Disulfide polymer grafted porous carbon composites for heavy metal removal from stormwater runoff

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HIGHLIGHTS

- The novel disulfide polymer grafted activated carbon composites were devised.
- Covalent bonds between disulfide polymer and carbon substrate have been proven.
- DiS-AC showed rapid kinetics on removing heavy metal in overall range of pH 6–8.
- DiS-AC showed high affinity towards even for trace amount of heavy metal in water.

GRAPHICAL ABSTRACT
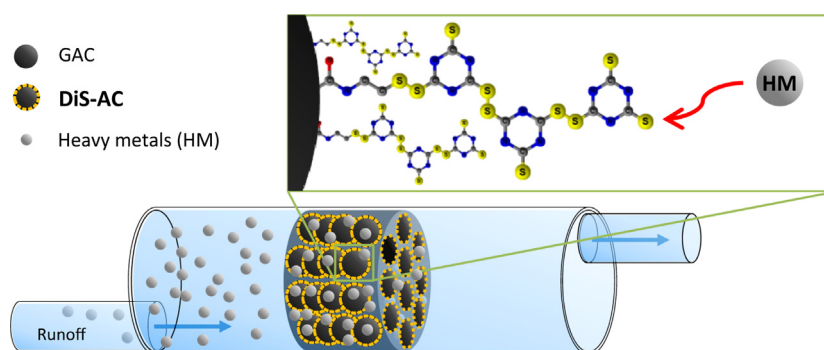
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ABSTRACT

The emerging concern of heavy metal pollution derived from stormwater runoff has triggered a demand for effective heavy metal sorbents. To be an effective sorbent, high affinity along with rapid sorption kinetics for environmental relevant concentrations of heavy metals is important. Herein, we have introduced a new composite suitable for trace metal concentration removal, which consists of cheap and common granular activated carbon covered with polymers containing soft bases, thiols, through acyl chlorination (DiS-AC). Material characterization demonstrated that the polymer was successfully grafted and grown onto the surface of the carbon substrate. The distribution coefficient for Cd^{2+} bonding was $89 \cdot 10^3$ L/kg at a solution concentration of 0.35 mg/L, which is notably higher than sorption affinities for Cd^{2+} seen in conventional sorbents. The sorption isotherm is well described by the Freundlich isotherm and within an hour, half of the initial trace (0.2 mg/L) concentration of Cd^{2+} was removed by the DiS-AC at a sorbent loading of 2 g/L. Therefore, the novel material DiS-AC promises to be an ideal candidate for filters treating stormwater runoff.

1. Introduction

Climate change has brought frequent, unexpected rainfall events that come along with the arising problem of stormwater runoff and subsequent drainage overflows [1]. A wide range of hazardous pollutants are released from these non-point sources and may cause epidemic

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problems to populations [2]. Among the pollutants, heavy metals are a notable problem, not only from urban stormwater runoff, but also in agricultural runoff. Urban stormwater runoff has limited natural infiltration due to the paved surface in cities, and thus a considerable amount of lead, copper, cadmium, and zinc from roads are washed off [3,4]. Additionally, roofs of buildings and atmospheric deposits also exacerbate heavy metal contamination during rainfall events [1,5]. Agricultural runoff also presents noticeable heavy metal pollution; in particular, heavy metals are a well-known problem in Europe and Asia due to the widespread heavy metal contamination of phosphate fertilizers [6,7]. Heavy metals are persistent, easily accumulated in biota, and result in adverse impacts on the human body. According to previous studies, heavy metal concentrations in stormwater runoff often exceed the emission limit values [8,9]. Even though there are already many proven existing ways of removing heavy metals from source waters, uncertainties revolving around stormwater runoff, such as the irregular and often poorly controlled flow or unpredictable concentrations of pollutant contained within will persist. Thus, decontamination of heavy metals from stormwater runoff has been extensively studied and different applications developed, such as wet detention ponds, filtration, and trapping in underground catchment basins. Wet detention ponds are widely applied in urban outskirts due to its simplicity, providing higher hydraulic retention times by buffering runoff flow during storm events [10]. However, wet detention ponds are hard to use in urban areas, as they require a large footprint. Therefore, catchment basins and filtration systems, which are relatively compact, are commonly used in cities. For heavy metals, removal by adsorption is proven to be an optimal technique compared to other mechanisms for efficient treatment of stormwater runoff [11,12]. Adsorption also provides for low investment costs due to the capability of treating large volumes of runoff within short time periods [12,13]. The most commonly used sorbents for removing heavy metals are sand, zeolite, and activated carbon [12]; however, applicability of these sorbents is limited when the treatment procedure needs instant removal of the pollutant coupled with high efficiency. Ideally, sorbents for contaminants in stormwater runoff should exhibit high selectivity and rapid sorption kinetics, as well as sufficient sorption capacity to increase the life length of the filter material. In recent years, a new generation of highly porous covalently bonded organic polymers that are extremely robust have been developed. These sorbents have been used for gas capture [14–16], solvent uptake [17], and groundwater remediation [18]. In our previous study [19], we have introduced a disulfide linked polymer network material, that involves thiol groups combined with triazine rings. In virtue of its chemical functionality, high sorption selectivity for soft Lewis acid heavy metal ions in the presence of earth metal ions was achieved [20]. Moreover, the sorption kinetics and metal sorption capacity was proven to be sufficient for use in stormwater runoff. The main challenge for using polymers in treatment filters is their small grain size, less than 50 μm, which may lead to hydraulic pressure overload and massive amounts of grain loss during the process.

