Removal of cadmium from airport derived stormwater by disulfide-polymer particles surface embedded on alginate beads

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Abstract Stormwater runoff water derived from airport areas gives severe cadmium contamination. To remove cadmium from the irregular amount of runoff water, a new sorbent material was introduced. Size-tunable alginate bead were successfully created with surface embedded high cadmium affinity disulfide-polymer particles (DiS-Alginate) suitable for high flow stormwater filters. Sorption and kinetic test were conducted at different concentrations of cadmium and compared with activated carbon. DiS-Alginate exhibited a maximum sorption capacity of 22.3 mg/g and almost 5 times higher sorption affinity than activated carbon. Moreover, the DiS-Alginate sorption mechanism was proven to be chemisorption that indicates rapid sorption kinetics. Therefore, DiS-Alginate appears to be a superior sorbent material for removing cadmium from airport stormwater.

Keywords: Airport runoff, disulfide-polymer, alginate beads, cadmium removal, column filling materials.

1. Introduction

Stormwater runoff is considered as huge non-point source of heavy metal ions in the surface water especially in airport regions [1][2]. Activities from airport everyday such as fueling operations, cleaning of aircraft, combustion of aviation are forming severe amount of precipitaion or atmospheric deposits. Moreover, considerable amount of aircraft de-icing/anti-icing fluids (ADAFs) are using worldwide to remove and prevent ice on aircrafts and it aggrevates the heavy metal pollution during cold seasons [2][3]. The presence of heavy metal ions in the water causes several adverse effects to living organisms. Among the heavy metal pollutions, cadmium is clearly established to have carcinogenic potential to humans and experimental animals [4][5]. Various cadmium concentrations in airport runoff are described to occur in the range 1 – 450 µg/L in different international airports even the accepted limit for airports regulations is 0.2 µg/L (Table 1). According to studies from United Stated environnmental protection agency [6] and Devon *et al.* [3], de-icing fluids detected to be containing 240 µg/L and 1500 µg/L, respectively. However, irregular amount of water at scattered rainfall events and various concentrations of pollutant concentrations hinder treatment of airport runoff. Hence, a highly efficient way of removing cadmium from the airport runoff is needed.

Recently, disulfide linked polymer networks for selective removal of heavy metal ions from water [7] has been published. This polymer networks showed rapid sorption kinetics with sufficient sorption capacity of heavy metal ions in the presence of competitive earth metal ions. In the previous study however only feasibility tests of polymer 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. Since the disulfide polymer is synthesized as a powder with an average diameter less than 1 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. In this study we therefore embedded disulfide polymer onto size-tuneable organic alginate beads (DiS-Alginate) and acheived bead size with an average diameter of 3 mm. These beads were tested for cadmium sorption and compared with a traditional used sorbent, high quality activated carbon.

Table 1. Cadmium concentration (µg/L) in airport runoff, de-icing fluid and accepted limit for airports regulations

Sites	Sampling site	Concentration	Reference
Airport complex in brazil	Wetland	90 - 450	[1]
Copenhagen airport	Runways, aprons, and other areas	0.263 - 0.453	[8]
Baltimore-Washington Int. airport	storm-water discharge pipe	3	[9]
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**	
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		1.5	[3]
Regulation		**Effluent limitation**	
Accepted limit for airports regulations for fresh water		0.2	[11][12]

2. Materials and Methods

2.1. Materials

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

2.2. Preparation of DiS-Alginate

Disulfide linked polymer network was prepared as described in previous study [7]. Briefly, by adding strong oxidant into the solution of thiocyanuric acid monomers and stirring for overnight. Thiols are oxidized and form disulfide link that end up with 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 firm up overnight. Subsequently, DiS-Alginate was washed with distilled water several times.

