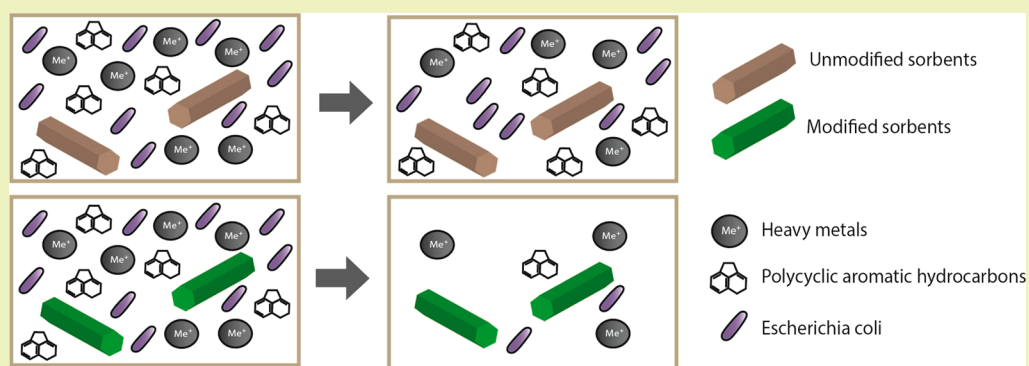


## Enhancement of Surface Runoff Quality Using Modified Sorbents

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## S Supporting Information



**ABSTRACT:** The objective of this study was to develop and test nanoparticle- and polymer-based bioactive amended sorbents to enhance stormwater runoff treatment in best management practices (BMPs). Red cedar wood and expanded shale were the sorbents tested. Red cedar wood chips (RC) were modified with 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride (TPA) and silver nanoparticles (AgNPs) at different mass loadings (0.36 mg/g, 0.67 mg/g, and 0.93 mg/g for TPA and 0.33 mg/g and 0.68 mg/g for AgNPs) to simultaneously improve the sorption of organic and inorganic contaminants and pathogenic deactivation in BMPs treating stormwater runoff. Unmodified expanded shale is often used as a filter material for stormwater treatment and was used as a base comparison. The results showed that TPA and AgNPs loading onto red cedar increased the Langmuir maximum sorption coefficient ( $Q$ ) for polycyclic aromatic hydrocarbons, up to 35 fold and 29 fold, respectively, compared to unmodified red cedar. In the case of heavy metals,  $Q$  for lead increased with increased loading of TPA and AgNPs, whereas no significant change in the  $Q$  value for cadmium was observed, while zinc and nickel sorption slightly decreased. The Langmuir maximum sorption coefficient of copper was higher for modified red cedar; however, no correlation was observed with TPA or AgNP loadings. The log reduction value (LRV) for *Escherichia coli* using unmodified red cedar was  $<1$  log, while modified red cedar exhibited LRV up to  $2.90 \pm 0.50$  log for 0.67 mg/g TPA-RC and up to  $2.10 \pm 0.90$  log for 0.68 mg/g AgNP-RC. Although AgNP-modified red cedar shows a comparable performance to TPA-RC, the high cost of production may limit the use of AgNP-amended materials. While TPA-modified red cedar has advantages of lower cost and lower toxicity, the fate, transport, and environmental implications of TPA in natural environments has not been fully evaluated. The findings from this study show that if BMPs were to incorporate the modified red cedar, stormwater treatment of PAH and *E. coli* could be enhanced, and the quality of the treated water will improve.

**KEYWORDS:** Stormwater runoff treatment, Bacteria deactivation, Nanomaterials, Poly(trihydroxysilyl)propyldimethyloctadecyl ammonium chloride, Organic and inorganic contaminants, Filter media, Sorption, Best management practices

## INTRODUCTION

Stormwater runoff contains polycyclic aromatic hydrocarbons (PAH), heavy metals, and pathogens that are discharged into natural surface and groundwater bodies, impairing ecosystems and compromising human health.<sup>1–3</sup> During and after precipitation events, these contaminants commonly exceed the maximum contaminant level (MCL) standards in runoff and receiving water bodies.<sup>1,4,5</sup> High concentrations of heavy metals and petroleum hydrocarbons, such as PAHs,<sup>3</sup> can compromise the ability to use stormwater for recharging aquifers or apply it

in gray water operations. The concentrations of *Escherichia coli* (*E. coli*) in runoff can exceed  $10^4$  colony-forming units (CFU) per 100 mL,<sup>1,6</sup> making stormwater runoff one of the major contributors of pathogens into surface and coastal waters.<sup>5,7</sup> The sources of pathogens in stormwater runoff are attributed to