In this study, a novel composite was introduced by grafting dangling thiol handles on the backbone of cheap and common granular activated carbon (DiS-AC) through acyl chloride surface modification. The successful polymer grafting was confirmed through extensive physical and chemical characterizations. Moreover, the composites exhibit high sorption affinity along with rapid kinetics, which can then be retrofitted on to common filtration column treatment systems for stormwater runoff.

2. Material and methods

2.1. Materials

Granular activated carbon (GAC, 2–3 mm particle grade) was purchased from Samchun Chemical Co. Nitric acid (60%) and sulfuric acid (47%), thiol chloride (99%), dimethylformamide, N,N-

diisopropylethylamine, cysteamine, sodium hydroxide, thiocyanuric acid, iodine, and potassium iodide were obtained from Sigma-Aldrich. Aqueous solutions of cadmium were prepared from 1000 mg cadmium standard solution ($CdCl_2$ in H_2O, Titrisol). All chemicals were used as received, unless otherwise stated. As a reference material, disulfide polymer was prepared by following the procedure previously published [19].

2.2. Surface modification of GAC

The surface modification processes were conducted in four steps, those being GAC oxidation, acyl chlorination [21], linear thiol attachment, and ultimately disulfide linked polymer grafting onto the substrate surface. Firstly in the aforementioned step processes, the GAC oxidation was performed with a 3:1 mixture of HNO_3 and H_2SO_4 for 24 h at room temperature to form carboxylic groups on the GAC surface. Secondly, acyl chlorination was achieved by stirring the oxidized GAC in dichloromethane while thionyl chloride was slowly added into the solution under N_2 atmosphere, in order to prevent hydrolysis of the newly formed acyl chloride groups; the solution was mixed under reflux for 24 h at 35 °C. Subsequently, the solvent was evaporated by rotary evaporator at 200 mbar of vacuum, followed immediately by a linear thiol attachment step. The thiol attachment was done by adding a mixture of 2 mmol of cysteamine dissolved in 180 mL of dimethylformamide to the acyl chloride activated GAC, followed by dropwise addition of 5.6 mmol of N,N-diisopropylethylamine. After 24 h of stirring at 80 °C, the cysteamine treated GAC was dried in vacuum at 80 °C for 12 h and dispersed again into 150 mL of sodium hydroxide solution with 3 mmol of trithiocyanuric acid for the last step. A strong oxidant containing an excess amount of iodine and potassium iodide was added dropwise into the mixture, while a temperature of 0 °C was maintained, until the mixture became a homogeneous solution; then, it was stirred overnight at room temperature. Finally, the surface modified composite (DiS-AC) was obtained and dried at 80 °C in a vacuum oven (See Fig. 1).

2.3. Characterization of the disulfide-linked polymer grafted activated carbon (DiS-AC)

Various characterization techniques were implemented on the materials produced throughout this study. Scanning electron microscopy (SEM, Quanta FEG 200 ESEM, FEI) was employed to observe the morphology of the materials and the Brunauer-Emmett-Teller (BET) surface area was measured by N_2 physisorption (3Flex, Micromeritics) after degassing the sample overnight under vacuum at 80 °C prior to measurement. Elemental analysis (EA, Vario Macro Cube, Elementar) was used to measure and calculate the composition of the materials, namely, carbon, nitrogen, and sulfur. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, data deconvolution was done by Thermo Avantage Software) was employed in order to determine the surface elemental profiles of the materials; samples were analyzed under vacuum with a monochromated Al-Kα X-ray source and an X-ray spot size of 400 μm. Thermo-gravimetric analysis (TGA, Discovery TGA, TA Instruments) was employed to evaluate the robustness and thermal stability of the materials, and subsequently coupled with Fourier-transform infrared spectroscopy (TGA-FTIR, Nicolet iS10, Thermo Scientific) to determine the functional groups degassed off samples during analysis.

