. Due to software limitations of the UltimakerCura version required for the Monoprice Mini Pro 3D printer, a simple grid pattern infill was used.

A clear, visual difference was noticeable between the lower infill densities (15 %, 20 %) and the higher fill densities (40 %, 50 %) based upon the 3D layer slices (Fig. 2). Experimentally, it was also apparent that the displacement of air for the sorbents with smaller cavities (higher fill densities) was problematic. Visible light microscopy images (Fig. 3) support this observation as the pore areas range from 1.2 mm^2 (30 %), 0.5 mm^2 (40 %), to 0.2 mm^2 (50 %). Since water is drawn through the sorbent by the action of vortex spinbar stirring, the smaller sorbent porosity can be problematic if the fill density is increased much past 50 %, unless a significant reduction in surface tension of the solvent can be realized or pressure is used to pump water through the sorbent bed.

3.2. Extraction and kinetics of VOC removal from water

Control experiments using only a stirbar (without a 3D printed sorbent) and a stirbar pressed into nonconductive PLA did not remove benzene, toluene, or ethyl benzene over the course of 5 h. However, for the conductive carbon black PLA, the percent extraction values in Table 1 over the course of 5 h show that a significant reduction in each of the VOCs was observed. The measured extraction efficiency order for the 5 h, 50 % fill density data correlates (r^2 = 0.96) with the trends in the organic carbon-water partition coefficient (K_{oc} = 61.7, 140, 204 for benzene, toluene, and ethyl benzene, respectively). AC modified filament appears well suited for the removal for simple, aromatic organic solvents; however, compounds with higher K_{ow}/K_{oc} values such as fused polyaromatic hydrocarbons (PAH) may have enhanced removal from aqueous solutions.

Competitive sorption of benzene, toluene, and ethyl benzene was modeled using a pseudo-second order equation $\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$ where q_e and q_t (mg g^{-1}) are the sorption capacity at equilibrium and at time t (min), respectively [8,9]. From the slope and y-intercept of plots of $\frac{t}{q_t}$ vs t, the pseudo-second order rate constant k (g mg^{-1} min^{-1}) was calculated. Strong linear plots ($r^2 > 0.995$) were obtained for toluene and ethyl benzene while slightly less linear plots were observed for benzene ($0.960 < r^2 < 0.999$). A linear relationship was found between the rate constants as a function of fill density for toluene and ethyl benzene

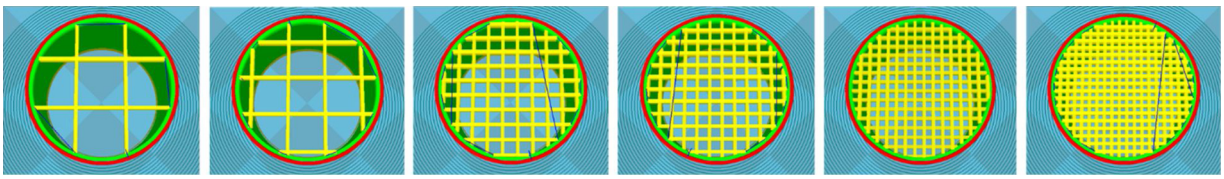

Fig. 2. Cura Ultimaker screen captures of infill layers of sorbent cylinders at fill densities of 15 %, 20 %, 25 %, 30 %, 40 %, and 50 %, left to right.

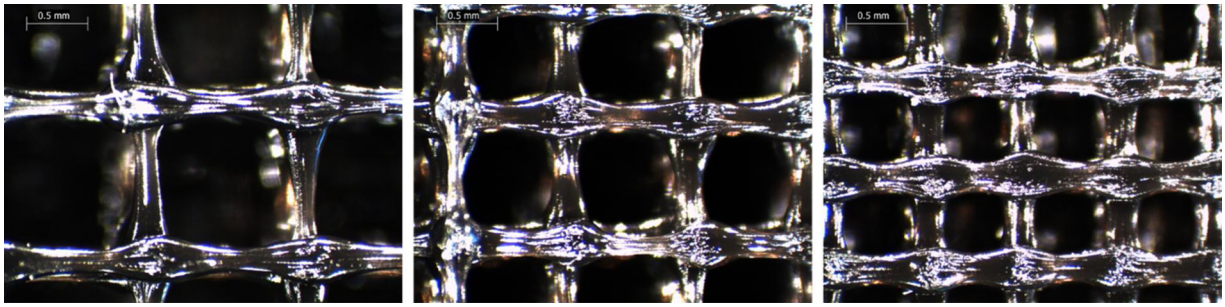

Fig. 3. Microscope images of 3D printed sorbents at fill densities of 30 %, 40 %, and 50 % left to right. A 0.5 mm scale bar is shown in the top left of each image.