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wildlife or pets<sup>8</sup> and to some degree human fecal contamination.<sup>7</sup> Exposure to pathogens can lead to serious illness, such as gastroenteritis or cholera.<sup>5,9</sup> Ideally, structural BMPs should simultaneously attenuate organic, inorganic, and microbiological contaminants. However, most stormwater BMPs are only effective in treating heavy metals and petroleum hydrocarbons<sup>10–12</sup> through filtration and sorption.<sup>13,11,12</sup> They are largely ineffective in treating pathogens.<sup>14–17</sup> Previous studies showed that materials such as organoclays amended with quaternary ammonium compounds exhibit higher sorption for PAHs and metals.<sup>18–21</sup> The quaternary ammonium polymer 3-(trihydroxysilyl)propyldimethyloctadecyl ammonium chloride (TPA) is used as a disinfectant material in environmental and medical applications such as in ceramic filters<sup>22</sup> and prosthetic devices.<sup>23</sup> Silver nanoparticles (AgNPs) are another well-known antimicrobial agent. Impregnating filter media with AgNPs effectively removes pathogens from aqueous solutions.<sup>24,25</sup> To our knowledge, these nanoparticles and the TPA polymer have never been used for stormwater runoff treatment.

One commonly used BMP is a tree filter, which consists of a subsurface biofiltration system that combines filtration, sorption, and phytoremediation processes for contaminant removal. However, previous studies have shown that contaminant removal is limited.<sup>13</sup> Hence, there is a need to find filter materials that can treat a variety of pollutants and can enhance the stormwater treatment performance of BMPs, such as tree filters. Hence, the objective of this study was to develop and test filter materials amended with nanoparticles or polymers that are capable of simultaneously removing PAHs, metals, and pathogens from stormwater runoff. For this study, red cedar (RC) wood chips and expanded shale (ES) were selected as the filter matrices. Expanded shale is a commonly used filter material in commercial tree filters, while the rot-resistance of red cedar, even under saturated conditions,<sup>26</sup> makes it a promising filter material. Here, we investigated the efficacy of TPA and AgNPs as amendments to RC and compared the contaminant removal performance to the unmodified expanded shale. The ultimate goal of this study is to offer new multifunctional filter materials for stormwater treatment.

## METHODS

**Materials.** Untreated red cedar wood was obtained locally (Liberty Cedar, West Kingston, RI). The wood was chipped, and the fraction of RC chips retained between 10 and 3.3 mm sieves was used for the experiments. This sieve size was chosen to avoid fines and larger wood chips as the former can reduce hydraulic conductivity and the latter could induce preferential flow paths. Expanded shale (ES; trade name Norlite), sorted between 13 and 19 mm (the size of ES used in tree filters), was obtained from Read Custom Soils (Hanover, MA). Both materials were washed and soaked in deionized water for a minimum of 2 weeks to leach out soluble matter. A 5% solution of 3-(trihydroxysilyl)propyldimethyloctadecyl ammonium chloride solution (TPA) (EPA product Reg. No. 83019-2) was obtained from Biosafe (Pittsburgh, PA). AgNPs were synthesized via Tollens method as described elsewhere,<sup>27</sup> using polyvinylpyrrolidone (PVP, average molecular weight 29,000 g/mol, Sigma-Aldrich) as a stabilizer.

Two common stormwater PAH compounds, acenaphthene and fluorene (purity grade of 98% or higher) were obtained from Sigma-Aldrich. The PAH solutions were prepared as described elsewhere.<sup>21</sup> PAH standards and deuterated PAH standards were obtained from Ultra Scientific, U.S.A. Metal reference standards containing 1000 mg/L  $\pm$  1% certified cadmium, copper, lead, nickel, and zinc were obtained from Fisher Chemical. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), disodium phosphate ( $\text{Na}_2\text{HPO}_4$ ), and sodium nitrate ( $\text{NaNO}_3$ ) were obtained from

Sigma-Aldrich. A nonpathogenic wild strain of *Escherichia coli* (*E. coli*) was obtained from IDEXX laboratories.

