



Selective removal of heavy metal ions by disulfide linked polymer networks



Dongah Ko^a, Joo Sung Lee^b, Hasmukh A. Patel^c, Mogens H. Jakobsen^d, Yuhoon Hwang^e, Cafer T. Yavuz^b, Hans Chr. Bruun Hansen^f, Henrik R. Andersen^{a,*}

^a Department of Environmental Engineering, Technical University of Denmark, Miljøvej 113, 2800 Kgs. Lyngby, Denmark

^b Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

^c Department of Chemistry, Northwestern University, Evanston, IL 60208 USA

^d Department of Micro and Nano technology, Technical University of Denmark, Ørstedes Plads, 345B, 2800 Kgs. Lyngby, Denmark

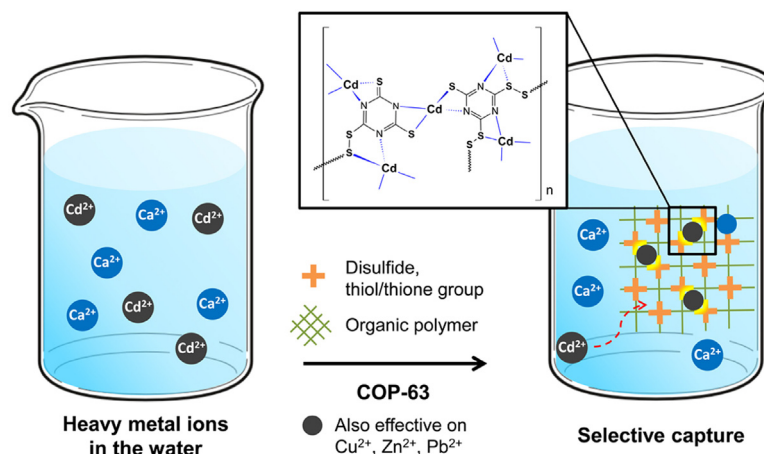
^e Department of Environmental Engineering, Seoul National University of Science and Technology, 232 Gongreung-ro, Nowon-gu, Seoul 01811, Republic of Korea

^f Department of Plant and Environmental Sciences, University of Copenhagen, Frederiksberg, Thorvaldsensvej 40, 1871 Frederiksberg C, Denmark

HIGHLIGHTS

- Disulfide/thiol polymer networks are promising as sorbent for heavy metals.
- Rapid sorption and high Langmuir affinity constant (a_L) for stormwater treatment.
- Selective sorption for copper, cadmium, and zinc in the presence of calcium.
- Reusability likely due to structure stability of disulfide linked polymer networks.

GRAPHICAL ABSTRACT



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ABSTRACT

Heavy metal contaminated surface water is one of the oldest pollution problems, which is critical to ecosystems and human health. We devised disulfide linked polymer networks and employed as a sorbent for removing heavy metal ions derived from contaminated water. Although the polymer network material has a moderate surface area, it demonstrated cadmium removal efficiency equivalent to highly porous activated carbon while it showed 16 times faster sorption kinetics compared to activated carbon, owing to the high affinity of cadmium towards disulfide and thiol functionality in the polymer network. The metal sorption mechanism on polymer network was studied by sorption kinetics, effect of pH, and metal complexation. We observed that the metal ions—copper, cadmium, and zinc showed high binding affinity in polymer network, even in the presence of competing cations like calcium in water.

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* Corresponding author.

E-mail address: henrik@andersen.net (H.R. Andersen).

1. Introduction

The heavy metal ions – cadmium, lead, copper, and zinc present in contaminated wastewater has been an epidemic problem to the environment and living organisms for millennia. Considerable amounts of heavy metals originate from industrial operations, mainly from mining, stormwater run-off and even agriculture [1–3]. Heavy metals accumulate in soils, plants, and animals due to their affinity for binding to solids and organisms [4]. The presence of heavy metal ions in water causes adverse effects on ecosystems and results in human health issues such as cancer and other chronic diseases [5]. Furthermore, through bioaccumulation and bio-magnification, the general public is vulnerable to both direct and indirect heavy metal ion consumption through food and water [1].

Among the sources of heavy metal contamination in surface water, stormwater runoff is of increasing interest to environmental engineers and regulators, since other sources have become better managed whereas stormwater runoff treatment is still treated to a limited extent, even though it is considered as wastewater in the EU legislation [6]. The limited extent of stormwater treatment is because runoff mostly occurs from a non-point source, unlike other sources of heavy metals [7]. Recently, changes in climate have added significant challenges to the stormwater runoff by changing precipitation patterns across the world to larger but more scattered rainfall events [8]. The concentration of heavy metals in stormwater varies by region and land use—residential areas, highways, industrial, farming areas and sources, such as vehicles (petrol, tire wear, brake linings), building materials (roofing, walls) [9,10], etc. Based on the recent scenario, the concentration of heavy metal ions in stormwater runoff often exceed water quality standard (WQS) values [11–13,2] in surface water. Various methods for removing heavy metals from wastewater, such as chemical precipitation [14], membrane filtration [15], ion exchange [16], and adsorption [17], have not been efficiently applied to the stormwater treatment due to the irregular occurrences of rain events and the highly variable concentrations of heavy metals in addition to other pollutants in the runoff [18]. Adsorption methods are better techniques compared to other methods for efficient treatment of contaminated stormwater due to low investment costs and because large volumes of stormwater can be treated within short time periods [19,20]. The sorption of heavy metal ions from water has been studied for decades. However, most of stormwater runoff studies have focused mainly on the heavy metal ions copper, zinc, lead, which mainly originates from building materials [21,22]. There have been only few studies of cadmium although it represent a significant contaminant originating from roads, airfields and parking lots [23].

The most widely applied sorption material is activated carbon (AC) since it has high porosity and low cost [24–26]. However, when AC is applied in water treatment it adsorbs a large variety of mostly non-ionic pollutants and nontoxic solutes, including major cations which compete for the sorption capacity of the material and cause it to become saturated quickly [17,27]. To overcome this hurdle, various minerals have been studied in passive geo-filters and these have been gradually employed for road runoff in Europe and North America [28] although these filters are only effective for selected pollutants such as lead, zinc, and organic pollutants [6]. Krishnan et al. [29] and Young et al. [30] previously evaluated the feasibility of a sulfur-crosslinked sorbent for the removal of soft acid metals. However, their study was limited to specific metal sorption without testing selectivity, and the sorption kinetics was too slow for use in stormwater cleaning.

The demand for new sorbents, which not only have a high surface area but which are also selective, continues to drive research into efficient and functionalized sorbent materials [31]. In a sit-

uation of growing environmental problems—global warming and water pollution, the breadth of potential applications is widening for these functionalized sorbents. Covalent organic polymers (COPs), which are porous networks of organic molecules interconnected by covalent bonds between monomers, were recently introduced as new, universal, and functionalized sorbents. Due to their robust properties [32], significant selectivity among gas molecules [33], low cost, and regenerability [34], COPs have been intensively studied in the field of carbon dioxide capture and storage [35]. COPs have vast potential for many kinds of pollutants and applications, and so their applicability in waste water treatment targeting heavy metal ions appears promising.