Table 1
Percent of VOC remaining in solution over 5 h for the six fill densities investigated.

time (min)	15%	20%	25%	30%	40%	50%
benzene						
0	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
30	89.3%	87.9%	84.4%	80.0%	80.4%	84.6%
60	82.8%	84.4%	78.1%	73.4%	72.1%	73.7%
90	78.5%	75.9%	71.7%	67.3%	64.1%	68.5%
120	77.9%	73.9%	68.9%	62.4%	57.3%	62.9%
180	72.7%	76.5%	64.2%	57.8%	51.3%	56.9%
240	67.5%	69.4%	57.7%	53.9%	49.8%	52.2%
300	68.6%	72.0%	55.7%	52.5%	49.8%	49.4%
toluene						
0	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
30	76.0%	73.7%	65.8%	61.4%	57.1%	55.5%
60	63.9%	65.3%	52.9%	50.1%	47.7%	44.7%
90	55.2%	52.2%	43.9%	41.1%	37.4%	35.4%
120	51.3%	47.9%	39.4%	35.5%	30.5%	30.6%
180	43.7%	46.0%	32.2%	29.4%	24.7%	24.5%
240	37.7%	37.7%	26.7%	25.6%	21.4%	20.8%
300	35.8%	37.9%	24.7%	24.3%	20.2%	18.7%
ethyl benzene						
0	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
30	55.3%	52.3%	43.3%	34.2%	34.6%	29.7%
60	40.8%	42.0%	31.8%	26.1%	25.5%	23.7%
90	32.9%	31.1%	24.3%	19.8%	19.2%	16.9%
120	29.1%	26.9%	20.9%	16.0%	13.8%	14.0%
180	22.6%	24.8%	16.7%	13.0%	11.8%	10.8%
240	18.1%	18.7%	12.6%	10.8%	9.7%	9.2%
300	17.0%	17.8%	11.2%	9.7%	8.2%	8.0%

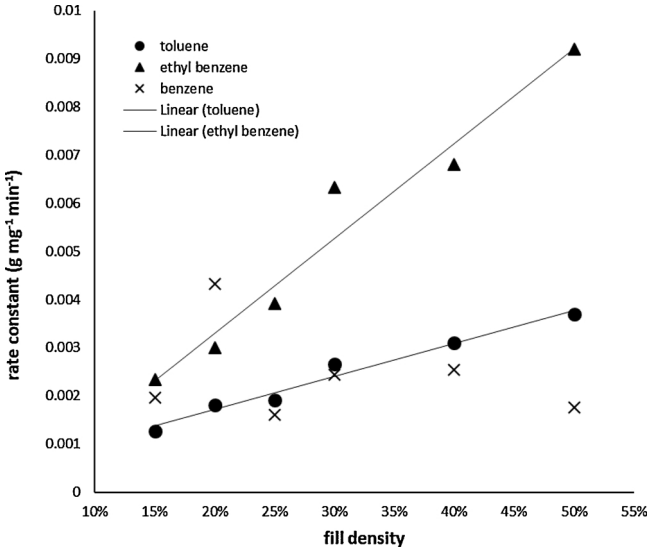

Fig. 4. Pseudo-second order rate constants for benzene, toluene, and ethyl benzene as a function of fill density. Linear regression lines are shown for toluene and ethyl benzene.

(Fig. 4), indicating that increased surface areas at the higher fill densities are advantageous for faster removal of VOCs from water. However, the rate constants for benzene were lower and did not follow any definite trend with fill density. Competitive solute-solute and solute-sorbent interactions for sorbent capacity may have affected benzene sorption in a mixture as opposed to a single-component system. For the cylinder sorbent design in Fig. 1, measured sorbent masses increased ~0.3 g per 10 % increase in fill density and as each cylinder required the same mass for printing the outer, solid wall of the cylinder and walled stir bar cavity, this reduction of mass effectively resulted in an increase of interior conductive PLA for extraction.

In this communication, the removal of VOC contaminants from water was achieved through 3D printing a sorbent from an unmodified, commercially available carbon black conductive PLA filament on a personal 3D printer. Future investigations will further explore 3D mesoporous structure control and other commercially available carbon-based 3D filament modifications for removal of select compound classes.

Funding sources

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declaration of Competing Interest

The authors declare a personal relationship.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jwpe.2020.101194.

References

[1] Z.X. Low, Y.T. Chua, B.M. Ray, D. Mattia, I.S. Metcalfe, D.A. Patterson, Perspective on 3D printing of separation membranes and comparison to related unconventional fabrication techniques, J. Membr. Sci. 523 (2017) 596–613.
[2] C. Fee, 3D-printed porous bed structures, Curr. Opinion Chem. Eng. 18 (2017) 10–15.
[3] C. Salmean, S. Dimartino, 3D-printed stationary phases with ordered morphology: state of the art and future development in liquid chromatography, Chromatographia 82 (1) (2019) 443–463.
[4] C. Fee, S. Nawada, S. Dimartino, 3D printed porous media columns with fine control of column packing morphology, J. Chromatogr. A 1333 (2014) 18–24.
[5] M.J. Sweetman, S. May, N. Mebberson, P. Pendleton, K. Vasilev, S.E. Plush, J.D. Hayball, Activated Carbon, Carbon Nanotubes and Graphene: Materials and Composites for Advanced Water Purification, C, Carbon Resour. Convers. 3 (2) (2017) 18.
[6] Proto-Pasta, Safety Data Sheet, 2018. https://www.proto-pasta.com/pages/documentation. (Accessed September 9, 2019.
[7] F. Daniel, N.H. Patoary, A.L. Moore, L. Weiss, A.D. Radadia, Temperature-dependent electrical resistance of conductive polylactic acid filament for fused deposition modeling, Int. J. Adv. Manuf. Tech. 99 (5–8) (2018) 1215–1224.
[8] Y.S. Ho, G. McKay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Process Saf. Environ. Prot. 76 (B4) (1998) 332–340.
[9] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (5) (1999) 451–465.