**Material Characterization.** The hydrodynamic sizes of the AgNPs were measured with dynamic light scattering (DLS) using a Zetasizer (Nano ZS, ZEN 3600, Malvern) at 25 °C in 1.3 mmol/L ionic strength medium. The surface area of the sorbents was measured using a multipoint BET method (Quantachrome NOWA 2200) with  $\text{N}_2$  as the sorbate. The hydrophobicity of the materials was determined by measuring the contact angle of water to modified red cedar using a contact angle goniometer (Rame-Hart)

**Laboratory Analysis.** TPA concentrations were analyzed using Hach Method 8337 on a Hach DR 2800 spectrophotometer. Metals, along with AgNPs (measured as total silver), were analyzed using a PerkinElmer inductively coupled plasma optical emission spectrometer (ICP-OES) 3100 XL. The fractions of silver nanoparticles and Ag ions were measured by filtering the samples through Amicon ultra-14 centrifugal filters (Millipore) at 3500 rpm for 30 min.

All PAH samples were prepared according to EPA method 610 and analyzed using a gas chromatograph coupled with a mass spectrometer (Shimadzu GC-MS QP2010). PAH samples were spiked with acenaphthene-d10 to quantify the extraction efficiency.

*E. coli* concentrations were determined using membrane filtration, applying m-FC broth with Rosolic acid (Millipore) and incubating the samples at 44.5 °C for 24 h. To enumerate *E. coli* sorbed onto the solid phase, samples were sonicated (QSonica, Q125) twice for 10 min at 20% amplitude in a phosphate buffer solution. The liquid phase was then analyzed by the aforementioned method.

**Experimental Methodology.** The laboratory experiments were divided into two phases. During the first phase, the loading capacity and stability of TPA and AgNP amendments on RC and ES were tested. This was achieved through batch sorption isotherms (loading capacity) followed by sequential desorption for a week (stability). In the second phase, building on the isotherm results obtained during the first phase, RC was modified with different TPA and AgNP loadings and evaluated in batch experiments for sorption capacity of PAHs and heavy metals and also *E. coli* disinfection performance.

**Phase I. Nanoparticle and Polymer Loading Capacity of Sorbents.** Batch isotherms were carried out in triplicates to determine the loading capacity of TPA and AgNPs onto the sorbent materials. For all experiments, a 1.3 mmol/L ionic strength medium using sodium chloride (NaCl) was used as a background solution in order to mimic surface water conditions in Rhode Island.<sup>27</sup> Detailed experimental procedures are in Text S1 of the Supporting Information. After conducting the sorption experiment, the samples were decanted and dried at 60 °C. Desorption of TPA and AgNPs from modified sorbent materials was determined through sequential desorption in DI water for a minimum of 24 h and up to 168 h, i.e., until aqueous concentrations were below the method detection limit of 0.2 mg/L for TPA and 0.01 mg/L for Ag. The method detection limit for Ag is below EPA MCL of 0.1 mg/L, while for TPA, no EPA MCL limit is defined. TPA is categorized as slightly toxic with oral  $\text{LD}_{50}$  above 5000 mg/L. The results from the desorption experiment were reported as total silver and TPA, respectively. The fractions of desorbed AgNPs and Ag ions are also measured and reported in Table S2 of the Supporting Information.

**Phase II. Organic and Inorganic Contaminant Removal Efficiency of Modified Sorbents.** Using the results obtained in phase I, RC was modified at different loadings of TPA and AgNPs (Table 1) to assess the ability to remove organic, inorganic, and microbiological contaminants as a function of loading. This process was required to adapt the lab-scale amending procedure to a large scale due to the large amount of the material required to perform all tests; details of this procedure are presented in Text S2 of the Supporting Information. Due to disintegration of ES when agitated for modification, this material was no longer tested. However, unmodified ES was used as baseline comparison for modified RC.

