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Acid Mine Drainage Remediation: Aluminum Chelation Using Functional Graphenic Materials

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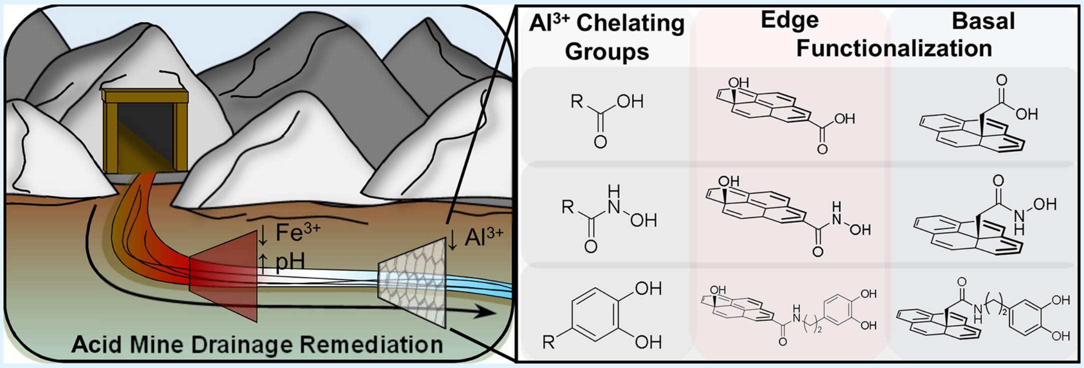

ABSTRACT: Acid mine drainage (AMD) is a pervasive source of metal pollution that severely impacts freshwater ecosystems and has a direct impact on human health. Conventional active and passive methods work very well for removing iron in AMD remediation, which is typically the highest metallic impurity. However, conventional passive remediation fails to remove all aluminum, which has severe ecological implications. Removal of aluminum ions using chelation, which traditionally uses small molecules that bind metals tightly for sequestration, holds promise. Yet, chelation strategies are limited because once introduced into surface water, small molecules are difficult to reclaim and often persist in the environment as pollutants. To address this, we have designed six unique scaffolds based on functional graphenic materials (FGMs) to create nonsoluble materials that could be placed at the end of a passive remediation process to remove persistent aluminum. When tested for efficacy, all six FGMs successfully demonstrated a reversible capacity to remove aluminum from acidic water, chelating up to 21 μg of Al/mg of FGM. Furthermore, when they were exposed to *E. coli* as an approximation for environmental compatibility, viability was unaffected, even at high concentrations, suggesting these FGMs are nontoxic and viable candidates for passive chelation-based remediation.

KEYWORDS: *graphene oxide, functional graphenic materials, acid mine drainage, water remediation, aluminum chelation*

1. INTRODUCTION

Acid mine drainage (AMD) is a pervasive source of pollution that severely impacts freshwater ecosystems[1,2] and has a direct impact on human health.[2−5] Most AMD originates from mines that have exposed rocks containing sulfide minerals. Sulfide minerals exposed to air and water are oxidized, resulting in the formation of sulfuric acid.[2,6,7] High concentrations of metal ions, such as iron, manganese, and aluminum, are dissolved by the acidic water and flow out into surface water.[6,7]

To remove these metals, the drainage water must be neutralized by raising the pH to affect precipitation of the metals. Currently, there are two major approaches to removing metals from AMD: (1) active remediation and (2) passive remediation. Active methods require a facility designed for continuous addition of a neutralizing agent, demanding intensive observation, labor, and cost. Passive remediation methods are preferable, requiring limited oversight. Passive methods take advantage of the natural flow of the water by creating landscapes including limestone rock beds and wetlands to naturally neutralize the AMD to encourage precipitation.[2,8,9] Passive methods work very well for removing iron, which is typically the highest metallic impurity. However, conventional passive remediation fails to remove all of the aluminum.[2] Best practices for aluminum removal require a more specialized passive remediation approach involving the installation of an anoxic, basic limestone drain that requires arduous routine maintenance.[10]

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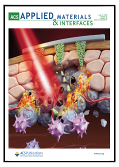