Herein, we report a disulfide-linked polymer networks (COP-63) for the removal of heavy metal ions—particularly cadmium—from contaminated water. COP-63 is synthesized using commercially available monomers following a catalyst-free facile synthetic route and synthesis can easily be scaled-up to grams scale. The polymer networks owe its removal ability to its porosity, and strong binding affinity of heavy metal ions such as cadmium, copper, and zinc, rationalized through the hard-soft acid and base (HSAB) theory. According to this theory, soft Lewis acids react preferentially with soft Lewis bases and hard Lewis acids with hard Lewis bases. This has been proven over the last decades and thus, it is commonly used to explain the stability of compounds, reaction mechanisms and pathways of metal-ligand interactions [36]. Scheme 1 depicts COP-63 sorption properties based on the HSAB theory where heavy metal ions in the water are selectively attracted to the disulfide groups and dangling thiol/thione groups in the organic polymer in presence of competing cations. Moreover, free electron pairs in nitrogen and sulfur of COP-63 are important for formation of coordination complexes with heavy metal ions [37,38]. COP-63 has high thermal and chemical stability [39,34], and it can thus be regenerated easily [32], thereby allowing for repetitive uses in water treatment applications.

We have investigated the kinetics of sorption and maximum equilibrium sorption capacity of COP-63, and compared with the sorption properties of a high-quality AC (Norit 1240W, activated by steam). Moreover, we have studied the sorption of selected heavy metals at different pH values, to estimate the role of protonation of the sulfur functionality and the effect of complexation. The competitive sorption and selectivity of specific heavy metal ions have also been investigated.

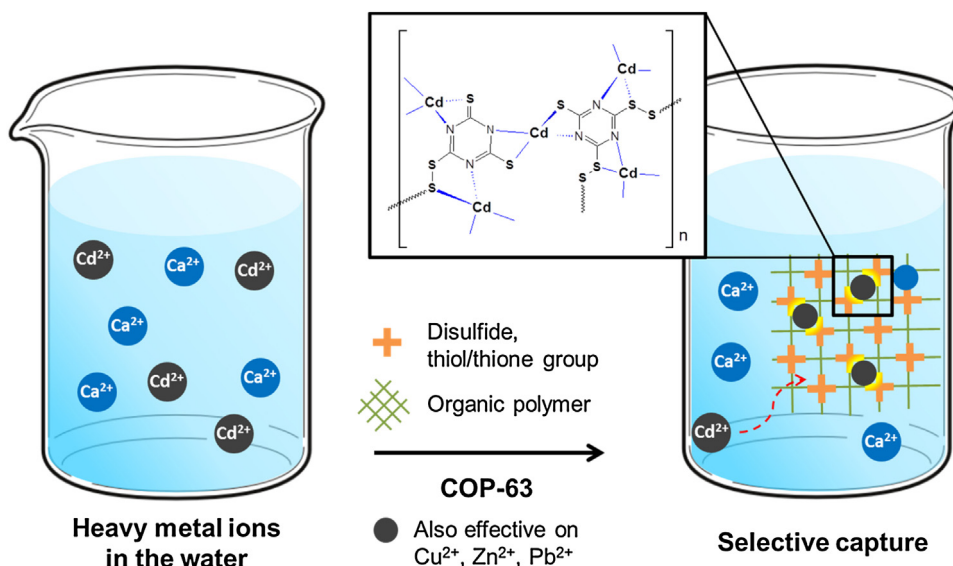
2. Experimental

2.1. Materials

Trithiocyanuric acid, sodium hydroxide, iodine, potassium iodide, and granular activated carbon (AC: Norit 1240W) were purchased from Sigma-Aldrich. Aqueous solutions of cadmium and lead were prepared from 1000 mg/L ICP standard stock solutions containing 2% w/w nitric acid purchased from Sigma-Aldrich. Zinc solutions were prepared from zinc standard stock solution for AAS, purchased from VWR, nickel solutions were prepared from chloride salt, while other metal ions solution were prepared from the nitrate salts. All chemicals were used as received, unless otherwise stated.

2.2. Synthesis of COP-63

A 250 mL round-bottom flask was placed in an ice bath, and 0.02 mol of trithiocyanuric acid dissolved in 100 mL of water containing 0.06 mol of NaOH. In a separate vial, an oxidizing solution was prepared by addition of 0.03 mol iodine into a saturated KI solution. Thereafter, the oxidant solution was slowly added to the



Scheme 1. Selective interactions among heavy metal ions and sulfur groups in covalent organic polymer suspended in water.

trithiocyanuric acid solution at 0–5 °C with stirring and the reaction mixture was stirred overnight at room temperature. Oxidation of thiol groups in the trithioscyanuric acid caused formation of disulfide bonds between the triazines and hence polymerization. The yellow precipitate was filtered and washed several times with deionized water and dried at 80 °C overnight in a vacuum oven.

2.3. Characterization of COP-63

Infrared spectra were measured with a Shimadzu IRTracer-100 ATR spectrometer. Elemental analysis was performed on a FLASH 2000 series from Thermo Scientific. To evaluate the porosity and BET surface area of COP-63, N₂ adsorption isotherms at 77 K were obtained with a Micromeritics 3Flex surface characterization analyzer after degassing the sample at 150 °C for 5 h under vacuum prior to measurement. Porosity was calculated based on the N₂-DFT pore size distribution model. Field Emission TEM 300 kV, Tecnai G2 F30 S-Twin and FEI Quanta 200 ESEM FEG were used for imaging the particle morphology. The charge and degree of COP-63 aggregation were measured according to zeta-potential and hydrodynamic diameter (HDD) on a Zetasizer 2000, Malvern, UK. Thermo-gravimetric analysis (TGA) was performed on a SHIMADZU-DTG 60A instrument by heating the sample to 800 °C in a nitrogen atmosphere at a rate of 10 °C min⁻¹.

2.4. Single metal sorption isotherms

Sorption isotherms were determined in solutions prepared from metal stock solutions and in presence of a 0.003 M NaHCO₃ buffer. pH values were adjusted by 1 M of HCl and NaOH, to fall into the range 6–7. Seven different metal concentrations, ranging between 1 and 75 mg/L, were used for the sorption isotherms, while AC was tested at four different concentrations. In a conical polyethylene (PE) tube, the cadmium solution was added to the sorbent (2 g/L). The tubes were shaken gently, and sampling started within a few minutes from start. For kinetic experiments, seven sampling times were selected (initial, 2 mins, 10 mins, 1 h, 4 h, 24 h, and 48 h). Sorbent and solution separation was performed using a 0.45 µm regenerated cellulose syringe filter (Sartorius, Minisart generated cellulose). Batches were shaken on an end-over-end rotator at 15 rpm and with a vibrating time of 5 s. All filtrates were acidified with 1% HNO₃. Cadmium at higher concentrations were deter-

mined by atomic absorption spectroscopy (FAAS, LOD: 0.016 mg/L) while lower cadmium concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, LOD: 0.1 µg/L). Very low cadmium concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS, LOD: 0.006 µg/L).

2.5. Multi-metal sorption test

A solution of five different heavy metal ions and one competitive alkaline earth metal ion, calcium, were mixed in a 0.003 M NaHCO₃ buffer solution. Initial pH values were adjusted to be in the range 6–7, by adding 1 M HCl or 1 M NaOH. The initial concentration of each heavy metal was fixed at 10 mg/L, while the concentration of the competitive metal ion was set in the range 10–100 mg/L. In a conical PE tube, the metal ion solution was added to COP-63 at a concentration of 0.2 g/L. Shaking and sampling were performed as described above. All filtrates were acidified with 1% HNO₃ and stored at 4 °C until measurement by ICP-OES (LOD: 1.3 µg/L for heavy metals, 13.2 µg/L for Ca).

2.6. Studies of the pH effect and heavy metal speciation

Solutions containing 10 mg/L of the heavy metal ions nickel, copper, cadmium, lead, and zinc, and 0.003 M of NaHCO₃, were adjusted to pH values within the range 3–10, using 1 M of HCl and NaOH and mixed with COP-63. Shaking and sampling were performed as described above. All filtrates were acidified with 1% HNO₃ and stored at 4 °C until measured by ICP-OES (LOD: 1.3 µg/L). Heavy metal speciation in solution depending on pH was calculated using the geochemical software code Visual MINTEQ ver. 3.0 [40]. In the calculations the temperature was set to 25 °C and all concentrations were the same as in the experiment.