Batch tests were carried out to determine the sorption capacity of the modified and unmodified sorbent materials for PAHs and heavy metals. A synthetic stormwater runoff stock solution, containing PAHs,

**Table 1. Amendment Loadings Achieved by Exposing Red Cedar to Aqueous Solutions of Either TPA or AgNPs**

bioactive agent	concentrations (mg/L)	amendments (abbreviation)
TPA	26	0.36 mg/g TPA red cedar (0.3TPA-RC)
	72	0.67 mg/g TPA red cedar (0.6TPA-RC)
	150	<sup>a</sup> 0.93 mg/g TPA red cedar (0.9TPA-RC)
AgNPs	20.8	0.33 mg/g AgNP red cedar (0.3AgNP-RC)
	52	<sup>a</sup> 0.68 mg/g AgNP red cedar (0.6AgNP-RC)

<sup>a</sup>Maximum possible loading.

metals, and inorganic salts, was prepared (Table S3, Supporting Information). All solutions were adjusted to a pH of 5.5. Details of the batch tests are described in Text S3 of the Supporting Information. Visual MINTEQ Ver.3.0, an equilibrium speciation software, was used to determine the speciation of metals in the synthetic runoff.

**Microbiological Contaminant Removal Efficiency by Modified Sorbents.** Two of the modified RC sorbents (0.6 mg/g TPA-RC and 0.6 mg/g AgNP-RC) along with unmodified RC and ES were selected to test bacteria deactivation efficiency. Five different initial *E. coli* concentrations relevant to stormwater runoff, ranging from  $10^2$ – $10^6$  CFU/100 mL, were used in the experiments.<sup>6,7</sup> Detailed experimental procedures are provided in Text S4 of the Supporting Information.

**Cost Analysis and Limitations.** The cost for the preparation of modified red cedar was calculated based on material costs incurred from lab-scale modifications. The total initial cost calculation for incorporating modified red cedar in a full-scale tree filter BMP system was based on a 5 cm thick layer of modified RC for a tree box filter with dimensions of 1.22 m × 1.83 m and a drainage area of 0.5 acre.

## RESULTS AND DISCUSSION

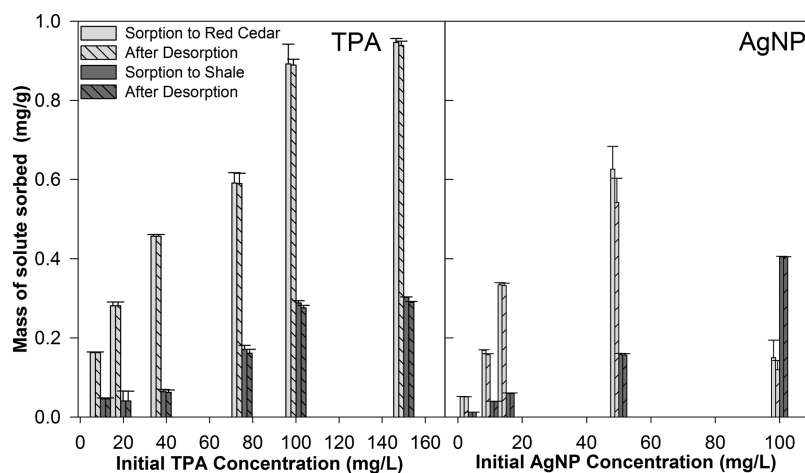
**Material Characterization.** The average hydrodynamic size of the AgNPs was  $38.5 \pm 3.5$  nm. The surface area of the modified RC increased with increased loading of AgNPs and TPA, for example, the surface area increased from  $4.89 \pm 0.092$  m<sup>2</sup>/g for UM-RC to  $7.98 \pm 0.42$  m<sup>2</sup>/g and  $6.01 \pm 0.23$  m<sup>2</sup>/g for 0.9TPA-RC and 0.6AgNP-RC. The contact angle of water for modified RC increased with loading of TPA and AgNPs (Table S4, Supporting Information). The contact angle was greater than 90° for 0.9TPA-RC and was greater than 70° for 0.6TPA-RC and 0.6AgNP-RC, indicating that modification with TPA and AgNPs made the material more hydrophobic.

**Phase I. Nanoparticle and Polymer Loading Capacity of Sorbents.** The TPA batch sorption on RC showed that between 37% and 98% of the initial mass of TPA in the aqueous phase was sorbed to the RC, with a maximum loading of  $0.93 \pm 0.03$  mg/g. For expanded shale (ES), the total mass of TPA sorbed was in the range of 30% to 75%, with a maximum loading of  $0.30 \pm 0.03$  mg/g. During the sequential desorption study, only  $0.54 \pm 0.30\%$  of the TPA initial mass sorbed was released from RC, while for ES, it was  $1.13 \pm 0.60\%$ .