2.4. Sorption kinetics studies

Three different cadmium concentrations were selected for determining the sorption kinetics of DiS-AC. All tests were conducted in triplicate, in addition to a control test. Firstly, 40 mL of 0.2, 0.35, and 0.5 mg/L cadmium chloride solution mixed with 3 mM of $NaHCO_3$ buffer were placed into polyethylene conical centrifuge tubes and
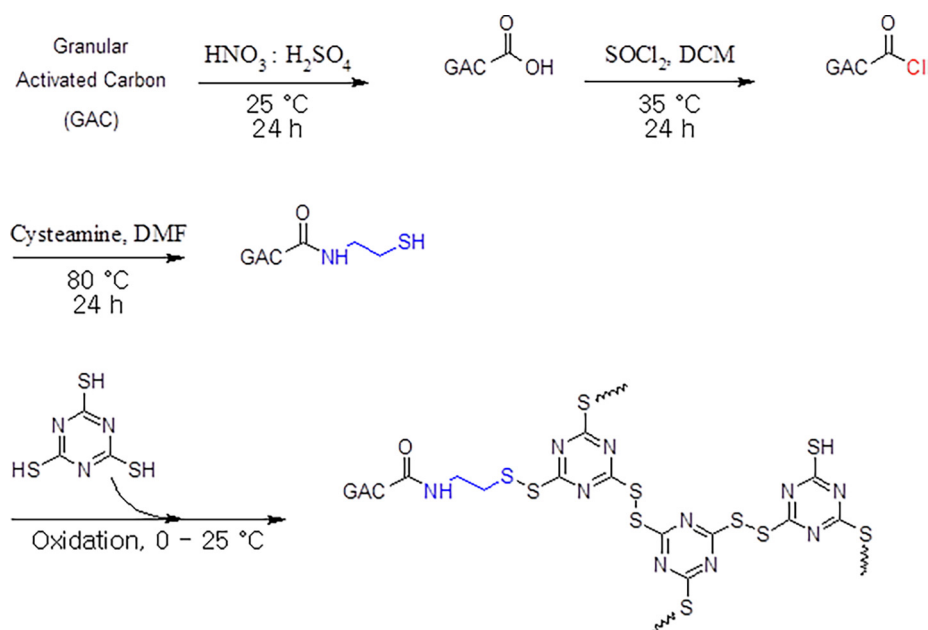
Fig. 1. The step-wise procedure of DiS-AC synthesis. Initially, bare GAC is oxidized and modified through acyl chlorination. Afterwards, cysteamine is attached to the surface. Finally, disulfide polymer grafting has been implied on the cysteamine treated GAC.

adjusted to approximately a pH of 8 by addition of 1 M HNO$_3$. The sample pH was stabilized for 1 h and initial samples were taken from the centrifuge tubes. Afterwards, 80 mg of DiS-AC were added to each centrifuge tube and sampling was performed at 2 min, 10 min, 1 h, 4 h, and 24 h. Each sample was centrifuged (1690*g*), then 1.5 mL of supernatant was collected and then acidified with 20 µl of HNO$_3$. Cadmium concentration was determined by graphite furnace atomic absorption spectrometer (GFAAS, Perkin Elmer, PinAAcle 900Z; LOD 0.1 µg/L).

2.5. Sorption as a function of pH

The effect of pH (6–8) on cadmium sorption to DiS-AC was scrutinized with the following procedure with replicates. A solution containing 10 mL of 0.5 mg/L cadmium chloride solution mixed with 3 mM NaHCO$_3$ buffer was adjusted to the desired pH by addition of 1 M HNO$_3$. The initial sample was collected after 1 h of pH stabilization, and then 20 mg of DiS-AC were added and shaken, and samples were taken after 1 h and 24 h. All samples were centrifuged and acidified with 20 µl of HNO$_3$, as described above. Samples were kept at 4 °C until measurement and cadmium concentrations were determined, as described above.

2.6. Maximum sorption capacity and sorption isotherm studies

Sorption isotherms were determined using four different cadmium concentrations with different DiS-AC dose (SI, Table A.1). Tests followed the same procedure as described above, except for the sampling times, which were 0 h and 24 h. Cadmium concentrations were determined as described above.

2.7. Sorption kinetics and isotherm fitting

To describe the sorption kinetics, both pseudo first-order and second-order kinetics models were tested. Pseudo first-order kinetics, suggested by Lagergren (1989) [22] were used for fitting the sorption kinetics using the linear form, of which is formulated as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

where, q_e and q_t are the amounts of metal ions adsorbed (mg/g) at equilibrium and time t, and k_1 is the rate constant of the sorption (1/

min).

The next sorption kinetics model, given by Ho and McKay (1999) [23], applied pseudo second-order kinetics, expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q_e})t \tag{2}$$

where, k_2 is the rate constant (g/mg·min) [23].

Sorption isotherm data were fitted by the Langmuir isotherm:

$$q_e = \frac{q_m a_L C_e}{1 + a_L C_e} \tag{3}$$

where, q_m is the maximum sorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate in solution (mg/L), and a_L is the Langmuir affinity constant (L/mg).

The data were also fitted by the Freundlich isotherm model:

$$q_e = K_F C_e^{1/n} \tag{4}$$

where, K_F is the Freundlich constant and $1/n$ is the heterogeneity factor.

The distribution coefficient for heavy metal bonding to the sorbent is given by [24]:

$$K_d \triangleq \frac{C_S}{C_w} = \frac{C_i - C_e}{C_e} \times \frac{V}{m} \tag{5}$$

where, C_i is initial concentration of cadmium in aqueous solution, C_e is the equilibrium concentration of cadmium in solution (mg/L), V (mL) the volume of solution, and m the mass of sorbent (g).

