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Applicability of disulfide-polymer particles surface embedded on alginate beads for cadmium removal from airport derived stormwater

Dongah Ko¹, Hyowon Kim², Hansaem Lee², Cafer T. Yavuz³, Henrik R. Andersen¹ and Yuhoon Hwang^{2,*}

¹ Department of Environmental Engineering, Technical University of Denmark, Bygningstorvet 115, 2800 Kgs. Lyngby, Denmark

² Department of Environmental Engineering, Seoul National University of Science and Technology, 232 Gongreung-ro, Nowongu, Seoul 01811, Republic of Korea.

³ Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea.

*Corresponding author: Yuhoon Hwang (yhhwang@seoultech.ac.kr)

Graphical abstract:

Highlights

- Disulfide/thiol functionalized composite was devised by embedding polymer on the alginate beads.
- Within 6 minutes, half of the cadmium ions were removed by novel composites, DiS-algi.
- Reactive column test for simulating conventional filter revealed the potential of DiS-algi filter.
- Filter regeneration tests proved reusability of DiS-algi filter.

Abstract

Stormwater runoff derived from airports causes severe cadmium contamination in excess of the maximum limit level and is difficult to treat due to the irregular contamination levels from scattered rainfall. To overcome this and remove cadmium from runoff, a new reactive filtration column is introduced. Sulfur functionalized polymer particles were successfully embedded onto the surface of alginate bead (DiS-algi) and simulated a real stormwater treatment filtration column. The DiS-algi shows 22.3 mg/g of batch and 877 $\mu\text{g/g}$ of continuous flow sorption capacity. Also, the results for the new sorption material show that within 6 mins half of the cadmium

was removed with 31 L/mg of Langmuir sorption affinity, outperforming an activated carbon filter. From a breakthrough test the reactive column shows complete uptake of cadmium from a contaminated flow, lasting two hours until reaching the breakthrough point. Furthermore, regeneration tests of the column verified its reusability. DiS-algi appears to be a viable new cadmium sorption material for airport derived stormwater runoff filtration systems.

Keywords: Airport stormwater runoff, cadmium removal, polymer composite sorbent, stormwater filtration

1. Introduction

Stormwater runoff is a huge non-point source of heavy metal ions for surface water, especially in airport regions [1],[2]. Daily activities at airports such as fueling operations, cleaning of aircraft, and combustion of aviation fuel give rise to severe amounts of precipitation and atmospheric deposits. Moreover, considerable amounts of aircraft de-icing/anti-icing fluids (ADAFs) are used worldwide to remove and prevent ice on aircrafts and this aggravates the heavy metal pollution during cold seasons [2],[3],[4]. The presence of heavy metal ions in water has several adverse effects on living organisms. It has been established that among the heavy metal pollutants, cadmium has carcinogenic potential to humans and experimental animals [5],[6]. Various cadmium concentrations in airport runoff occur in a range of 1 – 450 µg/L in different international airports, despite that the accepted flow limit for airports regulations is 0.2 µg/L (Table 1). The considerable amounts of cadmium ions released during aircraft cleaning since covers of aircraft wheels and brakes are composed by cadmium-plated components [7]. The cadmium-plating is standard material for the aircraft owing to advantages of the cadmium; such as sacrificial protection of steel, corrosion products with low volume, and compatibility with other components in the aircraft [8]. Also, de-icing fluids exacerbate the pollution of the cadmium and according to studies by the United States Environmental Protection Agency [9] and Devon et al. [3], de-icing fluids contain 240 µg/L and 1500 µg/L of cadmium, respectively. To remove heavy metals from stormwater runoff, various treatment methods have been applied such as wet detention ponds [10], filtration [11], and insertion of a catchment basin underground to avoid overflow in wastewater treatment systems. However, irregular amounts of water at scattered rainfall events and various concentrations of pollutant concentrations hinder treatment of airport runoff. Therefore, a highly efficient way of removing cadmium from airport runoff is needed. Recently, disulfide linked polymer networks for selective removal of heavy metal ions from water have been reported [12]. These polymer networks showed rapid sorption kinetics with sufficient sorption capacity of heavy metals in the presence of competitive earth metals based on the Hard Soft Acid Base (HSAB) theory. In a