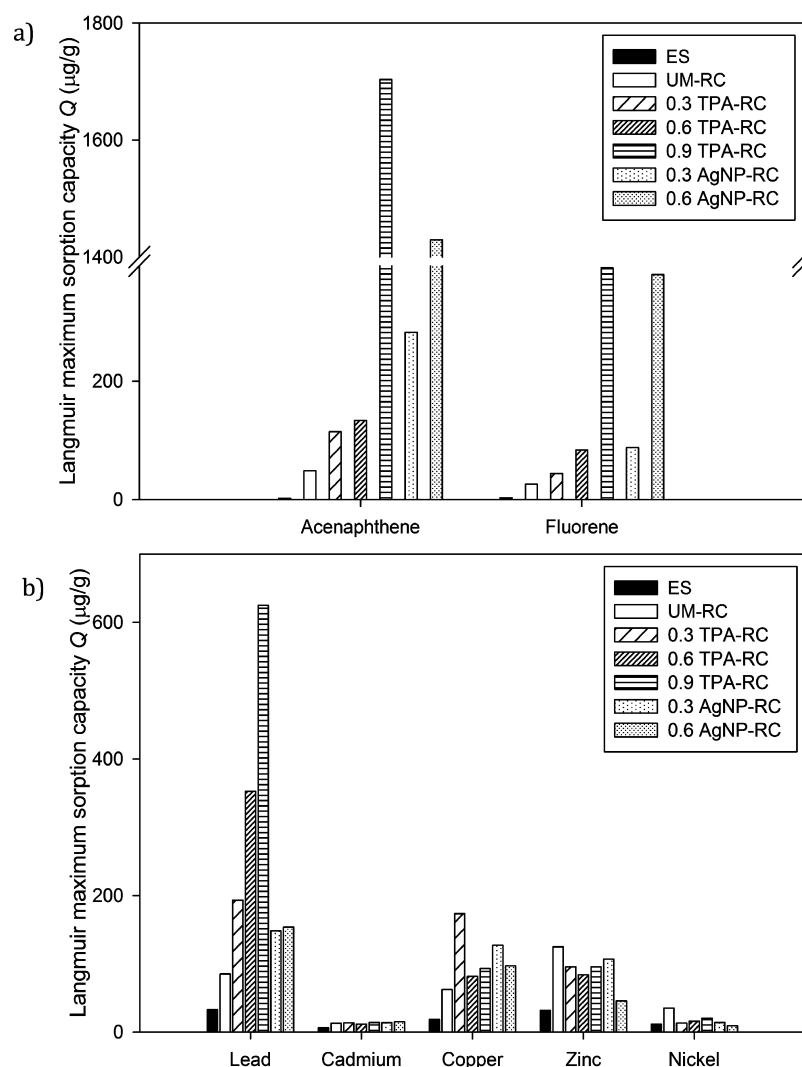
The higher sorption of TPA to RC is likely due to stronger interaction with the wood's molecules, such as lignin and cellulose.<sup>28</sup> The nonlinear shape of the sorption isotherm model (Figure S1a, Supporting Information) supports that TPA predominantly sorbs onto RC rather than diffusing into it, which would have been by linear sorption isotherm, indicative of Fickian transport processes. In comparison, ES contains little or no organic matter due to the extreme heating during expansion process.<sup>29</sup> This likely resulted in fewer sorption sites for TPA. The linearity of the ES isotherm (Figure S1a, Supporting Information) indicates that TPA may be partitioning into porous spaces in the shale.

The amount of AgNPs sorption to RC depended on the initial concentration of the AgNP solution. That is, RC sorbed up to 97% when the initial concentrations of AgNPs were below 21 mg/L. However, the AgNPs sorption to RC decreased to 75% and 10% when initial concentrations were at 52 and 104 mg/L, respectively. Maximum loading of AgNPs to RC was  $0.63 \pm 0.10$  mg/g.