3. Results and discussion

3.1. Physical properties of the DiS-AC materials

First evidence of the successful attachment of DiS-AC was gathered using scanning electron microscopy (SEM). The structure of bare GAC (Fig. 2a, c) exhibits a random and amorphous porous nature commonly found in all GACs [25]. However, after the surface modification and grafting of the polymer, the pores of GAC are substantially covered by polymer networks, as is visualized by the observed coating effect seen in SEM imaging (Fig. 2b, d).

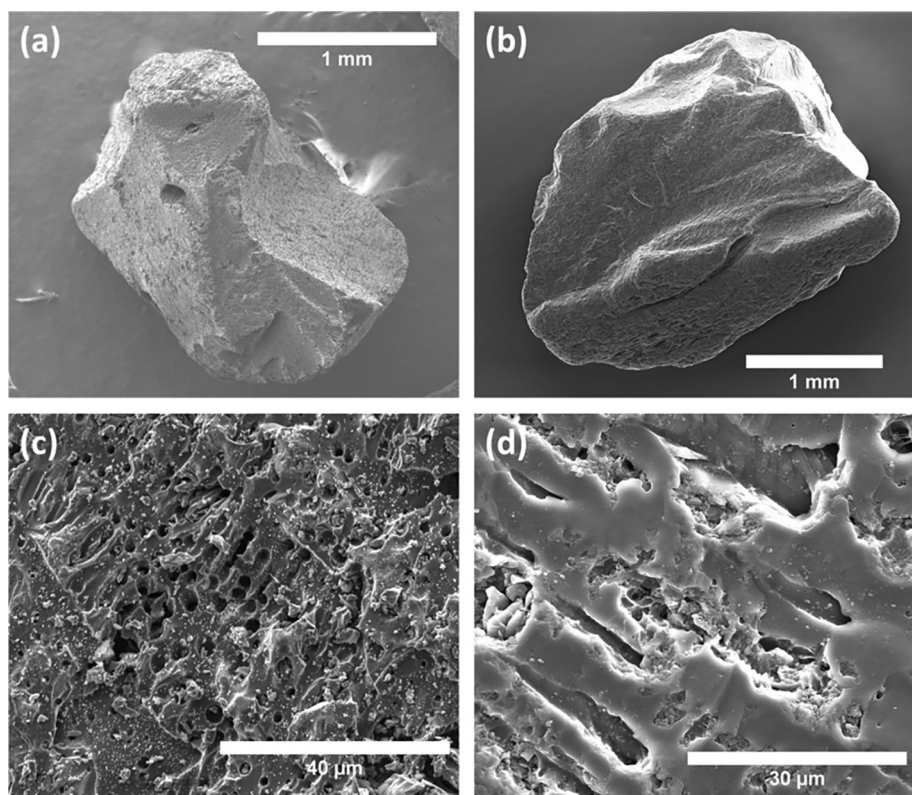The DiS-AC Brunauer-Emmett-Teller (BET) surface area was

Fig. 2. Scanning electron microscopy images of (a) overview morphology of GAC (b) overview morphology of DiS-AC (c) GAC surface and (d) DiS-AC surface.

determined to be 674 m^2/g, while the bare GAC possessed a slightly higher BET surface area of 943 m^2/g, indicating that the polymers have infiltrated and somewhat covered the porosity of the GAC. It is important to note that even though the grafted polymers appear to be blocking a discernible amount of pores of the GAC, there is still quite a high surface area remaining, due primarily to the porosity of polymer network itself.

3.2. Elemental composition and surface chemistry of the DiS-AC

The overall chemical composition was determined using elemental analysis (EA), finding that the DiS-AC consists of approximately 77.2% carbon, 1.5% nitrogen, and 1.4% sulfur. Assuming that there is a monomer unit of $C_6ON_4S_4H_5$ in the polymer, then the measured contents of nitrogen and sulfur corresponds to a content of 4% (by mass) of the polymer in the GAC, which is compatible with the experimental observation weight difference measured between bare GAC and DiS-AC. Surface elemental characterization of the different DiS-AC or GAC preparations was achieved using X-ray photoelectron spectroscopy (XPS). With a material penetration depth of 5–10 nm, XPS provides a convenient measure for the elemental make-up of specifically the surface of a particular material, making this an ideal method for confirming that polymers are grafted to the GAC surface. XPS determined that the carbon substrate surface (Fig. 3a) is primarily carbon (92%) with a minor amount of defects contained in the form of oxygen (8%) (Table 1). Acid oxidized carbon substrate expectedly contains slightly more oxygen (+ 2.4 to 10.4%), cysteamine (C_2H_7NS) grafted carbon substrate introduces the presence of nitrogen (2.6%) and sulfur (0.9%), and finally DiS-AC (Fig. 3b) yields slightly higher nitrogen (3.6%) and sulfur (1.0%) quantities due to the added presence of thiocyanuric acid monomer polymerized with cysteamine (Table 1).