previous study, however, only feasibility tests of polymers were conducted. In order for a sorbent to be applied for real water treatment systems, it should be compatible with constructing a column type filter for exhaustively treating the water in a reasonable time. For the rapid flow filtration, filter material should be bigger as effective grain size range, 0.4 to 2 mm [13]. Since the disulfide polymer is synthesized as a powder with an average diameter of less than 50 μm the direct usability of the polymer for stormwater treatment in a column is limited by the large hydraulic back pressure created by such small particles. To avoid this limitation in this study we have optimized the size of the column filling materials by embedding powdery polymer onto a bigger substrate. We therefore embedded the disulfide polymer onto size-tunable organic alginate beads (DiS-algi) and achieved bead size with an average diameter of 3 mm. These beads were tested for cadmium sorption and compared with a traditionally used sorbent, high quality activated carbon. Moreover, reactive columns were built with DiS-algi and simulated a real stormwater filtration system. Finally, regeneration tests on the column were conducted and the results verified its reusability.

Table 1 Cadmium concentration ($\mu\text{g/L}$) in airport runoff, de-icing fluid, and accepted limit for airports regulations

2. Experimental

2.1. Materials

Sodium alginate, calcium chloride hexahydrate, trithiocyanuric acid, sodium hydroxide, iodine, potassium iodide, and granular activated carbon (GAC: Norit 1240W) were purchased from Sigma-Aldrich. Sea sand (10-20 mesh) was purchased from Deajung Chemical and Metals. Cadmium solution was prepared from 1000 mg/L AAS standard stock solutions containing 0.1 M nitric acid purchased from Kanto Chemical. All chemicals were used as received, unless otherwise stated.

2.2. Preparation of disulfide-polymer particles surface embedded in alginate beads (DiS-algi)

A disulfide linked polymer network was prepared as described in a previous study [12]. Briefly, by adding a strong oxidant into the solution of thiocyanuric acid monomers and stirring overnight, thiols are oxidized and form a disulfide link, leading to the formation of a stable porous polymer. Afterwards, the beads were obtained by dropping a solution containing sodium alginate and 1.6 wt% disulfide polymer into 0.1 M CaCl_2 solution and firming up overnight. Subsequently, DiS-algi was washed with distilled water several times. The prepared DiS-algi was characterized to confirm successful preparation of the composite material. Elemental analysis was performed on a FLASH 2000 series from Thermo Scientific. Infrared spectra were measured with a Shimadzu IRTracer-100 ATR spectrometer. Imaging of DiS-algi was carried out on an optical microscope.

2.3. Batch test

2.3.1 Test procedure

Sorption isotherms were conducted in solutions prepared from metal stock solutions in the presence of a 0.003 M NaHCO_3 buffer. pH values were adjusted with 1 M HCl and NaOH, to be in a range of pH 6 to 7. Four different cadmium concentrations, ranging between 1 and 50 mg/L, were used for the sorption isotherms for both DiS-algi and granular activated carbon (GAC). In a conical polyethylene (PE) tube, the cadmium solution was added to the adsorbent. The tubes were shaken gently, and sampling started within a few minutes from the start. For kinetics experiments, six sampling times were selected (0, 2, 10, 60, 240, 1440, and 2880 mins). Sorbent and solution separation was performed using a 0.7 μm glass microfiber filter. Batches were shaken on an end-over-end rotator at 15 rpm. All filtrates were acidified with 1% HNO_3 . Cadmium concentrations were determined by Thermo Scientific Elemental Solaar M6 atomic absorption spectroscopy (FAAS, LOD: 0.026 mg/L).

2.3.2. Expression for sorption isotherm, sorption kinetics

At equilibrium (q_e), the maximum amount of metal ion sorption of the sorbent can be calculated by using 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 (mg/g), C_e represents the concentration of the adsorbate in solution (mg/L) at equilibrium, and a_L is the Langmuir affinity constant.

To determine the sorption behavior and kinetics, pseudo first-order and second-order kinetics models were applied. The pseudo first-order model was suggested by Lagergren (1989) and its linear form 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 adsorbed (mg/g) at equilibrium and time t . The rate constant of the sorption is shown as k_1 (1/min). The pseudo second-order kinetics was given by Ho and McKay (1999) applied to chemisorption and can be expressed as[17]:

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

where k_2 is the rate constant (g/mg·min).