2.7. Expression for sorption isotherm, sorption kinetics, and affinity

For sorbents with a fixed number of sorption sites, the maximum amount of metal ions sorbed to the polymer at equilibrium (q_e) can be calculated by use of the Langmuir isotherm equation:

$$q_e = \frac{q_m a_L C_e}{1 + a_L C_e} \quad (1)$$

where q_m is the maximum sorption capacity of the sorbent (mg/g), C_e is the equilibrium concentration of the adsorbate in solution (mg/L), and a_1 is the Langmuir affinity constant.

To describe the sorption kinetics, a pseudo first-order kinetic model was suggested by Lagergren (1989), the linear form of which is formulated as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

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

Another model for chemisorption was given by Ho and McKay (1999) applying pseudo second-order kinetics [41] which can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (3)$$

where k_2 is the rate constant (g/mg·min), while the other terms have the same meaning as in Eq. (2).

The affinity of the sorbent for binding of heavy metal ions can be expressed by the distribution of the metal between solid phase (C_s) and water (C_w) given by the distribution coefficient K_d (L/kg):

$$K_d \triangleq \frac{C_s}{C_w} = \frac{C_i - C_e}{C_e} \times \frac{V}{m} \quad (4)$$

where C_i and C_e are the initial and final concentrations (mg/L), respectively. V is volume of the solution (mL), and m is the mass of COP-63 used in the batch (g).

3. Results and discussion

3.1. Synthesis and characterization of COP-63

Polymerization of COP-63 was achieved through simple, one-pot synthesis involving a single monomer at ambient conditions. In the chemical structure of COP-63, each fragment has three disulfide groups that bridge to three other triazines [$C_3N_3S_3$] $_n$, and dangling thiol/thione groups at the end of polymer chains, see the structures of the monomer and the polymer in Fig. 1. The formation of disulfide linkages was confirmed by Fourier transform infrared spectroscopy (FT-IR) and elemental analysis (EA). The FT-IR spectra (Fig. 1) show peaks in the range 2899–3136 cm^{-1} for N–H stretching in triazine groups and these peaks became less when COP-63 formed. Three strong peaks at 1524, 1109, 742 cm^{-1} that correspond to the nonaromatic thione heterocycle stretching are shifted to aromatic trithiol stretching 1466, 1230, 825 cm^{-1} in the polymer, which reflects that a disulfide polymer has formed [42,43]. The peaks at 1109 and 1119 cm^{-1} represent C=S stretching in the monomer and COP-63, respectively. Peaks ranging between 460 and 540 cm^{-1} showed the formation of disulfide linkages in the COP-63 [44]. The absence of sharp S–H peaks [45] at 2500–2660 cm^{-1} and remaining C=S peaks in 1119 cm^{-1} confirms the substitution of thiol sites to disulfide and the existence of thiol/thione groups in COP-63 [43].

The elemental analysis showed that the COP-63 contain 52.5% S, 21.3% N, 19.8% C, 0.4% H, and 4.0% O. These fractions are comparable with the theoretical elemental percentage of COP-63: 0.46 mol H_2O (Theoretical S: 52.7%, N: 23.0%, C: 19.7%, H: 0.5%, and 4.0% O). BET measurements showed that COP-63 had a specific surface area of 150 m^2/g , with the majority of pores larger than 2 nm in diameter (Supplement Fig. S1); morphology characterization also showed the presence of pores in the polymer (Supplement, Fig. S6). It is expected that the pores larger than 2 nm pore size will provide faster accessibility between the sulfur functional groups and heavy metal ions during sorption. Thermogravimetric (TGA) analysis revealed that COP-63 is thermally stable up to 200 °C (Supplement, Fig. S4).

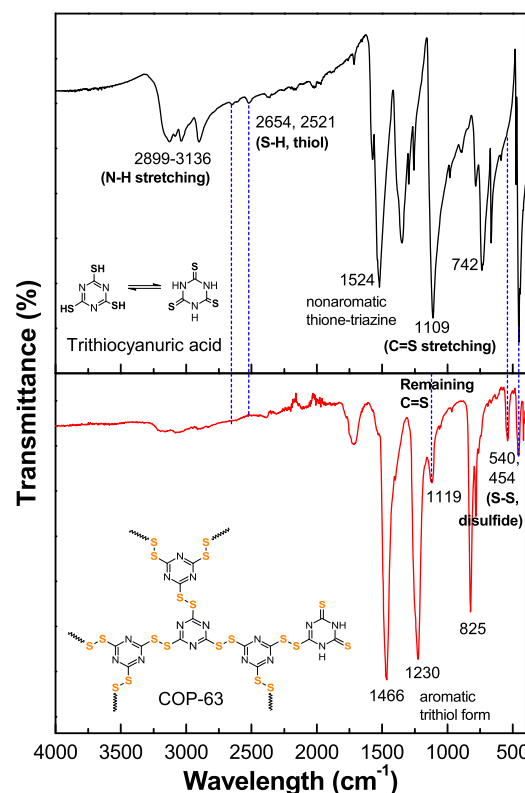


Fig. 1. FT-IR spectra of trithiocyanuric acid (black) and COP-63 (red). Distinctive absorption bands at 2899–3136 cm^{-1} (N–H, amine), 2500–2660 cm^{-1} (S–H, thiol), 700–1600 cm^{-1} (nonaromatic thione heterocycle), 800–1500 cm^{-1} (aromatic trithiol heterocycle), 1109, 1119 cm^{-1} (C=S, thione), and 460–540 cm^{-1} (S–S, disulfide). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

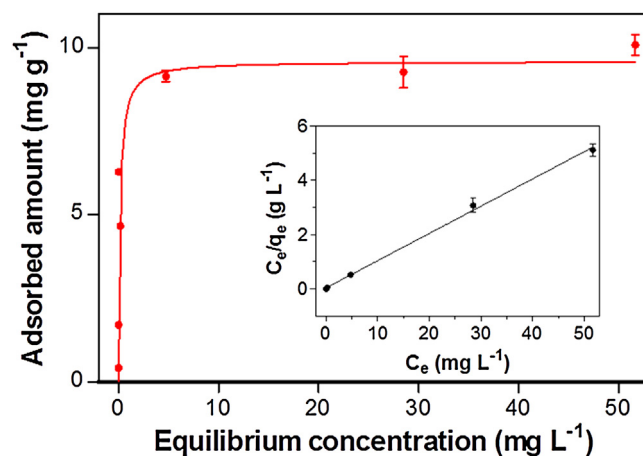


Fig. 2. Sorption isotherm for cadmium bonding to COP-63 and fitting by the Langmuir isotherm (Eq. (1)). Equilibration time of 48 h, pH 6–7, ambient conditions. Inset: Linearized form of Langmuir fitting, r^2 0.998. Error bars represent 95% confidence interval.

3.2. Heavy metal sorption equilibrium

To determine cadmium affinity and the sorption capacity of COP-63, sorption isotherms were produced. As shown in Fig. 2, the sorption isotherm data could be fitted successfully to a Langmuir sorption model.

The maximum sorption capacity of the sorbent (q_m) estimated from the Langmuir isotherm (Eq. (1)) reached 9.9 mg/g for COP-63, compared to 11.9 mg/g for AC (Supplement, Fig. S2). It is impor-

tant to note that the BET surface area of COP-63 was 150 m²/g, whereas the surface area of AC was 1100 m²/g. Based on the specific surface area, the cadmium maximum sorption capacity of COP-63 was 0.07 mg/m² compared to 0.01 mg/m² for AC. Thus, COP-63 has seven times higher sorption capacity per contact surface compared to AC. Moreover, the Langmuir affinity constant (a_L) of COP-63 was 3.43 L/mg compared with 0.39 L/mg for AC, illustrating that COP-63 has nearly 10 times higher sorption affinity compared to AC (Supplement, Table S1).