In order to gain further insight into the nature of the grafted polymer to the carbon substrate surface, a technique known as ion-etching was employed with the XPS instrument, in order to

consecutively strip away layers off the surface of a material to expose underlying components. The ion-etching removes on average 50 nm of material from the surface of the sample being analyzed. In particular, the sulfur S2p region was delved into and the associated sulfur chemistry was elucidated throughout subsequent layers (Fig. 3c, d). Fig. 3c illustrates the changing nature of the sulfur chemistry as layers are ion-etched off the surface. Fig. 3d gives the deconvoluted peaks seen in the depth profile, with four commonly observed peaks present [26,27]. The two primary peaks are attributed to disulfide S-S (163.9 eV) and sulfur oxide S-O (168.4 eV) while the two secondary peaks may be referred to S-C (165.4 eV) and S-H (163.2 eV); with the sulfur oxide groups very much present at the surface and quickly disappearing in the underlying layers. Therefore, XPS layer analysis proved that the surface of the material is covered by sulfur containing polymer.

3.3. Thermo-gravimetric analysis (TGA)

In order to determine the robustness and thermal stability of the produced materials, thermo-gravimetric analysis (TGA) was run on bare GAC and DiS-AC. Bare GAC demonstrated an overall drop in weight by roughly 13% at temperature rising from 30 to 900 °C, which is in agreement with a previous study of GAC surface modification using the same carbon substrate [21]; while DiS-AC resulted in an overall drop in weight by roughly 28% over the same temperature range (See Fig. 4).

It should be noted that there is an observable correlation in the disulfide polymer TGA curves and the grafted DiS-AC curves, in that there are similar mass loss trends at similar temperature profiles. It can be inferred that this indicates that the same material is being vaporized and degassed in both materials. Moreover, the weight loss of DiS-AC due to the polymer thermal degradation up to 250 °C is approximately 6%, which is similar to the calculated empirical grafted polymer percentage, i.e. 4%. For further confirmation, FTIR measurement was coupled with the TGA off-gas stream (TGA-FTIR) to qualitatively characterize those materials being degasses during TGA analysis, see
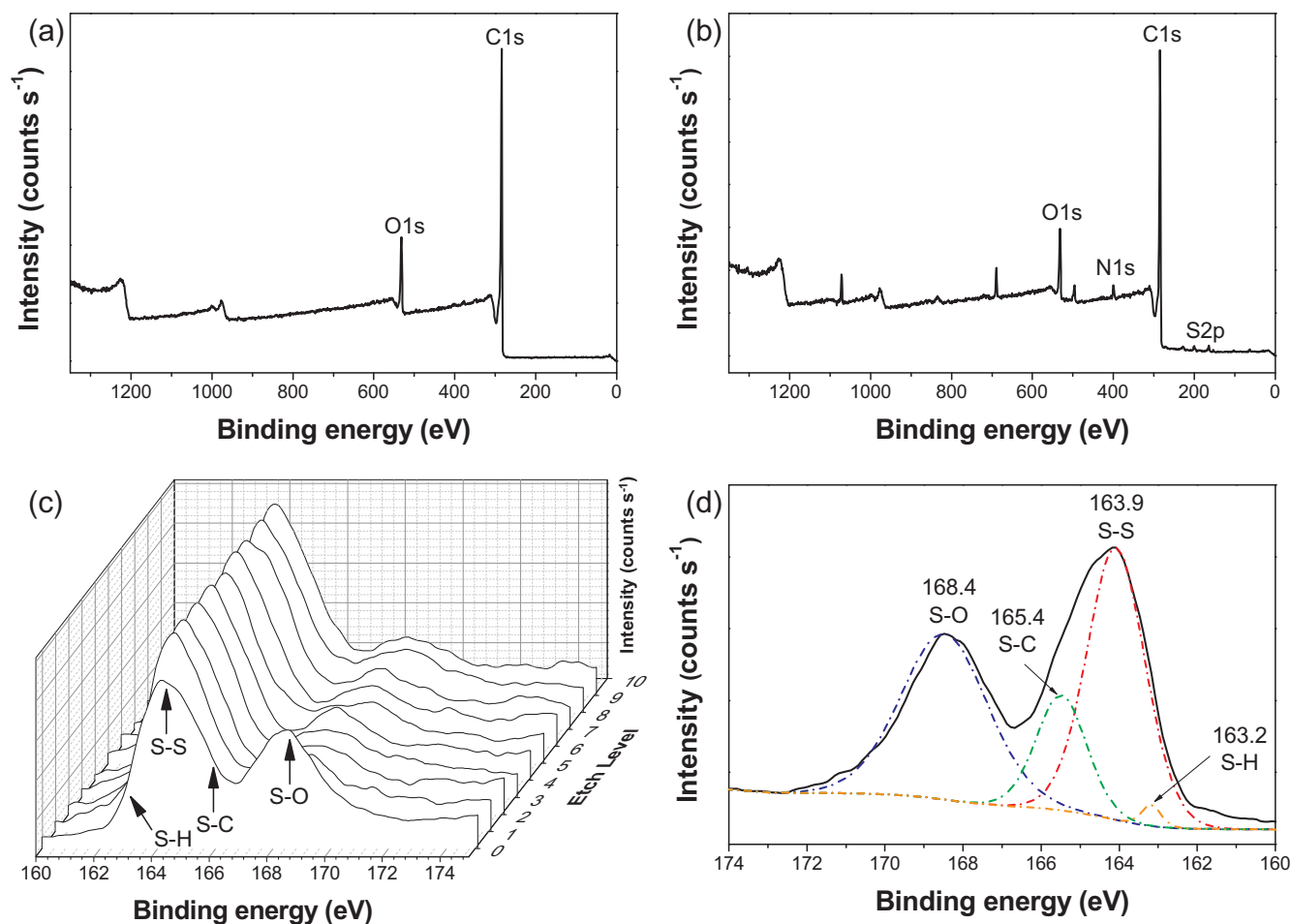
Fig. 3. X-ray photoelectron spectra. (a) Bare GAC survey scan. (b) Polymer grafted DiS-AC survey scan. (c) Depth profile for ion etched S2p scans for DiS-AC (note that the x-axis has been reversed to better display peak variation). (d) Peak deconvolution of S2p scan etch-0 (before etching took place) for DiS-AC.