2.3. Batch test

Sorption isotherms were conducted in solutions prepared from metal stock solutions in presence of a 0.003 M $NaHCO_3$ buffer. pH values were adjusted with 1 M of HCl and NaOH, to be in the range 6 –7. Five different cadmium concentrations, ranging between 1 and 50 mg/L, were used for the sorption isotherms for both DiS-Alginate and AC. In a conical polyethylene (PE) tube, the cadmium solution was added to the DiS-Alginate. The tubes were shaken gently, and sampling started within a few minutes from start. For kinetic experiments, six sampling times were selected (initial, 2 mins, 10 mins, 1 h, 4 h, and 24 h). Sorbent and solution separation was performed using a 0.45 µm regenerated cellulose syringe filter. Batches were shaken on an end-over-end rotator. 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).

2.4. Expression for sorption isotherm, sorption kinetics

At equilibrium (q_e) the maximum amount of metal ions sorption of sorbent can be calculated by using the Langmuir isotherm equation:

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

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_L 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:

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

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[13] which can be expressed as:

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

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

2.5. Characterization of disulfide polymer networks

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-Alginate was from optical microscope.

3. Results and Discussion

3.1. Physical and chemical characterization of the disulfide polymer

The images of disulfide polymer, pure alginate bead and DiS-Alginate with cross sectional area were obtained from optical microscope to compare their morphology (Figure 1). The disulfide polymer sizes were less than 1 μm however DiS-Alginate measured on average 3 mm. Moreover, disulfide polymer was embedded into the surface of alginate bead rather than being distributed through the alginate bead. Therefore accessibility of heavy metal into the polymer was not inhibited by the size of the alginate bead.

The polymerization of disulfide polymer was confirmed by comparing IR peaks and elemental analysis. The elemental analysis of disulfide polymer was resulted 19.8% C, 0.4% H, 21.3% N, 52.5% S, and 4.0% O and this fraction accordance to 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) [7]. The FT-IR spectra (Figure. 2) show peaks of aromatic trithiol stretching 1466, 1226, 823 cm^{-1} in the polymer, which reflects 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} showed the formation of disulfide linkages in the disulfide linked polymer networks [7].