2.4. Column operation

2.4.1 Operation procedure

The reactive column was made of a Pyrex glass tube of 1.2 cm inner diameter and 19.5 cm height. At the end point of the column, a stainless steel sieve with a 1 μm mesh was attached. Different flow rates were applied during the test. A metal solution was prepared by diluting 1000 mg/L cadmium stock solution in 1% nitric acid

with addition of a 0.003M NaHCO₃ buffer solution. All solutions were adjusted to be pH 6 to 7 before being added into the column by 5 M HCl and NaCl. In order to build the reactive column, sea sand was used as an inert filling layer and DiS-algi or GAC were placed between the sand layers. Flows were controlled by a peristaltic pump at 0.5 and 1 ml/min which gives retention time as 3.4 min and 6.8 min respectively. The eluent was filtered by using a 0.7 µm glass microfiber filter. Cadmium was detected by Thermo Scientific Elemental Solaar M6 atomic absorption spectroscopy (FAAS, LOD: 0.026 mg/L).

Figure 1 Schematic diagram of lab-scale reactive column of DiS-algi. The arrows indicate the direction of flow during the test.

2.4.2 Breakthrough curve analysis

The breakthrough time and curve are important characteristics for analyzing the sorption behavior of a column and determining parameters for the operation of a fixed bed column[18][19]. Effluent volume (V_{eff}) can be calculated from equation 4 as shown below:

$$V_{eff} = Qt_{total} \quad (4)$$

where t_{total} is the total flow time (min) and Q is the volumetric flow rate (ml/min).

The area below the breakthrough curve is calculated by integrating the adsorbed concentration as a function of time and it is used to determine the total adsorbed quantity (q_{total}) in the column, which can be expressed as:

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \quad (5)$$

where C_{ad} and t are respectively the adsorbed concentration (mg/L) and time (min).

The maximum capacity of the column (q_{eq}) is defined by the equation below:

$$q_{eq} = \frac{q_{total}}{w} \quad (6)$$

where w is the amount of adsorbent (g).

2.4.3 Regeneration

The reactive columns were washed by flushing selected washing agents. In this study three different washing agents were used, 0.01 M and 0.1 M EDTA and 0.1 M HCl. All steps followed the column sorption procedure except the flow rate, which was fixed at 0.5 ml/min.

3. Results and Discussion

3.1. Physical and chemical characterization of the disulfide polymer

The morphology of the disulfide polymer, DiS-algi, and cross-section images of the pure alginate bead and DiS-algi were obtained from an optical microscope for comparison (Figure 2). The disulfide polymer grain size is less than 50 μm while DiS-algi is around 3 mm, similar to the size of commercialized GAC (Figure S1). As shown in figure 2 (d), disulfide polymer was embedded in the surface of alginate beads rather than being dispersed in the alginate bead core, indicating that accessibility of heavy metal ions to the polymer would not be inhibited by the size of the alginate beads. This was also proven by testing the sorption ability for both a powdery polymer and DiS-algi (Figure S2).

Figure 2 Images obtained from optical microscope. (a) disulfide polymer (b) DiS-algi (c) cross section image of pure alginate bead and (d) cross section of DiS-algi.

The functionality of the disulfide polymer was confirmed by comparing the IR peaks and elemental analysis. The elemental analysis of the disulfide polymer yielded 19.8% C, 0.4% H, 21.3% N, 52.5% S, and 4.0% O, and this is consistent with the theoretical elemental percentage of disulfide linked polymer networks. (Theoretical C: 19.7%, H: 0.5%, N: 23.0%, S: 52.7%, and 4.0% O) [12]. The FT-IR spectra (Figure 3) show peaks of aromatic trithiol stretching 1466, 1226, 823 cm^{-1} in the polymer, reflecting that a disulfide polymer has formed. The peaks at 1120 cm^{-1} represent C=S stretching in the polymer networks. Peaks ranging between 456 and 533 cm^{-1} show the existence of disulfide linkages in the polymer networks [12]. As shown in the thermal stability graph in figure 3, DiS-algi follows the polymer stability trend, retaining its structure until 200 to 300 degrees C. Based on the overall physiochemical characteristics, it is proven that the functionalized polymer stably embedded in the surface of the substrate without any molecular degradation.

Figure 3 Infrared spectra of disulfide linked polymer networks with inset schematic of DiS-algi (left). Thermal stability comparison of disulfide linked polymer, alginate bead, and DiS-algi (right). Weight loss before 100

degrees C was ascribed to water evaporation. The DiS-algi and alginate bead weight losses were magnified 5-fold.