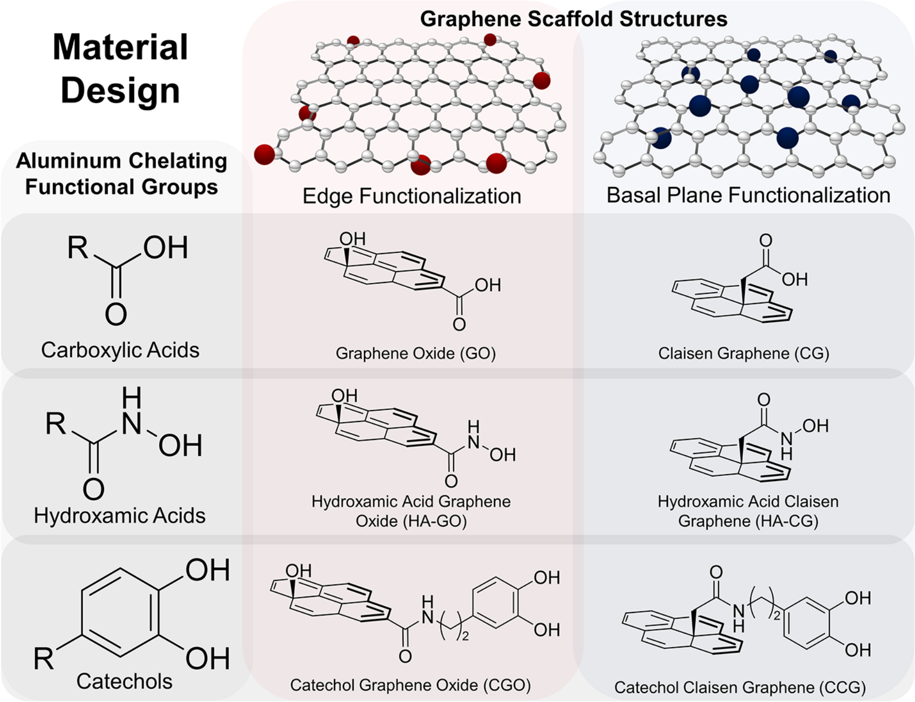

Figure 1. Material design of aluminum-chelating functional graphenic materials (FGMs) for acid mine drainage remediation. Aluminum-chelating functional groups (carboxylic acids, hydroxamic acids, and catechols) are represented on the left and the corresponding FGM scaffold containing the functional group is contained within the same row. Edge-functionalized FGMs are represented in red and basal-plane-functionalized FGMs are represented in blue.

The challenge of aluminum removal presents an ideal opportunity to employ material design to generate a more effective passive remediation method. One such approach would be to remove aluminum ions using chelation, which uses small molecules that bind metals tightly for sequestration. However, chelation strategies also suffer constraints because once they are introduced into surface water, small molecules are difficult to reclaim and often persist in the environment as pollutants.[11−13] To address this, chelators could be attached to a permanent, nonsoluble scaffold that could be placed at the end of a passive remediation process as a polisher to remove the persistent aluminum ions after most of the metals have been removed.[10]

A class of materials that show promise as insoluble chelation scaffolds are functional graphenic materials (FGMs). To synthesize FGMs, graphite is oxidized to graphene oxide (GO)[14,15] and subsequently modified to give the material tailored function. These materials provide scaffolds that are inexpensive, readily modified, and chemically sophisticated.[15] In this report, we used the chemical tunability of FGMs to covalently incorporate a variety of aluminum-chelating groups, such as carboxylic acids,[16,17] hydroxamic acids,[17,18] and catechols[17] to produce six unique FGMs. When tested for efficacy, all six FGMs successfully demonstrated the capacity to remove aluminum from acidic water. FGMs were also regenerable and stable for 1 week or more in acidic water. Thus, these FGMs fulfill our design criteria and show promise as a viable means for aluminum remediation.

2. MATERIALS AND METHODS

See Supporting Information for details.

3. RESULTS AND DISCUSSION

3.1. Material Design Rationale. To design recoverable aluminum-chelating materials, we need (1) an insoluble graphenic scaffold and (2) aluminum-chelating groups that can be attached to the scaffold (Figure 1).