Independent of the initial solution concentration, ES sorbed 96% to 99% of the initial mass of AgNPs with a maximum loading of  $0.40 \pm 0.02$  mg/g. In the case of AgNPs, desorption was variable for RC and depended on the AgNP mass sorbed to the sorbent. That is,  $2.50 \pm 2.94\%$  were desorbed if the AgNP loading was low (0.33 mg/g) and  $14.4 \pm 9.28\%$  if the loading was high (0.63 mg/g) (Figure 1b). Depending on the initial aqueous phase concentration of AgNPs, between 88% and 98% of the mass desorbed is in the form AgNPs, while the remainder is in form of Ag ions (Table S2, Supporting Information). For ES, desorption of AgNP was <0.01% relative to the initial mass of AgNPs sorbed, regardless of the initial aqueous phase AgNP concentration or mass sorbed (Figure 1b). The fraction of AgNPs and Ag ions desorbed from ES were below method



**Figure 1.** Polymer and nanoparticle loading capacity of sorbents. Mass sorbed during sorption experiments and mass retained after desorption for (a) TPA and (b) AgNPs on red cedar (RC) and expanded shale (ES). The data suggests that once amended the active compounds remain largely fixed on the substrate.



**Figure 2.** Langmuir maximum sorption coefficient  $Q$  of (a) PAHs and (b) heavy metals for expanded shale (ES), unmodified red cedar (UM-RC), and RC modified with TPA and AgNPs.

detection limit. The uptake of AgNPs can be due to trapping of AgNPs in the pores of the sorbent material and sorption due to van der Waal forces of attraction between AgNPs and the sorbents.

At concentrations below 52 mg/L, the hydrodynamic size of AgNPs is  $\leq 40$  nm, whereas at higher concentrations (104 mg/L), the average hydrodynamic size of the AgNPs increased to  $>80$  nm due to aggregation. This phenomenon was confirmed by TEM imaging (Figure S2, Supporting Information). The larger size could have hindered the sorption of AgNPs to the micropores in wood chips, whereas it did not reduce the uptake by ES due to the large pores present in expanded shale.<sup>29</sup>

**Phase II. Organic and Inorganic Contaminant Removal Efficiency of Modified Sorbents.** The results of the batch isotherm experiments for PAHs and heavy metals onto unmodified ES as well as unmodified and modified RC are non-linear (Figure 2). Assuming that the number of sorption sites is limited, the results were fitted to the Langmuir model

$$q = \frac{QbC_e}{(1 + bC_e)} \quad (1)$$

where  $q$  is the amount of solute sorbed ( $\mu\text{g/g}$ ),  $Q$  is the Langmuir maximum amount of solute that can be absorbed by the sorbent ( $\mu\text{g/g}$ ),  $b$  is the Langmuir adsorption coefficient, and  $C_e$  is the equilibrium aqueous solute concentration ( $\mu\text{g/L}$ ). The results from batch experiments show that during the experimental conditions RC and ES had reached saturation indicating a limited number of sorption sites (Figure S3, Supporting Information), thus confirming the appropriateness of the Langmuir type isotherm model. In order to compare the performance of all the materials, the Langmuir type model was applied to all data sets. The isotherm parameters for PAHs and metals for all sorbents were obtained using SigmaPlot 11 (Systat Software, Inc.) (Table 2). Except for ES, the goodness-of-fit using the Langmuir model was high ( $R^2 > 0.90$ ) for all isotherms.

**Polycyclic Aromatic Hydrocarbons.** The Langmuir maximum sorption capacity of PAH for ES is much lower compared to both unmodified and modified RC (Table 2), which may be a result of the vitrification process the expanded shale has undergone during thermal expansion, making it more inert by removing potential organic sorption sites.<sup>29</sup> In the case of RC, the value of  $Q$  for acenaphthene and fluorene increased with increased loadings of TPA and AgNPs (Figure 2). For example,



Table 2. Langmuir Maximum Sorption Capacity ( $Q$ ) for PAHs and Metals for All Sorbents<sup>a</sup>

contaminant		ES	unmodified RC	0.3TPA-RC	0.6TPA-RC	0.9TPA-RC	0.3AgNP-RC	0.6AgNP-RC
acenaphthene	$Q$ ( $\mu\text{g/g}$ )	2.3	48.6	114.6	133.7	1703.5	282.7	1429.2
fluorene	$Q$ ( $\mu\text{g/g}$ )	1.2	26.1	43.9	83.8	391.1	87.7	380.0
lead	$Q$ ( $\mu\text{g/g}$ )	33	85.14	193.3	352.6	625.1	148.4	153.8
cadmium	$Q$ ( $\mu\text{g/g}$ )	6.3	13.0	13.7	11.8	14.2	13.8	15.1
copper	$Q$ ( $\mu\text{g/g}$ )	18.7	62.3	173.4	81.8	93.2	127.1	97.06
zinc	$Q$ ( $\mu\text{g/g}$ )	31.7	124.9	95.6	84.1	95.7	106.7	45.8
nickel	$Q$ ( $\mu\text{g/g}$ )	11.6	35.3	13.25	15.8	20.36	14.23	9.2

<sup>a</sup>Both Langmuir adsorption coefficients ( $b$ ) and goodness-of-fit values ( $R^2$ ) are provided in the Supporting Information.

for acenaphthene,  $Q$  increased from 48.6  $\mu\text{g/g}$  for UM-RC to 1703.5  $\mu\text{g/g}$  for 0.9TPA-RC and to 1429.2  $\mu\text{g/g}$  for 0.6AgNP-RC (Table 2).