3.2. Sorption isotherm and kinetics of DiS-algi

To compare the sorption capacity of DiS-algi and GAC, sorption isotherms were fitted with Langmuir isotherms (eq. 1), as shown in Figure 4. The maximum sorption capacity of DiS-algi was calculated as 22.4 mg/g while that of GAC was 11.5 mg/g. It is also important to note that the Langmuir affinity constant (a_L) of DiS-algi was 31 L/mg, which is nearly 10^3 times higher than GAC's affinity constant of 0.03 L/mg (Table 2).

Figure 4 Langmuir sorption isotherm of DiS-algi plot with fitted line (red) and activated carbon plots with fitted line (black) from four different initial concentration batch tests.

Kinetic studies of DiS-algi also were conducted with GAC for comparison at four different cadmium concentrations (Figure 5). In the case of GAC, sorption in general was slow compared to DiS-algi, which has rapid sorption since sorption is related to not only diffusivity but also chemical attractions, as confirmed by the kinetics model. The kinetics is considered to be an important parameter for determining sorption behavior [20], and mostly physisorption well fitted by pseudo first-order kinetics (eq. 2) and chemisorption by pseudo second-order kinetics (eq. 3) [17],[21]. As a result of kinetics model fitting, DiS-algi was successfully fitted with the pseudo second-order kinetics whereas GAC showed better conformity to the pseudo first-order kinetics (Figure S3, SI).

Figure 5 Cadmium sorption kinetics studies of (a) GAC and (b) DiS-algi. Four different initial concentrations of cadmium were compared and differentiated by color; i.e., green, red, blue, and black represent 50, 25, 10, and 1 ppm, respectively.

Moreover, half of the cadmium ions were removed within 6 mins when DiS-algi was introduced into the polluted water. Compared with the half life time of GAC, 430 mins, DiS-algi has 70 times faster sorption at the same conditions (Table 2).

Table 2 Various data from sorption and kinetic studies of DiS-algi and GAC

In overall batch tests including isotherm and kinetic tests, DiS-algi showed superior sorption values compare with GAC. It is due to the disulfide and dangling thiols in the polymer which has higher affinity to attract soft acid metal ions, cadmium, based on HSAB theory [22]. Moreover, the strong coordination capability of backbone structure $C_3N_3S_3$ with transition metal ions explains exceptional sorption ability of DiS-algi [23]. The metal coordination bonds with thiol groups on disulfide linked polymer observed by IR spectra (Figure S5, SI). Besides, in the previous study [24] zeta potential of disulfide linked polymer showed negative charge at the range from pH 2.9 to pH 10.3 therefore, surface charge of DiS-algi also expected to have negative charge at a similar pH range for attracting positively charged cadmium ions in a solution.

3.3. Effectiveness of DiS-algi as column filling material

The reactive columns were built with DiS-algi and tested with two different flow rates along with a GAC column as a comparison (Figure 6). At a flow rate of 1 ml/min, both the DiS-algi and GAC columns did not have sufficient time for removing cadmium ions from the continuous flow. On the other hand, when the flow rate was reduced to 0.5 ml/min DiS-algi showed breakthrough at 137 minutes while GAC had it at 4 minutes. Therefore, a flow rate of 0.5 ml/min was selected for the remaining tests. Other optimized parameters for DiS-algi reactive column operation has been listed in Table S1 (SI). The effective volume, adsorbed amount, and maximum sorption capacity for the DiS-algi column were calculated using equation. 4-6 based on the selected flow rate tests.

Figure 6 Cadmium removal plot in fixed bed column with continuous flow rate 0.5 and 1 mL/min. Both DiS-algi and GAC plots were fitted by one-phase association equation with plateau. Red dots represent DiS-algi, black dots for GAC, and solid line showing 0.5 mL/min flow rate while dashed line for 1 mL/min flow rate.

The effective volume of the reactive column was derived as 68.5 mL and the total adsorbed amount of cadmium was 70 µg. The maximum capacity of the column was 877 µg/g while GAC only showed 64 µg/g of capacity. The DiS-algi reactive column thus has 15 times higher sorption capacity and faster kinetics compared to GAC, which is commonly used in stormwater treatment.