3.1.1. Graphenic Scaffolds. We targeted functional graphenic materials (FGMs) as the scaffolds of interest because of their insolubility, settling,[19] processability,[20,21] high surface area, versatility of chemical manipulation,[15] and spatial control of functional groups on the graphenic backbones.[15,22]

The insolubility, settling,[19] and processability[20,21] of FGMs enable recovery after use and regeneration for reusable, aluminum-chelating materials for AMD remediation. AMD remediation with aluminum-chelating FGMs could be accomplished using two approaches. The first approach could encompass the direct addition to water supplies, where the insolubility and settling of FGMs could be capitalized upon to recover materials from stream beds. The second approach is the utilization of FGMs as a filter. A litany of work has been reported on processing chemically diverse FGMs into filters, specifically for water purification.[23]

FGMs are ideal scaffolds because of their high surface area. These graphenic materials can be accessed inexpensively using graphite as a precursor material. Graphite is composed of two-dimensional sheets of carbon atoms bound together, where many sheets aggregate to form the bulk material. With use of a modified Hummers' method,[15,24,25] the large surface area of graphite sheets is exposed through exfoliation and installation of oxygen groups, yielding atomically thin sheets of graphene oxide (GO) (Figure 1, Scheme S1).[15]

The plethora of functional groups found on GO creates an opportunity for versatile chemical manipulation and spatial

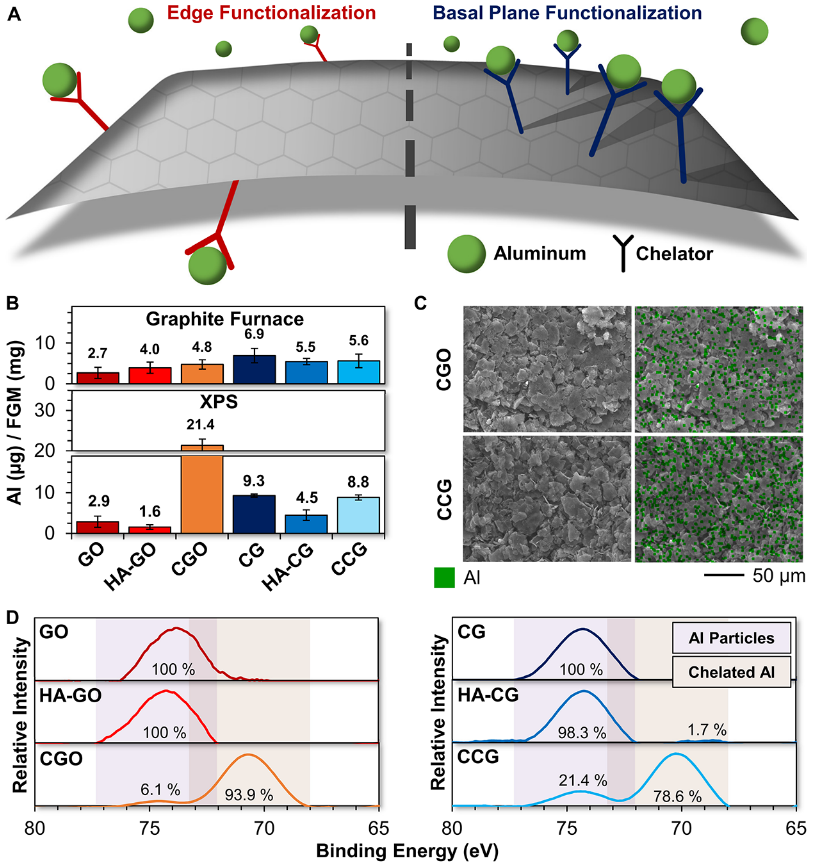

Figure 2. Aluminum-chelating capacity of functional graphenic materials (FGMs). Edge functionalization with carboxylic acids (graphene oxide, GO), hydroxamic acids (hydroxamic acid graphene oxide, HA-GO), and catechols (catechol graphene oxide, CGO) are shown in dark red, red, and orange, respectively. Basal plane functionalization with carboxylic acids (Claisen graphene, CG), hydroxamic acids (hydroxamic acid Claisen graphene, HA-CG), and catechols (catechol Claisen graphene, CCG) are shown in dark blue, blue, and light blue, respectively. (A) Schematic representation of the spatial distribution of aluminum-chelating groups on the graphenic backbone for edge and basal plane functionalization. (B) The mass of aluminum removed from a stock solution treated with FGMs, measured via a graphite furnace (top). The mass of aluminum adsorbed onto the surface of FGMs after treatment, as determined from the survey scans acquired using X-ray photoelectron spectroscopy (XPS) (bottom). The bars are the average of $n = 3$ samples and the error bars represent the standard deviation. (C) Energy-dispersive X-ray (EDX) spectroscopy of FGM samples, where measured adsorbed aluminum is displayed in green. (D) High-resolution XPS spectra of aluminum adsorbed onto the surface of FGMs. The peaks at 74.5 eV (shaded purple) are representative of adsorbed aluminum particles whereas the peaks at 70.5 eV (shaded orange) represent chelated aluminum ions. The relative percentages of the adsorbed aluminum particles and chelated aluminum ions were determined from the total area under the Al 2p curve.