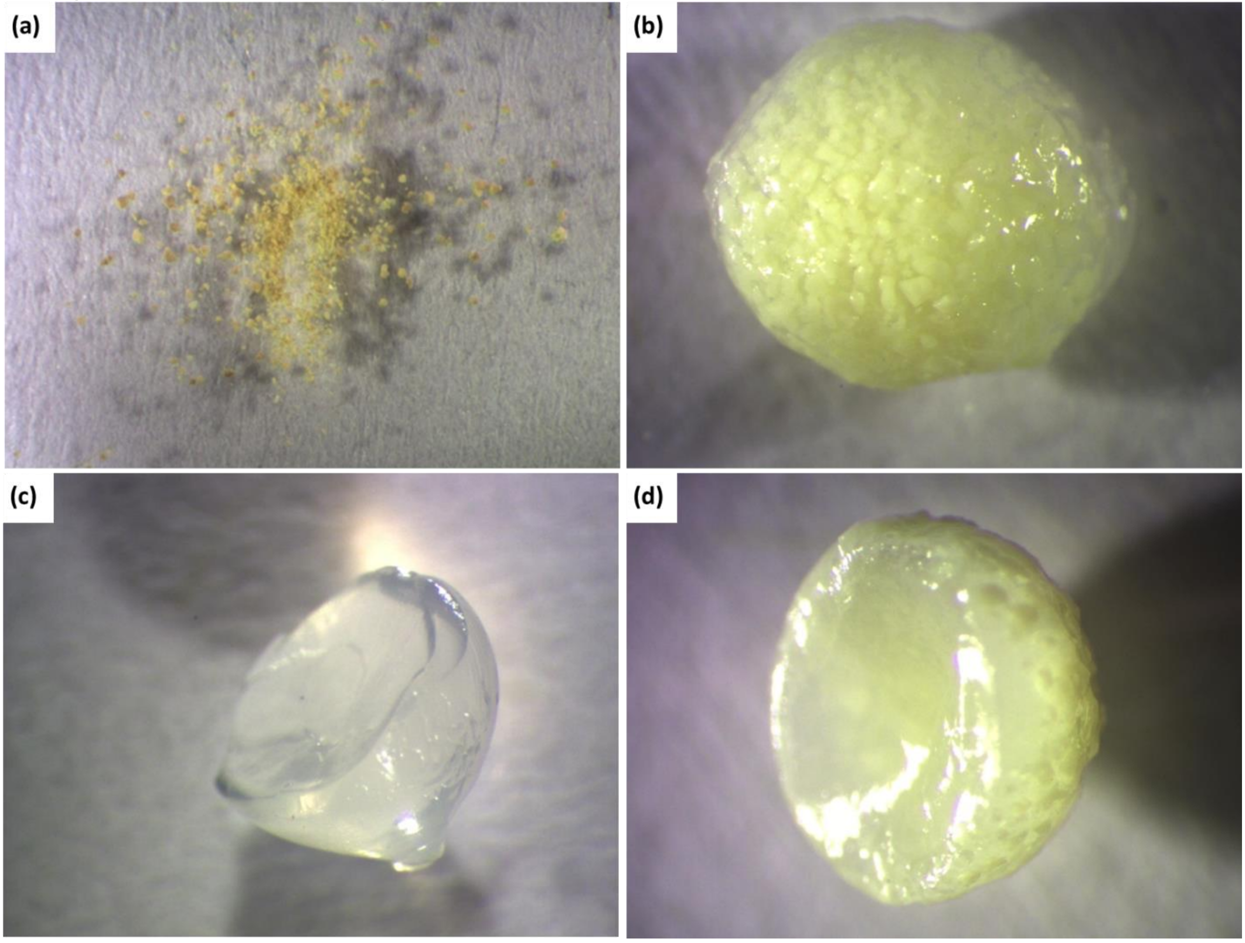

Figure 1. Images obtained from optical microscope. (a) disulfide polymer (b) DiS-Alginate (c) cross section image of pure alginate bead and (d) cross section of DiS-Alginate.

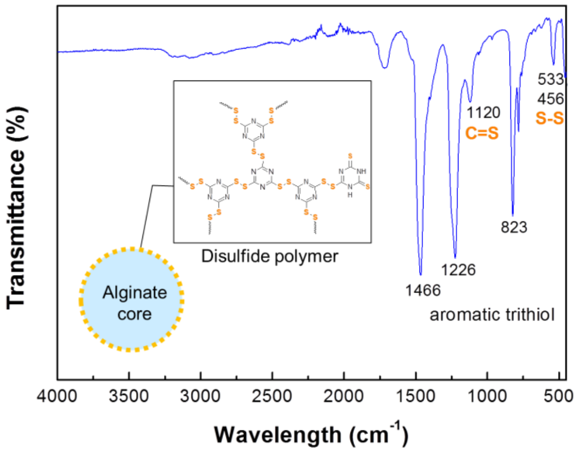

Figure 2. Infrared spectra of disulfide linked polymer networks. (Inset: schematic of DiS-Alginate.)

3.2. Cadmium equilibrium adsorption isotherms

To compare the sorption capacity of DiS-Alginate and AC, sorption isotherms were fitted as shown in Figure 3. The maximum sorption capacity of DiS-Alginate was 22.3 mg/g and it was 19.6 mg/g for AC. It is important to mention that Langmuir affinity constant (a_L) of DiS-Alginate was 32 L/mg and for AC it was just 6 L/mg, indicating that disulfide polymer coated bead has above 5 fold higher sorption affinity than AC.