Table 1
Surface atomic percentages of the different steps of the surface modified GAC, as determined by XPS.

Element	GAC	GAC-oxidized	GAC-cysteamine	DiS-AC
C	92.0	89.6	83.9	80.5
O	8.0	10.4	9.8	9.5
N	–	–	2.6	3.6
S	–	–	0.9	1.0
Other	–	–	2.9	5.3

Fig. 5.

Initially, at the ambient instrument analysis temperature (i.e. 36 °C), no discernible peak pattern is found in the spectra of the DiS-AC being analyzed; however, after overlooking the peaks stemming from water/humidity in the sample spectra at 100 °C, starting at 200 °C the peaks in the spectra of the grafted polymer begin to emerge. Functional groups, including C=O, N−H, and C−N, can be detected at 1720, 1530, and 1390 cm^{-1}, respectively. Evidence of the grafted polymer also appears in the FTIR spectra; around 200 – 300 °C, the first peak for C-S is observed, as was also reported by Halas et al. (2010) [28]. Furthermore, a series of peaks attributed to the C-S bond are found in the range of 720–615 cm^{-1}, typical of organo-sulfur compounds [29], that become more and more pronounced as the analysis temperature increases. Finally, although typically having an extremely weak signal in IR analysis [30], two very minor peaks corresponding to the S-S disulfide bond are observed at 495 and 470 cm^{-1} at the very high temperatures during analysis.
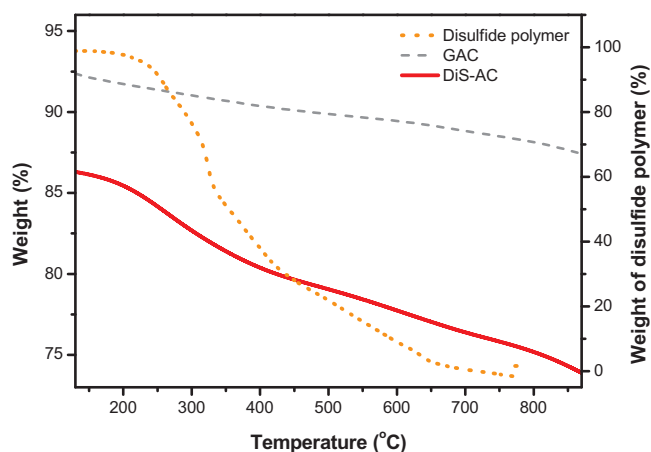

Fig. 4. Thermo-gravimetric analysis of bare GAC (dashed line), the pure disulfide polymer (dotted line), and the grafted polymer DiS-AC (solid line).