control of functionality on the graphenic backbone. Here, our aim was to install water-stable functional groups on the graphenic backbones so that these materials could withstand long-term use in AMD conditions. GO contains spatially separated, distinct oxygen groups that serve as excellent chemical handles for targeted functionalization on either the edge or the basal plane of sheets (Figure 1, Scheme S2). The edges of GO sheets are populated by carboxylic acids, whereas the basal plane of GO contains tertiary alcohols and epoxides.[15] The basal plane groups on GO can be modified, but most modifications result in water-labile functional groups that rapidly degrade. Carboxylic acids on GO sheet edges are the most stable functional groups, limiting GO to edge functionalization for our intended application. To target edge functionality, carboxylic acids on the edge of GO sheets can be activated to produce hydroxamic acid and catechol edge-functionalized FGMs.

The instability of basal plane functionalization of GO can be circumvented by applying the Claisen reaction. Specifically, the tertiary alcohols found on the basal plane of GO can be transformed into carboxylic acids via a Johnson-Claisen rearrangement, producing an FGM known as Claisen graphene (CG) (Scheme S2). These basal plane carboxylic acids found on CG can then be manipulated using the same chemistries as GO, enabling the production of basal-plane-functionalized FGMs (Scheme S2).[22,25] The high heat necessary for the Claisen reaction, however, significantly reduces the other functional groups on the graphenic backbone, limiting this material to basal plane modification.[22]

3.1.2. Aluminum-Chelating Groups. We employed hard soft acid base (HSAB) theory to identify functional groups that bind aluminum. With use of HSAB theory, acids and bases are divided into hard and soft designations, where hard classifications include small, highly charged species and soft classifications include large species with low charge. According to HSAB theory, hard acids form more stable compounds with hard bases and soft acids form more stable compounds with soft bases.

Aluminum is a hard acid; thus, we targeted chemical moieties classified as hard bases that have been previously reported to chelate aluminum: carboxylic acids,[16,17] hydroxamic acids,[17,18] and catechols[17] (Figure 1).

3.2. Generation of Aluminum-Chelating FGMs. Here, we demonstrate facile chemistries that install aluminum-chelating groups (carboxylic acids, hydroxamic acids, and catechols) on either the edge or basal plane of the graphenic scaffolds, generating six aluminum-chelating FGMs. All FGMs were derived from the same batch of graphene oxide (GO) to enable direct comparisons of the chemical composition and material performance of FGMs. More details are provided in the Supporting Information.

3.2.1. Carboxylic Acid-Functionalized FGMs. FGMs containing carboxylic acids on the edge or basal plane of flakes were successfully synthesized, yielding graphene oxide (GO) and Claisen graphene (CG), respectively. Fourier transform infrared (FTIR) spectroscopy demonstrates that GO and CG contain a carboxylic acid stretch at 1720 cm^{-1} (Figure S1). Deconvolution of high-resolution carbon spectra obtained from X-ray photoelectron spectroscopy (XPS) also reveals a carboxylic acid peak at 289.0 eV for both GO and CG (Figures S2 and S3).

3.2.2. Hydroxamic Acid-Functionalized FGMs. We produced edge-functionalized hydroxamic acid GO (HA-GO) and basal-functionalized hydroxamic acid CG (HA-CG), using carbodiimide activation of carboxylic acids[26] on GO and CG, respectively (Scheme S2). This represents one of the first times hydroxamic acids have been installed on a graphenic material. To confirm that hydroxamic acids were covalently installed on the edge and basal plane of graphenic sheets, a multifaceted characterization approach including XPS, FTIR spectroscopy, and proton nuclear magnetic resonance (^1H NMR) spectroscopy was used.

Elemental XPS confirmed hydroxamic acid FGMs contained nitrogen (Figure S2), which is an element unique to hydroxamic acids. Furthermore, the nitrogen content of HA-GO and HA-CG was consistent with the number of carboxylic acids on GO and CG that could be used for functionalization. FTIR and ^1H NMR spectroscopy analysis (Figures S4 and S5) confirmed that hydroxamic acid FGMs did not contain nitrogen impurities from the synthetic pathway (see Supporting Information for discussion). Thus, the nitrogen content detected in the hydroxamic acid FGMs via XPS was a result of hydroxamic acid functionalization of the graphenic backbone.