3.3. Sorption kinetics

The kinetics of sorption is one of the important parameters, providing insights into the sorption mechanism [46]. Fast sorption kinetics for heavy metal adsorption is important, as it determines the size of the filter that is required relative to the water flow to be treated. This is particularly important in the treatment of stormwater runoff, which occurs sporadically but in large volumes and therefore requires fast sorption kinetics [47]. In the kinetic tests, 98% of total cadmium was removed by both sorbents, i.e. COP-63 and AC, within 3000 min (Fig. 3a). However, in terms of rate of sorption, COP-63 and AC exhibited significant differences (Fig. 3a, inset).

To find the best-fitting kinetic model for the sorption data, both the pseudo first-order kinetic (Eq. (2)) and the pseudo-second order kinetic models (Eq. (3)) were fitted (Fig. 3b,c). By comparing model fits, the pseudo second-order kinetic model returned the best fit for COP-63 ($r^2 = 0.999$). In contrast, the data for AC were better described by the pseudo first-order model ($r^2 = 0.985$) (Supplement, Fig. S3). This may conform with a strong chemical sorption to COP-63 and physical sorption to AC [48,49].

It is highly relevant for the application of sorbents to note that the half-life ($t_{1/2}$) for the removal of cadmium by AC is 63 min, whereas the half-life ($t_{1/2}$) for sorption by COP-63 is 4 min. Thus, COP-63 displays much faster cadmium sorption than AC, and hence filters with much lower residence times can be made by using COP-63 compared with AC.

COP-63 demonstrated excellent affinity to sorb cadmium from water, as K_d reached 4.29×10^5 L/kg at the equilibrium concentration of 1 µg/L (Supplement, Table S1). Based on the study reported by Shin et al. (2007), a K_d value of 10^4 L/kg is considered quite good, and a K_d value of 10^5 L/kg is considered excellent [50].

3.4. Effect of pH on metal complexation and the protonation of active sorption sites

Unlike physical sorption, COP-63 contains specific active disulfide and thiol-binding sites for heavy metal ions. In order to utilize these active sites, both a negative charge on the polymer (here determined as the zeta potential) and diffusion of metal ions to active sites are important. Strong binding of cations can be expected when sorptive surfaces are negatively charged [51,52] in addition to the formation of strong covalent bonds between metal ions and the bonding sites [53]. Diffusion can be determined by aggregating COP-63 particles, expressed by the hydrodynamic diameters of the particles. Aggregation tends to increase the distance metal ions will diffuse from a solution to the active binding site, thus slowing the sorption kinetics. To investigate the efficiency of COP-63 active sites, the zeta potential and hydrodynamic diameter (HDD) at five different pH values were examined (Table 1).

As shown in Table 1, the lowest zeta potential was observed at intermediate pH, i.e. pH 6–8, ranging from −32.4 to −33.7 mV. Moreover, the smallest HDD size was seen at pH 6–8, which may provide the faster contact of heavy metal ions to active sites. Therefore, COP-63 can be expected to have the highest chemical removal

Table 1

Mean value of zeta potential (mV) and hydrodynamic diameter (HDD) (µm) of COP-63 at different pH (Supplement, Fig. S5).

pH	Zeta Potential (mV) Mean values of two measurements	HDD (µm) and standard deviation
2.9	−3.4	1.5 ± 0.5
5.3	−26.8	0.4 ± 0.1
6.7	−33.45	0.3 ± 0.1
8.0	−32.1	0.3 ± 0.1
10.3	−31.1	0.4 ± 0.1

capacity of heavy metal ions at intermediate pH — which aligns well with typical pH values of stormwater runoff. It is worth noting that at high pH (pH 10.3) values, COP-63 particles show slightly weaker negative zeta potential and a higher HDD diameter, albeit they are almost similar to the values in the intermediate pH range. Hence, even at a high pH, COP-63 is expected to have similar sorption properties as at intermediary pH. On the other hand, at pH 5.3 and 2.9, COP-63 shows a significantly higher hydrodynamic diameter and smaller zeta potential, which leads to aggregation of particles that may slow down the rate of sorption [53].

To evaluate the binding of the heavy metal ions to sulfur functional active sites versus pH, tests were carried out to determine the sorption of five heavy metal ions at eight different pH values. Furthermore, for each heavy metal solution, speciation was calculated by Visual MINTEQ to evaluate the major species in solution (Fig. 4).

Sorption data for intermediate pH values (pH 6–8) show the highest removal efficiency—as expected—based on zeta potential and HDD values. However, exceeding the intermediate pH range, sorption declined though zeta potential and HDD of the polymer was similar with values at intermediate pH values. This can be explained by metal ion speciation in solution. When pH exceed the intermediate pH range, metal ions form negatively charged metal complexes, which apparently do not bind to a negatively charged active polymer site, even though COP-63's active sites are still available. Heavy metal removal efficiency decreases at low pH, where the zeta potential is smaller and HDD is higher. Moreover, at a low pH, there is significant competition between H⁺ and metal cations for binding sites, which decreases sorption efficiency [54]. In conclusion, the highest chemical sorption capacity appears at an intermediate pH of 6–8, in accordance with sufficient negative surface charge, high contact area for COP-63's active sites, and optimal speciation of metal ions in solution.

3.5. Selective sorption

In conventional water treatment processes, AC is a widely used heavy metal sorbent. However, the sorption of other major cations, such as cadmium and magnesium, competes with the sorption of heavy metal cations and hence reduces the efficiency of AC for heavy metal binding in many types of wastewater, such as stormwater. Hence, in order to be efficient in real treatment applications, a sorbent must not only have sufficient sorption capacity and fast sorption kinetics, but it should also show high selectivity of the target metal ions. Thus, selective metal sorption studies in the presence of competitive cation were conducted to demonstrate the selectivity of COP-63. Four different heavy metal ions commonly occurring in polluted water streams, namely copper, nickel, lead, and zinc, were selected besides cadmium. As a competitor, one of the most abundant divalent cations in water, calcium, was added at different concentrations.

As shown in Fig. 5, the presence of calcium has different effects on the sorption of heavy metal ions to COP-63 and AC. The most pronounced differences is seen for copper removal, where COP-