Finally, the modification with TPA and AgNPs increased the hydrophobicity of the RC as confirmed by contact angle measurements (Table S4, Supporting Information). While the  $C_{18}$  chain of the TPA molecule is enhancing the hydrophobicity of RC, in the case of AgNP-RC, it is the PVP coating on AgNPs. The increase in surface hydrophobicity of RC resulted in an increase in PAH sorption after the amendment of RC with both AgNPs and TPA. This is due to the hydrophobic interactions between PAH and modified RC. In addition, PAHs can also partition onto the organic phase created by TPA and PVP on modified RC.

**Heavy Metals.** The results obtained from the Visual MINTEQ model show that at pH 5.5 the metal speciation in the synthetic stormwater is dominated (73.5% to 87.6%) by the divalent cations ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ ) and otherwise consists of predominantly sulfate salts of, e.g.,  $\text{PbSO}_4$  (Table S6, Supporting Information). The percentage of metals available for sorption was taken into account for batch isotherm calculations, and the Langmuir isotherm model was used for quantitative comparison of the sorption capacity between the unmodified and modified materials.

Of all sorbents tested, the unmodified ES exhibited the lowest  $Q$  for all metals (Table 2). In the case of RC,  $Q$  for Pb increased from 85.14  $\mu\text{g/g}$  for unmodified RC to 625  $\mu\text{g/g}$  for 0.9TPA-RC and 153.8  $\mu\text{g/g}$  for 0.6AgNP-RC (Table 2). For Cu, the TPA and AgNP amendments enhanced the sorption of Cu compared to unmodified RC. However, no correlation could be identified between amendment loading and Cu sorption (Table 2). The modification of RC with TPA and AgNPs did not have an impact on  $Q$  for Cd and slightly decreased in the case of Zn and Ni (Table 2).

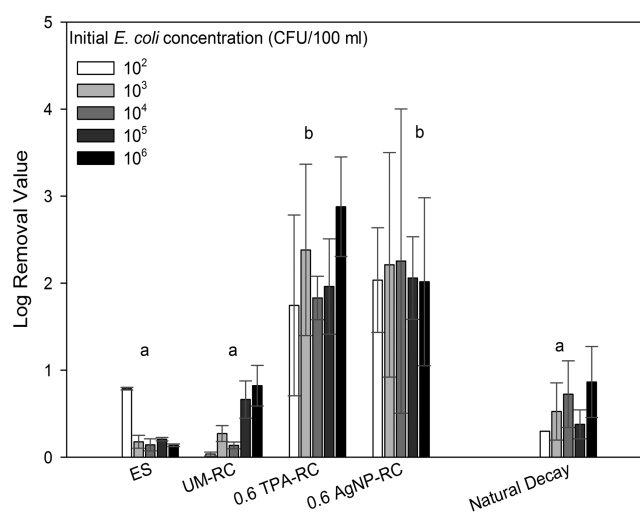
The enhanced maximum sorption capacity  $Q$  of modified RC for Pb and Cu, as well as the unchanged  $Q$  for Cd, indicates that modification of RC is not limiting the retention of these metals and in fact increases it. The hydroxyl groups present in the TPA molecule provides attractive sorption sites for metals, whereas the oxygen and nitrogen present in PVP can form metal complexes.<sup>30</sup> The increase in Pb and Cu sorption could be due to bonding with hydroxyl groups on TPA and formation of complexes with PVP present on AgNPs. In addition, the increase in surface area of modified RC (Table S4, Supporting Information) likely provided more sorption sites for these metals. However, the reasons for the slight decrease in  $Q$  for Zn and Ni (Table 2) is unclear. No correlations with physicochemical properties or interactions with the amendments were found to explain the different sorption behavior of these metals to modified RC. Therefore, further studies are required

to gain insight on the sorption behavior of these metals onto modified RC.