3.2.3. Catechol-Functionalized FGMs. Edge and basal plane functionalization of graphenic materials with catechol moieties was accomplished using thionyl chloride amidation. We have previously reported the successful synthesis of catechol GO (CGO) and catechol CG (CCG).[25] Briefly, GO and CG are treated with thionyl chloride to convert carboxylic acids into acyl chlorides, which are more reactive electrophiles. Then activated GO and CG are coupled to an amine-containing catechol, generating an amide linkage between the graphenic backbone and the catechol (Scheme S2).

Here, CGO and CCG were successfully coupled with catechols. FTIR spectroscopy shows the characteristic carboxylic acid stretch at 1720 cm^{-1} for GO and CG. After catechol conjugation, the carboxylic acid stretch shifts to 1705 cm^{-1} and increases in intensity for CGO and CCG, suggesting the formation of an amide bond (Figure S1). Furthermore, an element unique to the catechol molecule (nitrogen) was detected by XPS in CGO and CCG (Figure S2). Deconvolution of XPS high-resolution nitrogen spectra showed the presence of an amide peak at 398.8 eV for CGO and CCG (Figure S6), confirming that some of the catechol molecules in CGO and CCG were covalently bound to the graphenic backbone.

3.3. Chelation Capacity and Regeneration of FGMs. All six of our FGMs-chelated aluminum in AMD-like conditions at pH 4. Here, FGMs were exposed to acidic water contaminated with high concentrations of aluminum, and the capability of FGMs to chelate aluminum was confirmed using two approaches. One method analyzed the amount of aluminum removed from solution using a graphite furnace (Figure 2B). The second method analyzed the amount of aluminum on the recovered FGMs via XPS (Figure 2B,D) and energy-dispersive X-ray (EDX) spectroscopy (Figure 2C). Although the graphite furnace analyzes bulk samples and XPS examines surface properties, these results corroborate that FGMs have the capacity to remove up to 21 μg of aluminum/mg of FGM.

The aluminum chelation capacity of FGMs is influenced by the amount and identity of chemical moieties on the graphenic scaffold. Graphite furnace and XPS analyses suggest that basal-functionalized FGMs chelate more aluminum than edge-functionalized materials (Figures 2, Figures S7 and S8). We hypothesize the advantage of basal plane functionalization may be a result of more functionalization and intersheet chelation, where intersheet chelation is represented in Figure S9. The basal plane of FGM sheets have a larger surface area to install more functional groups when compared to the edge of sheets. We found that basal plane FGMs had more carboxylic and hydroxamic acids than their edge-functionalized counterparts (Figures S3 and S8). Basal-functionalized materials may form stronger associations with aluminum through intersheet chelation, which is less favorable for edge-functionalized FGMs (Figure S9). Furthermore, CG, CGO, and CCG containing carboxylic acid and catechol moieties chelated the most aluminum (up to 21.4 μg/mg for CGO).

The amount of aluminum pollution at different AMD sites can vary over orders of magnitude. Furthermore, aluminum concentrations at individual AMD sites fluctuate seasonally.[8] Consequently, our technology would be most efficacious as a polisher to remove persistent aluminum in AMD environments that have already been remediated for iron (i.e., at pH 4 or higher).

High-resolution aluminum XPS demonstrates that aluminum is removed in different chemical forms by FGMs. All six FGMs removed aluminum as aluminum particles because of a characteristic peak at 74.5 eV (Figure 2D). We hypothesize that oxygen groups on the edge and basal plane of FGMs may serve as nucleation sites for aluminum precipitation. CGO and CCG also contained a peak at 74.5 eV, indicating the materials also promoted aluminum precipitation. However, catechol FGMs also had a more predominant peak at 70.5 eV, resulting from chelated aluminum ions.

We tested the reversibility of chelation to determine if FGMs could be regenerated for reuse (Figure S10). Aluminum was sequestered in two forms on FGMs: as aluminum ions, held in coordination complexes, and as particulate precipitates. Aluminum was completely removed from edge- and basal-modified FGMs containing carboxylic and hydroxamic acids. However, only 49% and 57% of aluminum was removed from CGO and CCG, respectively. In these FGMs, all particulate aluminum was removed, but the ionic aluminum remained, demonstrating the irreversibility of the chelation bond with catechol groups. This was confirmed by the 70.5 eV peak in the high-resolution XPS aluminum spectra (Figure S10).