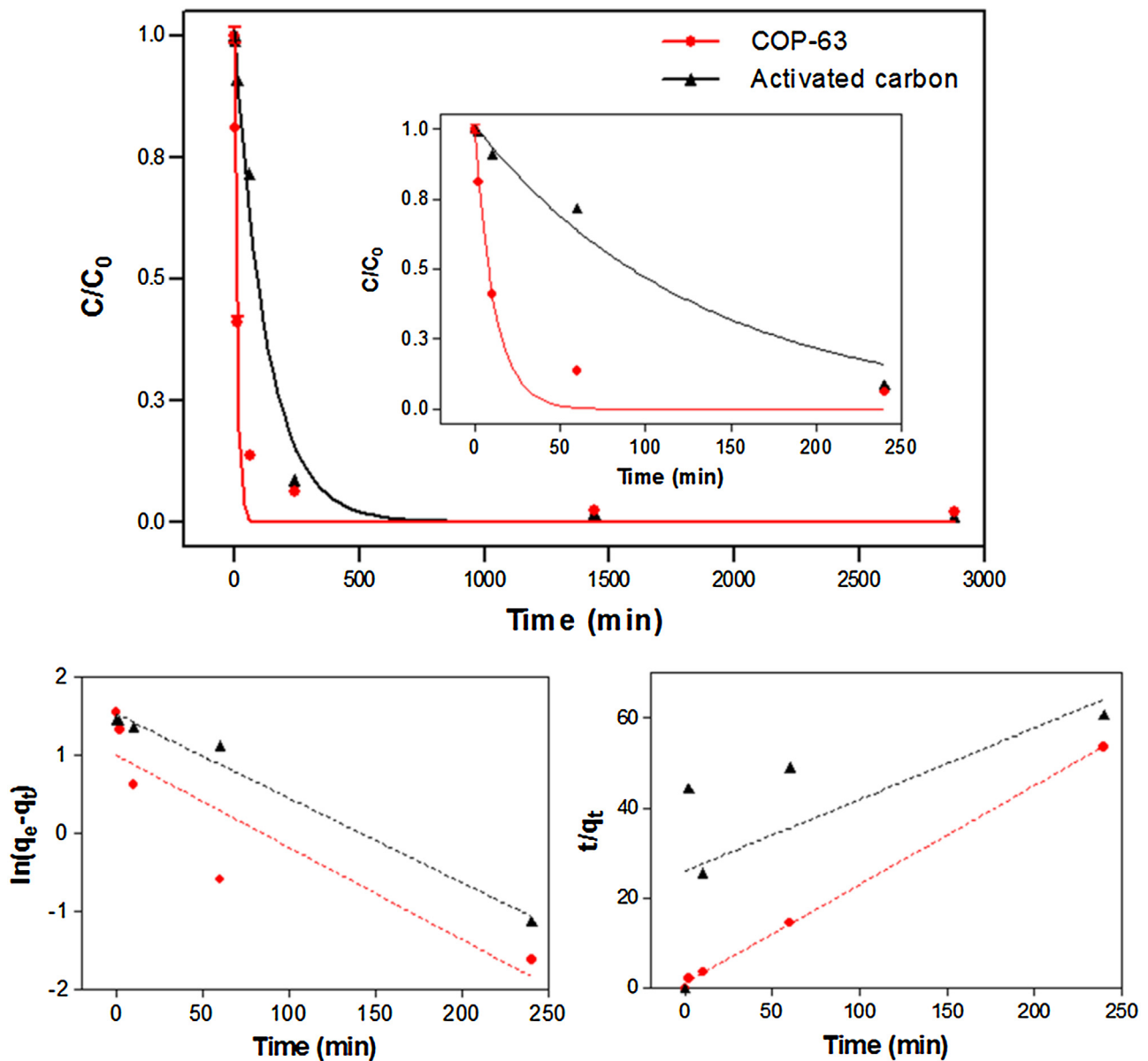


Fig. 3. Kinetics of cadmium sorption to COP-63 and AC. (a) Removal of cadmium in solution plotted versus time and lines due to fitting by the first-order kinetic model (Eq. (2)). Initial concentration was 10 mg/L. Error bar refers to standard deviation ($n=3$) Inset: Enlarged graph from start to 240 min. (b) Pseudo first-order kinetics model (Eq. (2)) fitted by linear regression for cadmium sorption on COP-63 and AC. (c) Fitting of the pseudo sec-ond-order kinetics model (Eq. (3)) to sorption data (red symbols: COP-63, black symbols: AC). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

63 has much stronger bonding than AC, while calcium has a very minor effect on heavy metal bonding to COP-63 but a marked effect on the bonding of copper to AC. In the case of zinc, lead, cadmium, and nickel, any increase in the concentration of calcium positively affects the sorption of the heavy metals. It is important to note that for zinc and cadmium, COP-63 again shows higher selectivity than AC in the presence of calcium. For nickel and lead, on the other hand, COP-63 has less selectivity compared to AC under the test conditions. This is explained by the hard-soft acid base (HSAB) theory, since a soft base (COP-63) was dispersed in the solution containing soft acids (heavy metal ions). Among heavy metal ions, copper and cadmium are well-known soft acids and have higher polarizability, which in turn results in the higher tendency of electron distortion to contribute to affinity. However, nickel, lead, and zinc are defined as “borderline acids” that have less affinity to soft bases compared to strong soft acids [55]. In conclusion, the selectivity studies show

that COP-63 has high binding affinities to copper, cadmium, and zinc in the presence of up to 10 times higher concentrations of calcium in water.

3.6. Treatment perspective

Mines et al. [56] demonstrated that COP could be grafted easily and inexpensively onto granular AC to create a functional polymer shell. Briefly, surface-oxidized AC was treated with thionyl chloride, followed by the addition of melamine, to create a backbone containing a COP monomer covalently bound on the AC surface. The precursors were polymerized to create an amino-functionalized COP structure on the AC surface. The resulting COP was found to be covalently bound to AC, while it maintained the sorption functionality of the pure COP polymer [56]. Similarly, COP-63 could be grafted onto AC by replacing melamine with trithiocyanuric acid,