**Microbiological Contaminant Removal Efficiency of Modified Sorbents.** Two modified sorbents (0.6TPA-RC and 0.6AgNP-RC) were tested for bacteria deactivation efficiency and were compared to unmodified RC and ES. The disinfection performance of the materials was calculated as log removal value (LRV)

$$\text{LRV} = \log(\text{initial } E. \text{ coli concentration}) - \log(\text{final } E. \text{ coli concentration}) \quad (2)$$

Final *E. coli* concentration is the total *E. coli* in aqueous phase and sorbed to the sorbents. The average LRV for the unmodified RC and ES was always below 1 (Figure 3). For the



**Figure 3.** Deactivation of *E. coli* at increasing concentrations using unmodified and modified materials (0.6TPA-RC and 0.6Ag-RC). Both the 0.6TPA-RC and 0.6Ag-RC were significantly more effective at deactivating *E. coli* compared to the unmodified materials ( $p < 0.001$ ). The data presented are averages of nine samples. Individual significant differences between the materials are indicated by the letters a and b in the figure.

modified materials, the average LRV values ranged from  $1.74 \pm 1.04$  log to  $2.90 \pm 0.50$  log for 0.6TPA-RC. In the case of 0.6AgNP-RC, the average LRV value ranged from  $2.03 \pm 0.60$  log to  $2.10 \pm 0.90$  log. Overall, the deactivation performance shows that the modified materials are significantly more effective at deactivating bacteria compared to unmodified ES and RC ( $p < 0.001$ ) (Figure 3). Previous studies showed that the impregnation of TPA and AgNPs onto surfaces enhanced the deactivation of *E. coli*.<sup>22</sup> Several mechanisms have been suggested for disinfection using AgNPs. These include damage

to bacteria by pitting the cell membrane, lysis of cells caused by silver ion release, or damage of the cell by the reactive oxygen species formed on the surface of the AgNPs. The biotoxicity of TPA has been explained mainly by the positively charged quaternary amine groups attracting *E. coli* and C<sub>18</sub> groups the piercing membrane and causing cell disruption<sup>31</sup>

**Cost Analysis and Limitations.** The contaminant removal performance and bacterial deactivation of both TPA- and AgNP-modified RC compare well and significantly enhanced water quality compared to unmodified RC. However, the selection of which antimicrobial agent to use for modification will be driven by the costs of amending the materials. The initial modification cost for RC using AgNPs is higher compared to TPA (Table S7, Supporting Information). For instance, to modify 1 kg of RC at similar loadings (~0.6 mg/g), AgNP modification costs \$57.90/kg versus \$10.30/kg for TPA (Table S7, Supporting Information). When installing these amendments in a field-scale BMP, such as a tree filter, less than 8% of the total initial cost incurred was for the TPA amendment compared to a 35% increase for AgNP. The toxicological data as determined by previous studies also suggests that TPA is less toxic compared to AgNPs (Table S8, Supporting Information). Further, the antimicrobial performance of AgNPs primarily depends on silver ion release. Over time, the silver ion release from AgNPs may decrease and thus could result in the reduction of antimicrobial efficiency.

Overall, TPA has a cost advantage over AgNPs in addition to lower toxicity and better contaminant removal performance. The long-term performance of TPA is currently unknown and requires further studies. These need to include investigations of TPA behavior at different water chemistry conditions.

In summary, this study reveals that conventional materials such as unmodified expanded shale and red cedar have very limited pathogen treatment capabilities. However, RC amended with TPA and AgNPs both increased antimicrobial properties by orders of magnitude. The amendments also enhanced PAH sorption while not hindering the sorption of most metals. These findings show that modified sorbent materials can enhance the stormwater treatment efficiency of BMP filters. The high cost involved in amending the sorbent with AgNPs and the higher toxicity may prevent the use of AgNP-modified materials in BMPs. Conversely, TPA-modified RC has the advantage of lower cost, lower toxicity, and higher contaminant and pathogen removal performance, making it the overall better choice as a filter medium for use in BMPs, such as tree filters. However, the long-term performance and effectiveness of TPA-modified RC under natural environmental conditions has yet to be studied.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental procedures in Text S1–S4, supporting graphics and images in Figures S1–S3, and additional information in Tables S1–S8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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