3.4. Kinetics of cadmium sorption for DiS-AC

The trends of the sorption kinetics at three different initial concentrations (0.2, 0.35, and 0.5 mg/L) are comparable when normalized to the initial concentrations (Fig. 6a). Hence, the lowest initial concentration of 0.2 mg/L was selected for kinetics fitting, using pseudo first-order kinetics (Eq. (1)) and pseudo second-order kinetics (Eq. (2)) (Fig. 6b, c). Both kinetics models fit well with the data based on the
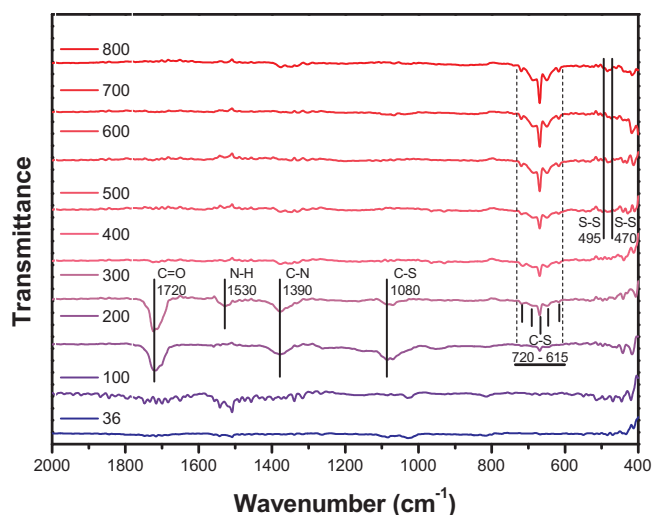
Fig. 5. TGA-FTIR analysis of DiS-AC, plotted as a function of TGA analysis temperature (i.e. 36 – 800 °C). Peaks at 495 cm^{-1} and 470 cm^{-1} correspond to the S-S disulfide bond. Peaks from 615 cm^{-1} to 720 cm^{-1} and 1080 cm^{-1} indicate typical organo-sulfur bonds. Peaks at 1390 cm^{-1}, 1530 cm^{-1}, and 1720 cm^{-1} are representing C−N, N−H, and C=O bonds, respectively.
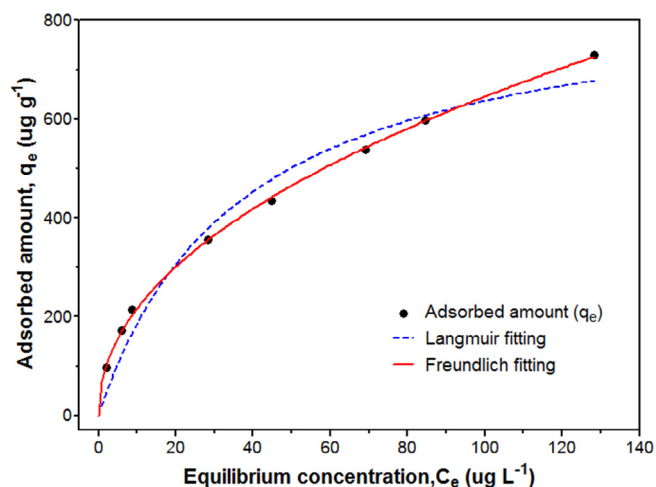

Fig. 7. Sorption isotherms of cadmium ion sorption on disulfide-linked polymer grafted carbon substrates (DiS-AC). The red solid line represents the non-linear fitting of data by the Freundlich model, while the blue dashed line represents fitting by the Langmuir model.

Table 2
Parameters corresponding to the Freundlich sorption isotherms and solid-water partitioning coefficients (K_d) at a solution concentration of 0.35 mg/L for DiS-AC.

	Freundlich			K_d (L/kg)
	K_F	n	R^2	
DiS-AC	73	2.12	0.99	$89.5 \cdot 10^3$

correlation coefficient. Within 53 min of contact time, half of the initial cadmium was sorbed onto the DiS-AC at a loading of 2 g/L, while standard GAC reported in a similar adsorption study with a loading of 4 g/L took 2.5 h to reach half saturation [31]. To predict real-world performance of DiS-AC in an actual stormwater filter, the required amount of DiS-AC needed in one filter has been calculated based on industry specifications [32,33], and applied in the appropriate equations for sorption determination. Assuming that the rate of sorption increases proportionally to the dose of filtering (active sorption sites) material, the DiS-AC applied in real-column type packed filter will be expected to remove approximately 97% of cadmium within 10 s.

3.5. Sorption isotherm and maximum capacity

The Langmuir and Freundlich isotherms were fitted onto the cadmium sorption plots of DiS-AC (Fig. 7). The parameters along with correlation coefficients are given in Table 2.

The Freundlich fitting was found to be far better (r^2 = 0.99) than the Langmuir fitting (r^2 = 0.77) (SI, Fig. A.1). The conformity with the

Freundlich equation indicates that the DiS-AC is a multisite sorbent, in contrast to the Langmuir model that assumes a uniform surface [34]. This also points to the inherent randomness of how the grafted polymer adheres to the surface of the GAC. It is important to note that the present experiment focused only on trace amounts of cadmium, for particular relevance with stormwater runoff applications; hence, the plots only cover the region prior to the point where the plateau effect starts in the Langmuir isotherm.

The Freundlich constant, K_F, reflects the affinity of the sorbate [35]; and, with a K_F of DiS-AC of 73 [(mg g^{-1})(mg^{-1})$^{1/n}$], this is roughly 50 times higher affinity compared to GAC and 174 times higher when
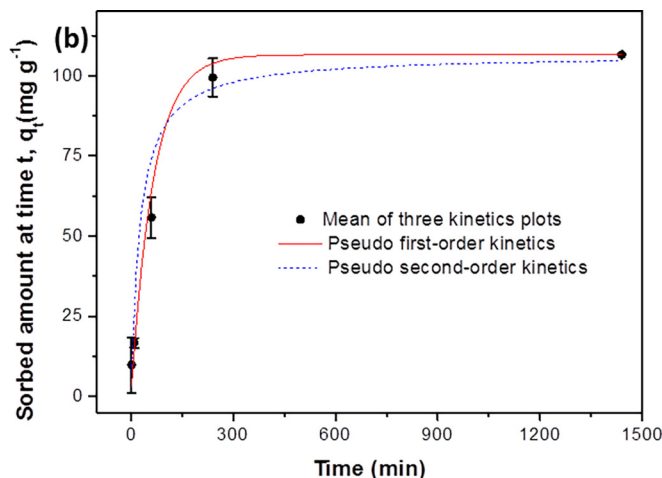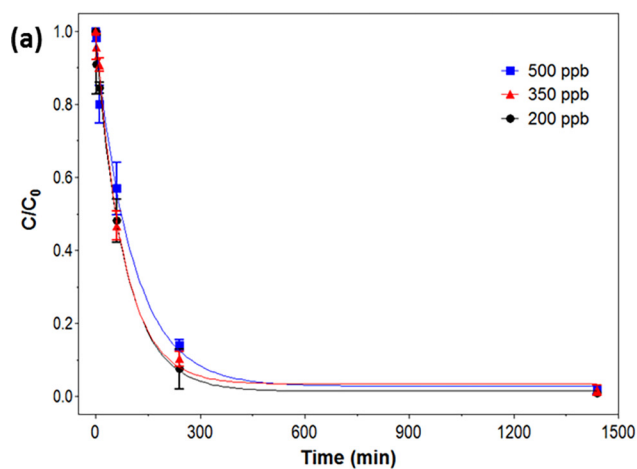