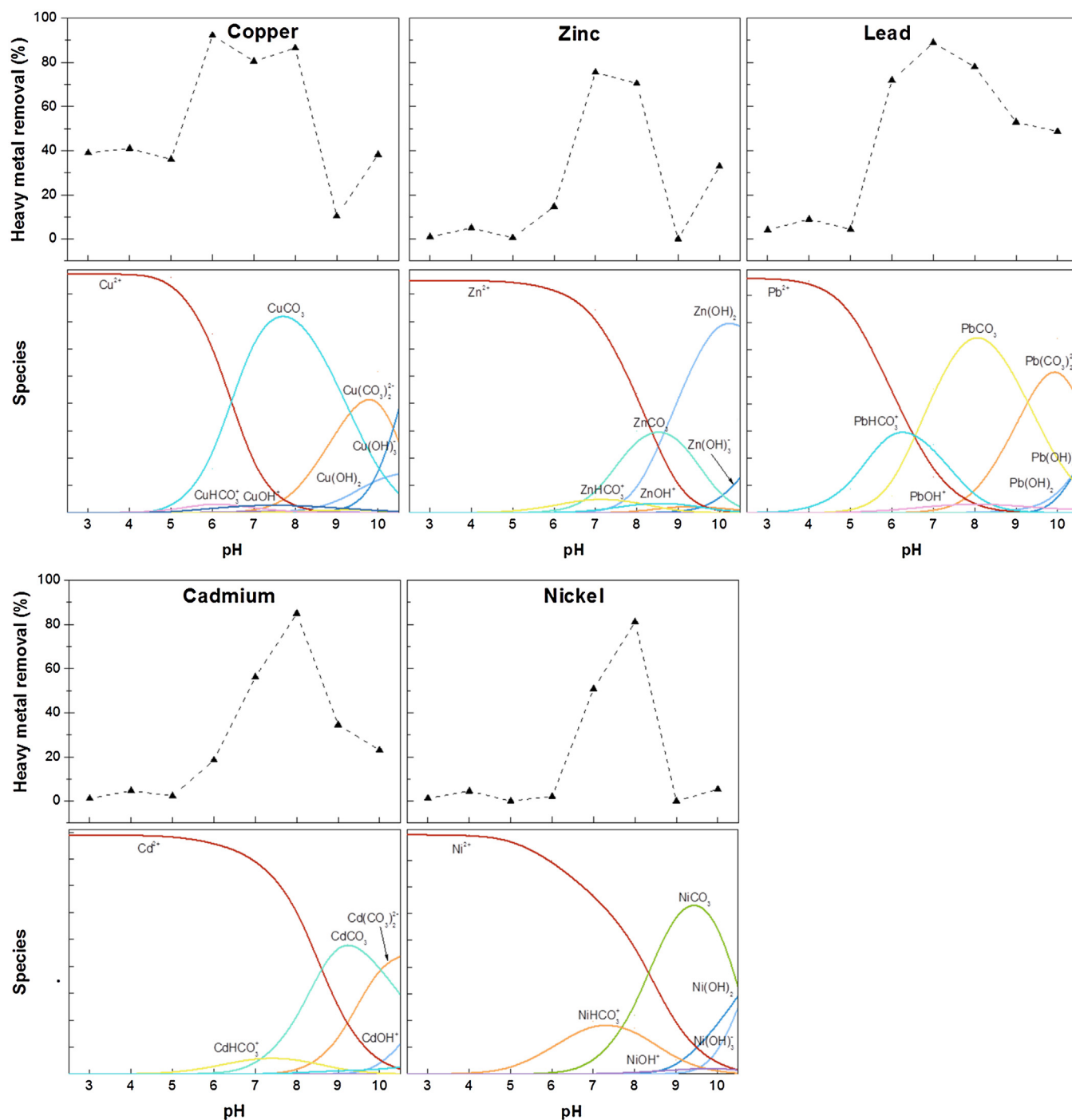


Fig. 4. Binding of copper, zinc, lead, cadmium and nickel to COP-63 at different pH compared with solution speciation computed by Visual Minteq. The plot with a dashed line in dark is the observed metal ion removal percentage, while the colored lines show the speciation.

followed by the same polymerization reaction as described in this work. This would form granular AC-sized beads with the sorption capacity and kinetics of COP-63 at an ideal particle size and mechanical strength for building filters that would thus express faster sorption kinetics and higher selectivity for the sorption of soft acid metals compared to high-quality activated carbon. It is likely that such a material would also be highly stable to allow for regeneration, due to the covalent bonding between AC and COP, which is known to tolerate heat (Supplement, Fig. S4) and chemical regeneration (Supplement, Fig. S7).

4. Conclusions

In this study, disulfide-linked covalent organic polymer, COP-63, was used as a sorbent for selective heavy metal removal from contaminated waters. COP-63 has almost similar maximum sorption capacity for heavy metals as high-quality AC on a mass basis while COP-63 has a seven times higher sorption capacity than AC on a specific surface area basis. The COP-63 has faster sorption kinetics, and thereby half of heavy metal ions are removed from a solution within 4 min ($t_{1/2}$), which is 16 times faster than AC. The chemisorption mechanism of the polymer networks was confirmed by kinetic and pH effect studies that confirmed heavy metal binding on disul-

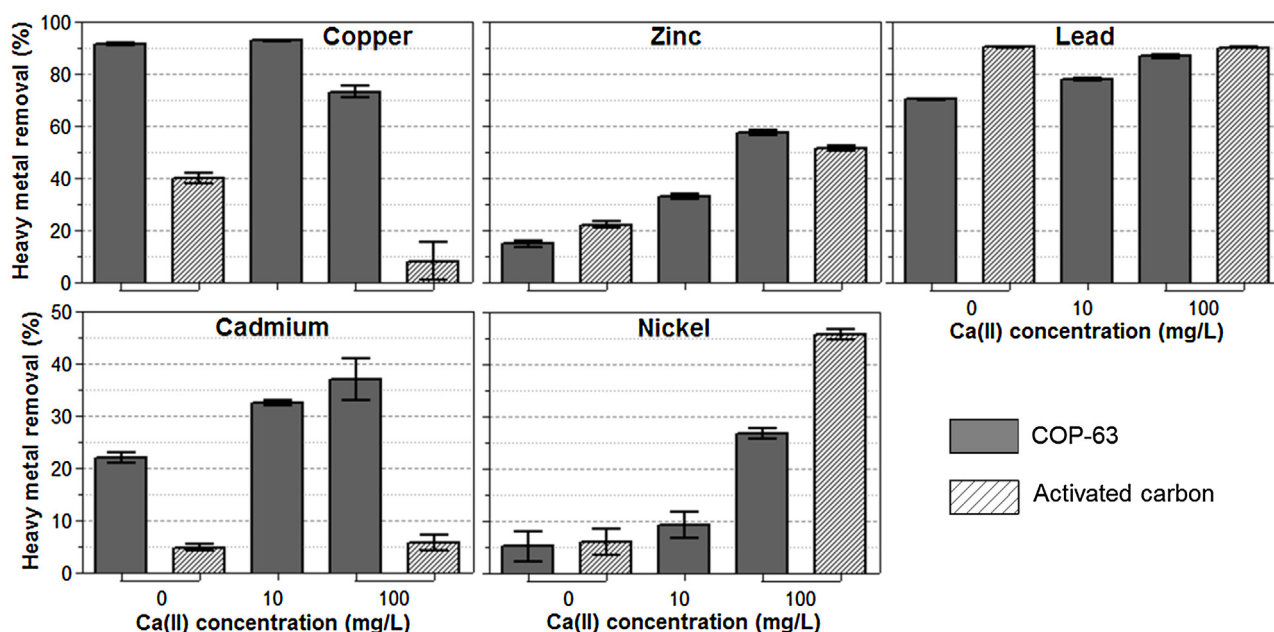


Fig. 5. Selective sorption of five different heavy metal ions in the presence of calcium as a competing cation to COP-63 and AC. Three different concentrations of calcium ions (0, 10 and 100 mg/L) were added to heavy metal ion solutions at pH 6–7 (Initial metal concentrations: 10 mg/L each, sorbent concentration: 0.2 g/L, contact time: 24 h). Error bars represent standard deviation (n = 3).

fide and thiol sites. The zeta potential of COP-63 and the metal speciation significantly affected sorption of metal ions at different pH. It was observed that the targeted heavy metal ions such as copper, cadmium, and zinc, show high binding affinity to COP-63 in the presence of 10 times higher concentrations of alkaline earth metal ions in water. COP-63 has sufficient sorption capacity with fast kinetics and has strong binding affinity with heavy metal ions. Hence, COP-63 can be a potential sorbent for stormwater treatment where peak flows cause short residence times.

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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.jhazmat.2017.03.007>.