An increase of pH has been shown during a simultaneous sorption test from pH 6.2 to 7.8 due to the hydrolysis of materials as well as cationic exchange [25] (Figure S4, SI). This is general response of pH seen in many other previously reported sorbents [25][26].

3.4. Regeneration study

The regeneration test of reactive column was conducted with different flushing agents, EDTA and HCl, and between them HCl shows better desorption ability. At low concentrations EDTA does not show any desorption ability whereas highly concentrated EDTA could extract cadmium ions from the column, however it showed high fluctuation. Therefore, repeated sorption and desorption tests were carried out with 0.1M HCl and the mass of cadmium in the column during repeated tests also was calculated (Figure 7).

Figure 7 Sorption-desorption repeated test on reactive column using 0.1 M of HCl as flushing agent for desorption. Black-solid and blue-dashed lines are indicating effluent cadmium concentration and mass of cadmium in reactive column, respectively.

As shown in Figure 7, the mass of cadmium in the reactive column decreases slightly due to the remaining cadmium after the regeneration step. The reactive column uptakes 133 μgCd in the first sorption test and it decreases to 98 and 91 μgCd at the second and third sorption tests, respectively. However after the first run, the cadmium uptake capacity of the column stabilized and breakthrough curves were retained for three iterations of cyclic sorption tests.

4. Conclusion

In this study, a DiS-algi reactive column was introduced to simulate cadmium removing from airport derived stormwater runoff. The maximum sorption capacity of DiS-algi reached 22.3 mg/g while GAC shows a value of 11.5 mg/g and nearly 10^3 times higher sorption affinity is shown in DiS-algi compared to GAC. Moreover, the DiS-algi sorption mechanism was proven to be chemisorption by a pseudo-second order kinetics model and this mechanism gives rapid sorption kinetics with 6 mins of cadmium half life time. From the breakthrough tests, we found that the maximum capacity of the reactive column was 877 $\mu\text{g/g}$, and cadmium ions were completely removed by this reactive column for 2 hours until it reached to breakthrough point. Furthermore, regeneration tests proved the reusability of the column. Consider the sufficient sorption capacity with rapid kinetics and reusability of the reactive column, DiS-algi holds promise as a column filling material in airport derived stormwater treatment systems for removing cadmium.

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Figure captions

Figure 6 Schematic diagram of lab-scale reactive column of DiS-algi. The arrows indicate direction of flow during test.

Figure 7 Images obtained from optical microscope. (a) disulfide polymer (b) DiS-algi (c) cross section image of pure alginate bead and (d) cross section of DiS-algi.

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Figure 6 Cadmium removal plot in fixed bed column with continuous flow rate 0.5 and 1 mL/min. Both DiS-algi and GAC plots were fitted by one-phase association equation with plateau. Red dots represent DiS-algi, black dots for GAC, and solid line showing 0.5 mL/min flow rate while dashed line for 1 mL/min flow rate.

Figure 7 Sorption-desorption repeated test on reactive column using 0.1 M of HCl as flushing agent for desorption. Black-solid and blue-dashed lines are indicating effluent cadmium concentration and mass of cadmium in reactive column, respectively.

Table 3 Cadmium concentration ($\mu\text{g/L}$) in airport runoff, de-icing fluid and accepted limit for airports regulations

Sites	Sampling site	Concentration ($\mu\text{g/L}$)	Reference
Airport complex in brazil	Wetland	90 - 450	[1]
Copenhagen airport	Runways, aprons, and other areas	0.263 - 0.453	[10]
Baltimore-Washington Int. airport	storm-water discharge pipe	3	[11]
Seattle-Tacoma int. Airport	-	0.15 – 0.38	[10]
Poland airport	High capacity of passenger movement	0.08 – 5.28	[2]
De-icing fluid		Concentration ($\mu\text{g/L}$)	
De-icing Fluid Ethylene glycol based fluid		240	[6]
Propylene glycol based fluid		6.7	[6]
Aircraft de-icing/anti-icing fluids with 80% glycols		1500	[3]
Regulation		Effluent limitation	
Accepted limit for airports regulations for fresh water		0.2	[11],[12]

Table 4 Various data from sorption and kinetic studies of DiS-algi and GAC

	Maximum sorption capacity (mg/g)	Langmuir affinity constant (L/mg)	Half life time* (min)
DiS-algi	22.4	31	6
GAC	11.5	0.03	430
*Initial cadmium concentration 1 mg/L			