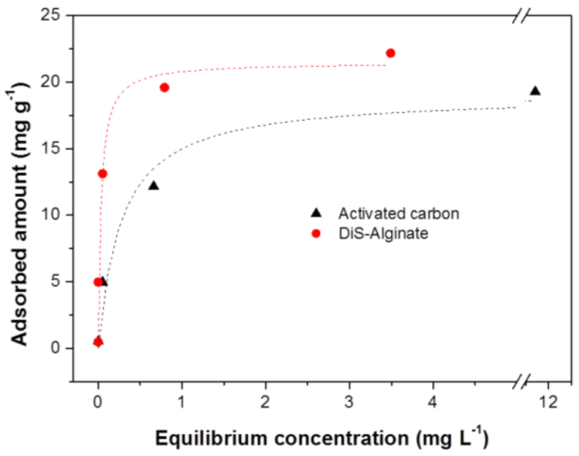

Figure 3. Langmuir sorption isotherm of DiS-Alginate (red, dashed line) and activated carbon (black, dashed line) from five different initial concentration batch tests. Plots are representing measured data.

The kinetic studies also conducted for two different adsorbents with four different concentration of cadmium (Figure 4). In the case of AC, sorption from 240 min gets slower due to the weak concentration diffusion however, DiS-Alginate has rapid sorption since sorption is derived with not only diffusivity but also chemical attractions. The sorption mechanism was also confirmed by kinetics fitting. Kinetic is considered as important parameter for determining physisorption fitted by pseudo first order kinetics and chemisorption by pseudo second order kinetics. AC was fitted on to pseudo first order kinetics (r^2 = 0.99) while disulfide polymer coated bead was successfully fitted with pseudo second order kinetics (r^2 = 1).

3. Conclusion

In this study, DiS-Alginate was introduced to remove cadmium from airport stormwater runoff water. Maximum sorption capacity of DiS-Alginate reached 22.3 mg/g while AC shows 19.6 mg/g and nearly 5 times higher sorption affinity shown in disulfide polymer coated bead compare to AC. Moreover, DiS-Alginate sorption mechanism proven to be chemisorption that gives rapid sorption kinetics. Consider the sufficient maximum sorption capacity and sorption affinity with rapid kinetics, disulfide polymer coated bead in promise to be a column filling material in airport wastewater system for removing cadmium from the runoff.

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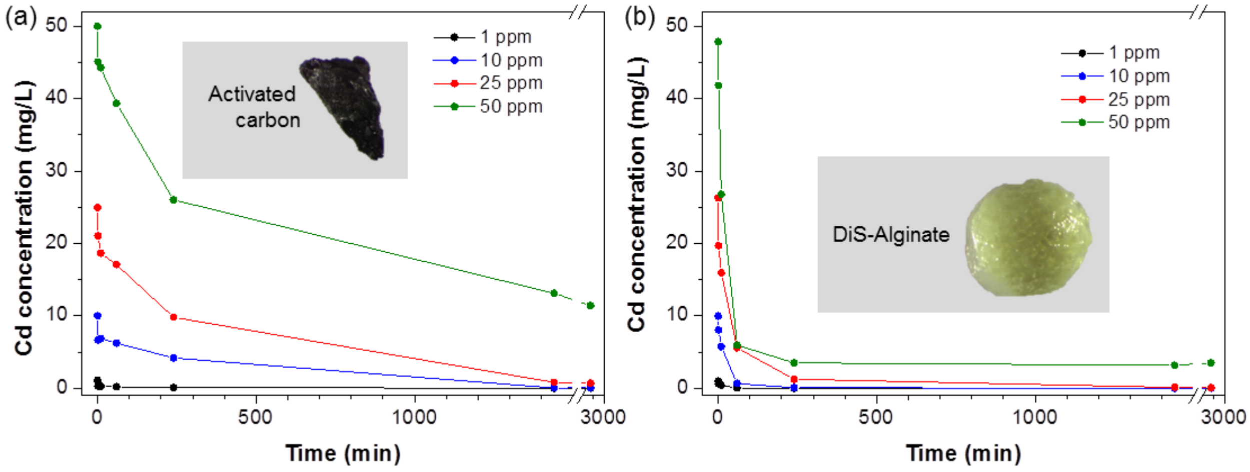

Figure 4. Cadmium sorption kinetic study of (a) AC and (b) DiS-Alginate**.** Four different initial concentration of cadmium were compared.

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