References

- [1] J.O. Duruibe, M.O.C. Ogwuegbu, J.N. Ekwurugwu, Heavy metal pollution and human biotoxic effects, *Int. J. Phys. Sci.* 2 (2007) 112–118, <http://dx.doi.org/10.1016/j.proenv.2011.09.146>.
- [2] S.T. Ingvertsen, M.B. Jensen, J. Magid, A minimum data set of water quality parameters to assess and compare treatment efficiency of stormwater facilities, *J. Environ. Qual.* 40 (2011) 1488–1502, <http://dx.doi.org/10.2134/jeq2010.0420>.
- [3] F. Zhang, Y. Li, M. Yang, W. Li, Content of heavy metals in animal feeds and manures from farms of different scales in Northeast China, *Int. J. Environ. Res. Public Health* 9 (2012) 2658–2668, <http://dx.doi.org/10.3390/ijerph9082658>.
- [4] K. Vijayaraghavan, S. Rangabhashiyam, T. Ashokkumar, J. Arockiaraj, Mono- and multi-component biosorption of lead(II), cadmium(II), copper(II) and nickel(II) ions onto coco-peat biomass, *Sep. Sci. Technol.* 51 (2016) 2725–2733, <http://dx.doi.org/10.1080/01496395.2016.1212889>.
- [5] A. Ihsanullah, A.M. Abbas, T. Al-amer, M.J. Laoui, M.S. Al-marri, M. Nasser, M. Khraisheh, M. Ali, Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications, *Sep. Purif. Technol.* 157 (2016) 141–161, <http://dx.doi.org/10.1016/j.seppur.2015.11.039>.
- [6] K. Cederkvist, M. Jensen, S. Ingvertsen, P. Holm, Controlling stormwater quality with filter soil—event and dry weather testing, *Water* 8 (2016) 349, <http://dx.doi.org/10.3390/w8080349>.
- [7] I. Fraga, F.J. Charters, A.D. O'sullivan, T.A. Cochrane, A novel modelling framework to prioritize estimation of non-point source pollution parameters for quantifying pollutant origin and discharge in urban catchments, *J. Environ. Manage.* 167 (2016) 75–84, <http://dx.doi.org/10.1016/j.jenvman.2015.11.003>.
- [8] S. Asam, D. Spindler, S. Julius, B. Bierwagen, Stormwater management in response to climate change impacts: lessons from the chesapeake bay and great lakes regions, *United States EPA* 66 (2016) <https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=309540>.
- [9] P. Wu, Y. Zhou, Simultaneous removal of coexistent heavy metals from simulated urban stormwater using four sorbents: a porous iron sorbent and its mixtures with zeolite and crystal gravel, *J. Hazard. Mater.* 168 (2009) 674–680, <http://dx.doi.org/10.1016/j.jhazmat.2009.02.093>.
- [10] D.P.H. Laxen, R.M. Harrison, The highway as a source of water pollution: an appraisal with the heavy metal lead, *Water Res.* 11 (1977) 1–11, [http://dx.doi.org/10.1016/0043-1354\(77\)90175-0](http://dx.doi.org/10.1016/0043-1354(77)90175-0).
- [11] R. Pitt, A. Maestre, R. Morquecho, The National Stormwater Quality Database (NSQD, Version 1.1), 1st Annu. Stormwater, 2004, pp. 1–9 http://unix.eng.ua.edu/~rpitt/Research/ms4/Paper/MS4_Feb_16_2004_paper.pdf.
- [12] P. Göbel, C. Dierkes, W.G. Coldewey, Storm water runoff concentration matrix for urban areas, *J. Contam. Hydrol.* 91 (2007) 26–42, <http://dx.doi.org/10.1016/j.jconhyd.2006.08.008>.
- [13] T. Fletcher, H. Duncan, P. Poelsma, S. Lloyd, Stormwater flow and quality, and the effectiveness of non-proprietary stormwater treatment measures: a review and gap analysis, *Tech. Rep.* (2004) 1–171.
- [14] M.M. Matlock, B.S. Howerton, D.A. Atwood, Chemical precipitation of heavy metals from acid mine drainage, *Water Res.* 36 (2002) 4757–4764, [http://dx.doi.org/10.1016/S0043-1354\(02\)00149-5](http://dx.doi.org/10.1016/S0043-1354(02)00149-5).
- [15] K. Jasiewicz, R. Pietrzak, Metals ions removal by polymer membranes of different porosity, *Sci. World J.* (2013) 2013, <http://dx.doi.org/10.1155/2013/957202>.
- [16] A. Dąbrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange

- method, *Chemosphere* 56 (2004) 91–106, <http://dx.doi.org/10.1016/j.chemosphere.2004.03.006>.
- [17] B. Sancey, G. Trunfio, J. Charles, J.F. Minary, S. Gavoille, P.M. Badot, G. Crini, Heavy metal removal from industrial effluents by sorption on cross-linked starch: chemical study and impact on water toxicity, *J. Environ. Manage.* 92 (2011) 765–772, <http://dx.doi.org/10.1016/j.jenvman.2010.10.033>.
 - [18] P. Mahbub, G.A. Ayoko, A. Goonetilleke, P. Egodawatta, S. Kokot, Impacts of traffic and rainfall characteristics on heavy metals build-up and wash-off from urban roads, *Environ. Sci. Technol.* 44 (2010) 8904–8910, <http://dx.doi.org/10.1021/es1012565>.
 - [19] H. Genç-Fuhrman, P. Wu, Y. Zhou, A. Ledin, Removal of As, Cd, Cr, Cu, Ni and Zn from polluted water using an iron based sorbent, *Desalination* 226 (2008) 357–370, <http://dx.doi.org/10.1016/j.desal.2007.02.117>.
 - [20] K.S. Hui, C.Y.H. Chao, S.C. Kot, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash, *J. Hazard. Mater.* 127 (2005) 89–101, <http://dx.doi.org/10.1016/j.jhazmat.2005.06.027>.
 - [21] P. Göbel, J. Zimmermann, C. Klinger, H. Stubbe, W.G. Coldewey, Recommended urban storm water infiltration devices for different types of run-off under varying hydrogeological conditions, *J. Soils Sediments* 8 (2008) 231–238, <http://dx.doi.org/10.1007/s11368-008-0020-6>.
 - [22] M.B. Jensen, K. Cedervist, P.E.R. Bjerager, P.E. Holm, Dual porosity filtration for treatment of stormwater runoff: first proof of concept from Copenhagen pilot plant, *Water Sci. Technol.* 64 (2011) 1547–1557, <http://dx.doi.org/10.2166/wst.2011.186>.
 - [23] T. Wium-andersen, A.H. Nielsen, T. Hvitved-, J. Vollertsen, Heavy Metals, PAHs and Toxicity in Stormwater Wet Detention Ponds, Novatech, 2010.
 - [24] S.B. Lalvani, T. Wiltowski, A. Weston, Metal ions removal from wastewater by adsorption, *ACS Div. Fuel Chem. Prepr.* 42 (1997) 877–878.
 - [25] P. Hadi, M.H. To, C.W. Hui, C.S.K. Lin, G. McKay, Aqueous mercury adsorption by activated carbons, *Water Res.* 73 (2015) 37–55, <http://dx.doi.org/10.1016/j.watres.2015.01.018>.
 - [26] M. Singanan, Removal of lead(II) and cadmium(II) ions from wastewater using activated biocarbon, *ScienceAsia* 37 (2011) 115–119, <http://dx.doi.org/10.2306/scienceasia1513-1874.2011.37.115>.
 - [27] R. Xu, G. Zhou, Y. Tang, L. Chu, C. Liu, Z. Zeng, S. Luo, New double network hydrogel adsorbent: highly efficient removal of Cd(II) and Mn(II) ions in aqueous solution, *Chem. Eng. J.* 275 (2015) 179–188, <http://dx.doi.org/10.1016/j.cej.2015.04.040>.
 - [28] K. Tota-Maharaj, P. Parneet, Investigating the influence of geotextile layers as biofilm granular filters to treat stormwater, *Urban Water J.* 12 (2015) 559–569, <http://dx.doi.org/10.1080/1573062X.2014.916726>.
 - [29] K. Anoop Krishnan, K.G. Sreejalekshmi, V. Vimexen, V.V. Dev, Evaluation of adsorption properties of sulphurised activated carbon for the effective and economically viable removal of Zn(II) from aqueous solutions, *Ecotoxicol. Environ. Saf.* 124 (2016) 418–425, <http://dx.doi.org/10.1016/j.ecoenv.2015.11.018>.
 - [30] S.K. Yong, W.M. Skinner, N.S. Bolan, E. Lombi, A. Kunhikrishnan, Y.S. Ok, Sulfur crosslinks from thermal degradation of chitosan dithiocarbamate derivatives and thermodynamic study for sorption of copper and cadmium from aqueous system, *Environ. Sci. Pollut. Res.* 23 (2016) 1050–1059, <http://dx.doi.org/10.1007/s11356-015-5654-5>.
 - [31] G. Zhou, J. Luo, C. Liu, L. Chu, J. Ma, Y. Tang, Z. Zeng, S. Luo, A highly efficient polyampholyte hydrogel sorbent based fixed-bed process for heavy metal removal in actual industrial effluent, *Water Res.* 89 (2016) 151–160, <http://dx.doi.org/10.1016/j.watres.2015.11.053>.
 - [32] H.A. Patel, F. Karadas, J. Byun, J. Park, E. Deniz, A. Canlier, Y. Jung, M. Atilhan, C.T. Yavuz, Highly stable nanoporous sulfur-bridged covalent organic polymers for carbon dioxide removal, *Adv. Funct. Mater.* 23 (2013) 2270–2276, <http://dx.doi.org/10.1002/adfm.201202442>.
 - [33] H.A. Patel, S.H. Je, J. Park, D.P. Chen, Y. Jung, C.T. Yavuz, A. Coskun, Unprecedented high-temperature CO₂ selectivity in N₂-phobic nanoporous covalent organic polymers, *Nat. Commun.* 4 (2013) 1357, <http://dx.doi.org/10.1038/ncomms2359>.
 - [34] D. Ko, H.A. Patel, C.T. Yavuz, Synthesis of nanoporous 1,2,4-oxadiazole networks with high CO₂ capture capacity, *Chem. Commun. (Camb.)* 51 (2015) 2915–2917, <http://pubs.rsc.org/en/Content/ArticleHTML/2015/CC/C4CC08649j>.
 - [35] Z. Xiang, R. Mercado, J.M. Huck, H. Wang, Z. Guo, W. Wang, D. Cao, M. Haranczyk, B. Smit, Systematic tuning and multifunctionalization of covalent organic polymers for enhanced carbon capture, *J. Am. Chem. Soc.* 137 (2015) 13301–13307, <http://dx.doi.org/10.1021/jacs.5b06266>.
 - [36] R.M. LoPachin, T. Gavin, A. DeCaprio, D.S. Barber, Application of the Hard and Soft, Acids and Bases (HSAB) theory to toxicant – target interactions, *Chem. Res. Toxicol.* 25 (2012) 239–251, <http://dx.doi.org/10.1021/tx2003257>.
 - [37] H. Zhuang, L. Yang, J. Xu, F. Li, Z. Zhang, H. Lin, J. Long, X. Wang, Robust photocatalytic H₂O₂ production by octahedral Cd₃(C₃N₃S₃)₂ coordination polymer under visible light, *Sci. Rep.* 5 (2015) 16947, <http://dx.doi.org/10.1038/srep16947>.
 - [38] M.M. Matlock, K.R. Henke, D.A. Atwood, D. Robertson, Aqueous leaching properties and environmental implications of cadmium, lead and zinc Trimercaptotriazine (TMT) compounds, *Water Res.* 35 (2001) 3649–3655, [http://dx.doi.org/10.1016/S0043-1354\(01\)00091-4](http://dx.doi.org/10.1016/S0043-1354(01)00091-4).
 - [39] H.A. Patel, D. Ko, C.T. Yavuz, Nanoporous benzoxazole networks by silylated monomers their exceptional thermal stability, and carbon dioxide capture capacity, *Chem. Mater.* 26 (2014) 6729–6733.
 - [40] J.P. Gustafsson, Visual MINTEQ, 2012, <http://vminteq.lwr.kth.se/>.
 - [41] Y.S. Ho, Review of second-order models for adsorption systems, *J. Hazard. Mater.* 136 (2006) 681–689, <http://dx.doi.org/10.1016/j.jhazmat.2005.12.043>.
 - [42] M.S. Patel, Exceptional organic solvent uptake by disulfide-linked polymeric networks, *RSC Adv.* 4 (2014) 24320, <http://dx.doi.org/10.1039/c4ra03355h>.
 - [43] Z. Zhang, J. Long, L. Yang, W. Chen, W. Dai, X. Fu, Xuxu Wang, Organic semiconductor for artificial photosynthesis: water splitting into hydrogen by a bioinspired C₃N₃S₃ polymer under visible light irradiation, *Chem. Sci.* 2 (2011) 1826–1830.
 - [44] C.N.R. Rao, R. Venkataraghavan, T.R. Kasturi, Contribution to the infrared spectra of organosulphur compounds, *Can. J. Chem.* 42 (1964) 36–42.
 - [45] P. Tingaut, R. Hauert, T. Zimmermann, Highly efficient and straightforward functionalization of cellulose films with thiol-ene click chemistry, *J. Mater. Chem.* 21 (2011) 16066, <http://dx.doi.org/10.1039/c1jm11620g>.
 - [46] I. Ali, V.K. Gupta, Advances in water treatment by adsorption technology, *Nat. Protoc.* 1 (2006) 2661–2667, <http://dx.doi.org/10.1038/nprot.2006.370>.
 - [47] R. Field, M.P. Brown, W.V. Vilkelis, Stormwater Pollution Abatement Technologies, US Environmental Protection Agency, Cincinnati, OHIO, 45268, 1994.
 - [48] R.E. Morsi, M.Z. Elsayee, Polyaniline nanotubes: mercury and competitive heavy metals uptake, *Am. J. Polym. Sci.* 5 (2015) 10–17, <http://dx.doi.org/10.5923/j.ajps.20150501.02>.
 - [49] G. Zhou, C. Liu, L. Chu, Y. Tang, S. Luo, Rapid and efficient treatment of wastewater with high-concentration heavy metals using a new type of hydrogel-based adsorption process, *Bioresour. Technol.* 219 (2016) 451–457, <http://dx.doi.org/10.1016/j.biortech.2016.07.038>.
 - [50] B.Y. Shin, G.E. Fryxell, W. Um, K. Parker, S.V. Mattigod, R. Skaggs, Sulfur-functionalized mesoporous carbon, *Adv. Funct. Mater.* 17 (2007) 2897–2901, <http://dx.doi.org/10.1002/adfm.200601230>.
 - [51] M. Dai, The effect of zeta potential of activated carbon on the adsorption of dyes from aqueous solution: I. The adsorption of cationic dyes: methyl green and methyl violet, *J. Colloid Interface Sci.* 164 (1994) 223–228, <http://dx.doi.org/10.1006/jcis.1994.1160>.
 - [52] D.-Q. Lin, P.J. Brixius, J.J. Hubbuch, J. Thömmes, M.-R. Kula, Biomass/adsorbent electrostatic interactions in expanded bed adsorption: a zeta potential study, *Biotechnol. Bioeng.* 83 (2003) 149–157, <http://dx.doi.org/10.1002/bit.10654>.
 - [53] Y. Zhang, M. Yang, N.G. Portney, D. Cui, G. Budak, E. Ozbay, M. Ozkan, C.S. Ozkan, Zeta potential: a surface electrical characteristic to probe the interaction of nanoparticles with normal and cancer human breast epithelial cells, *Biomed. Microdevices.* 10 (2008) 321–328, <http://dx.doi.org/10.1007/s10544-007-9139-2>.
 - [54] H. Genç-Fuhrman, P.S. Mikkelsen, A. Ledin, Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater using high-efficiency industrial sorbents: effect of pH, contact time and humic acid, *Sci. Total Environ.* 566–567 (2016) 76–85, <http://dx.doi.org/10.1016/j.scitotenv.2016.04.210>.
 - [55] J.A. Lemire, J.J. Harrison, R.J. Turner, Antimicrobial activity of metals mechanisms, molecular targets and applications, *Nat. Rev. Microbiol.* 11 (2013) 371–384, <http://dx.doi.org/10.1038/nrmicro3028>.
 - [56] P.D. Mines, D. Thirion, B. Uthuppu, M.H. Jakobsen, H.R. Andersen, C.T. Yavuz, Covalent organic polymer functionalization of activated carbon surfaces through acyl chloride for environmental clean-up, *Chem. Eng. J.* 309 (2017) 766–771, <http://dx.doi.org/10.1016/j.cej.2016.10.085>.