Fig. 6. (a) Sorption kinetics for cadmium sorption to DiS-AC in batch experiments, with a DiS-AC loading of 2 g/L, examined at three initial cadmium concentrations and plotted using normalized y-axes. (b) Pseudo first-order kinetics and pseudo second-order kinetics fittings for an initial cadmium concentration of 0.2 mg/L. Error bars represent the standard deviation for replicates.
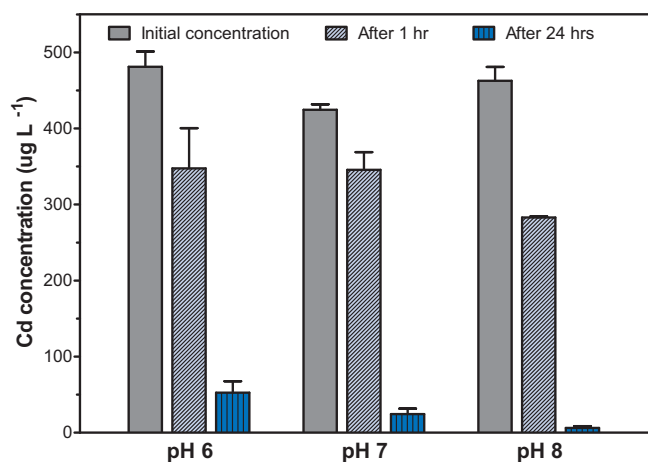
Fig. 8. Effect of pH on the sorption of DiS-AC in batch experiments, with 2 g/L sorbent dosage at 0.5 mg/L cadmium solution concentration. Grey columns represent the initial concentration of cadmium, light blue columns represent the concentration after 1 h of reaction time, and dark blue columns represent the remaining cadmium concentration after 24 h of reaction time. The error bars represent the standard deviation for replicates.

compared to sand, both of which are commonly used for stormwater filtration [36,37] (SI, Table A.2). The heterogeneity and sorption favorability factor, n, was calculated from the Freundlich fitting. The value n > 1 reflects sorption with a high affinity between the sorbate and the sorbent; therefore, in this study, DiS-AC has a value of n = 2.12, indicating chemical sorption of cadmium [38,39]. The distribution coefficient (K_d) of DiS-AC at a solution concentration of 0.35 mg/L was $89 \cdot 10^3$ L/kg, which is 7.6 times higher compared to original GAC (SI, Table A.2).

3.6. Effect of pH on cadmium sorption

The sorption tests at different pHs have shown that DiS-AC efficiently retains cadmium in the pH range 6–8 (Fig. 8).

At equilibrium and an initial cadmium concentration of 0.5 mg/L, the removal percentages of cadmium were 89%, 94%, and 99% at pH 6, 7, and 8, respectively. The most effective sorption was revealed at a condition of pH = 8, with rapid sorption kinetics and higher capacity compared to other pH ranges. It is important to note that stormwater runoff in urban areas has fluctuating pH conditions within the ranges of pH 6 – 8 [40]. Therefore, DiS-AC sorption could adequately work without any need for pH adjusting pre-treatment. Moreover, the sorption characteristics of DiS-AC, which are dependent on pH conditions, were in accordance with the sorption characteristics of the disulfide-linked polymer by itself [19].

4. Conclusion

A new type of carbon substrate covered with dangling thiol handles (DiS-AC) synthesized through acyl chlorination is suggested as a stormwater runoff filtration sorbent. Both physical and chemical characterization of the material confirmed that the polymer with thiol handles are successfully grafted and grown onto the surface of the amorphous carbon substrate. Based on cadmium sorption tests, DiS-AC exhibited a distribution coefficient of $89 \cdot 10^3$ L/kg for sorbing cadmium, which is 37 times higher compared to conventional GAC sorbents. Furthermore, half of the trace amounts of cadmium ions were removed within an hour at a sorbent loading of 2 g/L. Additionally, applicability of the DiS-AC filter material at variable pHs between 6 and 8, typical for stormwater runoff pH, has been demonstrated. In conclusion, a novel material is introduced, which is a promising candidate for removing heavy metal contamination from stormwater runoff.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2018.04.192.

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