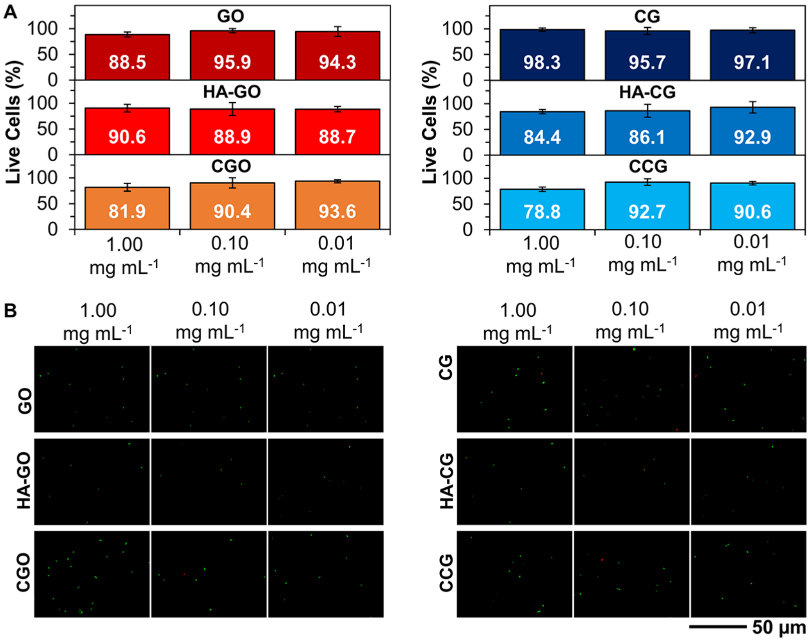

Figure 3. Microbial compatibility of FGMs with *E. coli* using the LIVE/DEAD BacLight assay. (A) Percentage of live bacteria after exposure to 0.01, 0.1, and 1.0 mg mL^{-1} of FGMs for 16 h at 37 °C. The percentage of live bacteria is normalized to the no treatment control. Bars represent the average of $n = 3$ replicates and the error bars are the standard deviation. (B) Fluorescence microscopy images of bacteria after exposure to 0.01, 0.1, and 1.0 mg mL^{-1} of FGMs for 16 h at 37 °C. Note that green fluorescence (live cells) results from the SYTO 9 stain, whereas red fluorescence (dead cells) is due to the propidium iodide stain.

The long-term stability of chelating groups on FGMs in AMD-like conditions suggest materials could be used for extended periods of time. Here, we found chelating groups on FGMs were stable in AMD-like conditions (pH 4) for 1 week or longer. Appreciable chemical changes in FGMs were not observed by XPS (Figures S11−S13) (see Supporting Information for an additional discussion).

3.5. Ecological Impact of FGMs. Small concentrations of FGMs that may enter the environment are expected to have minimal ecological effects because of the compatibility of FGMs. Previously, our group demonstrated the compatibility of FGMs with mammalian models in vitro and in vivo.[27,28] However, there is a still a pervasive consensus that FGMs have bactericidal effects, which could be detrimental to microflora essential to ecological food chains. Recent studies have shown that FGMs are not bactericidal; rather, FGM impurities account for the reported antimicrobial activity of these materials.[29] Considering this, we have found FGMs are well-tolerated by *Escherichia coli*, even in unrealistically high concentrations (0.01−1.0 mg mL^{-1}) (Figure 3A,B and Figures S14−S22)).

4. CONCLUSION

Here, we report the synthesis of six unique FGMs that covalently incorporate a variety of metal-chelating groups, such as carboxylic acids, hydroxamic acids, and catechols. When tested for efficacy, all six FGMs successfully demonstrated a reversible capacity to remove aluminum from acidic water, chelating up to 21 μg/mg of FGM. Furthermore, when they were exposed to *E. coli* as an approximation for environmental compatibility, the viability was unaffected, even at high concentrations, suggesting these FGMs are nontoxic. Thus, these FGMs fulfill our design criteria and show promise as a viable means for aluminum remediation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c06958.

Additional experimental data and methods, results and discussion, reaction schemes, figures, and references (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AMD, acid mine drainage; FGM, functional graphenic material; GO, graphene oxide; CG, Claisen graphene; HA-GO, hydroxamic acid graphene oxide; HA-CG, hydroxamic acid Claisen graphene; CGO, catechol graphene oxide; CCG, catechol Claisen graphene; HSAB, hard soft acid base; FTIR, Fourier transform infrared; XPS, X-ray photoelectron spectroscopy; ^{1}H NMR, proton nuclear magnetic resonance; EDX, energy-dispersive X-ray

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