

Adsorption of dissolved copper and zinc on sand and iron oxide-coated sand (IOCS) for urban stormwater treatment: effects of pH, chloride, and sulfate

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ABSTRACT

This study investigated the adsorption efficiencies of dissolved copper (Cu(II)) and zinc (Zn(II)) on sand and iron oxide-coated sand (IOCS), which were considered as potential filter materials for treating urban stormwater runoff. Through a series of batch adsorption experiments, we compared adsorption efficiencies between sand and IOCS and examined the effects of varying stormwater conditions including pH, the coexistence of copper and zinc, and concentrations of chloride and sulfate ions. Surface area and point of zero charge of the sand media largely increased by coating iron oxides. IOCS always showed greater and stable removal of Cu(II) and Zn(II) with greater removal efficiency for Cu(II) than Zn(II). The effect of pH on the removal efficiency of Zn(II) by IOCS was minimal at pH 6–8 whereas the removal efficiency of Cu(II) by IOCS profoundly increased at pH > 7 likely due to the precipitation of copper hydroxide. The coexistence of Cu(II) and Zn(II) decreased their adsorption efficiencies by IOCS due to their competition for the available sites on the IOCS surface but with less decrease compared to sand. Adsorption efficiencies of sand and IOCS decreased as the concentrations of the Cl⁻ and SO₄²⁻ increased with smaller effects on IOCS than on sand. Competitions of the heavy metal ions with other cations such as Ca⁺ and Na⁺, the counter-ions for Cl⁻ and SO₄²⁻, might be the main cause of the decreased adsorption. The results of this study suggest that the use of IOCS as a filter media for the urban stormwater treatment can be potentially beneficial compared to conventional filter media such as sand because it can provide more stable and efficient removal of heavy metals contained in the stormwater runoff under varying chemical conditions.

Keywords: Adsorption; Sand; Iron oxide coated sand (IOCS); Copper; Zinc; Chloride; Isotherm

1. Introduction

Urban stormwater runoff has been recognized as one of the leading causes of pollution in rivers, lakes and estuaries [1]. Toxic organic compounds, nutrients and heavy metals are the primary pollutants found in urban stormwater runoff, impacting humans and other living organisms [2,3]. Heavy metals have been of particular concern due to their elevated concentrations in urban stormwater

runoff, impairing receiving waters [4]. Copper and zinc are the two predominant heavy metal species observed in urban stormwater runoff [2,5]. Major urban sources of copper and zinc include brake pads and other vehicle parts, vehicle combustions, building exteriors, and metal-containing pesticides [6,7]. Copper, even at very low concentration levels, can bioaccumulate and pose potential threats to human health and the ecosystem [8]. Existing literature

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reports that accumulation of copper in the human body can damage organs such as brain, skin, pancreas and heart [9,10]. Excessive intakes of zinc also cause problems such as anemia, fever, vomiting and skin inflammation [11]. Therefore, managing urban stormwater runoff, especially at its early stage of formation, is of great significance.

Currently available stormwater treatment techniques such as low-impact development and best management practices use sedimentation or filtration mechanisms to reduce peak flows and pollutant loads [12]. Existing studies have suggested that these techniques efficiently remove particles and particle-bound pollutants [12] but are less efficient in removing dissolved fractions of the pollutants including dissolved heavy metals [13]. In particular, copper and zinc in urban stormwater runoff are dominantly present in the dissolved form [4,14] and are poorly removed by conventional sedimentation and filtration practices [15]. To increase the removal efficiency of the dissolved heavy metals in stormwater runoff, various filter media have been examined including sand, calcite, zeolite, iron oxide-coated sand (IOCS), and recycled materials such as iron filings and plant driven materials [16–18].

IOCS has recently been drawing increased attention for treating stormwater runoff due to its high efficiency in removing microorganisms, turbidity and heavy metals [19–21]. The oxides of iron, especially α -Fe₂O₃ and α -FeOOH, are components that are broadly distributed on the surface of the earth [22]. Due to their relatively large surface area and high adsorption capability, iron oxide particles have been considered as an efficient sorbent for environmental pollutants [23,24]. However, it is difficult to separate iron oxide particles from the water after the adsorption process due to their extremely small sizes. IOCS has been prepared to address this separation problem by depositing iron oxides on the surface of sand [25].

Adsorption of heavy metals on filter media such as sand and IOCS can be influenced by the coexisting ions due to their interactions and competitions over active sites on the media surface [15,26]. In particular, urban stormwater typically contains a variety of metallic and non-metallic ionic species [27], which can affect the adsorption efficiency. In particular, the widespread use of de-icing salts in urban areas during winter seasons results in high levels of Cl⁻ in stormwater runoff, decreasing the removal efficiency of heavy metals in stormwater runoff using the adsorption process [28,29].

In this study, we examined how different conditions of major coexisting ions and pH in water can affect the adsorption capacity of heavy metals on IOCS using a series of batch experiments, and thereby evaluate the potential applicability of IOCS for treating urban stormwater runoff. Divalent copper (Cu(II)) and zinc (Zn(II)) were selected as the study of heavy metals because they are the two prevalent heavy metal ions found in urban stormwater runoff. The specific objectives of the present study are (1) to compare adsorption efficiency of the tested heavy metals between sand and IOCS, (2) to investigate the effect of pH and coexistence of the heavy metals on the adsorption capacity of IOCS, and (3) to investigate the effects of the coexisting anions, Cl⁻ and SO₄²⁻, which are the two prevalent anions found in urban stormwater runoff [27].

2. Materials and methods

2.1. Preparation of adsorbents

IOCS was prepared following the procedure proposed by Lo et al. [30]. Raw sand was sieved to have a diameter range of 0.5–0.6 mm before use. The sieved sand was soaked in 1 M HCl solution for 24 h as pretreatment, and was repeatedly rinsed for multiple times using ultrapure water, and then was placed in the oven at 105°C until it was completely dried up. Solutions of 1 M FeCl₃ and 6 M NaOH, 100 mL each, were fully mixed and stirred. A 100 mL of mixed solution was evenly mixed with the pretreated sand in a conical flask, which was then placed in a temperature-controlled orbital shaker operated at 90°C for 6 h, until the moisture was completely dried up. The mixture was repeatedly rinsed using ultrapure water until the water ran clear, and then was placed in the oven at 105°C until it was completely dried up. The iron (Fe) content and the surface area of the prepared IOCS were determined using an acid digestion method [31], and the Brunauer–Emmett–Teller (BET) method (Autosorb-iQ 2ST/MP, Quantachrome, USA), respectively.

2.2. Determination of the point of zero charge (pH_{pzc})

The point of zero charge (pH_{pzc}) was determined using the salt addition method [32]. A 0.1 M NaNO₃ solution was prepared, and its pH was adjusted to 4, 5, 6, 7, 8, 9, 10 and 11 using 0.1 M HNO₃ and 0.1 M NaOH. A 40 mL of the prepared solution was mixed with 0.2 g of sand or IOCS sample, and was then agitated at the temperature of 30°C for 24 h. The pH value of each solution was measured to calculate the pH difference (Δ pH) before and after the agitation. The pH value at Δ pH = 0 was taken to be pH_{pzc}.

2.3. Batch experiments

A series of batch experiments were conducted to examine adsorption kinetics and adsorption capacity of Cu(II) and Zn(II) on the adsorbents. Experimental solutions containing 1,000 μ g/L Cu(II) and/or 1,000 μ g/L Zn(II) were prepared from CuSO₄·5H₂O and ZnSO₄·7H₂O: an experimental solution containing only Cu(II) or Zn(II) is termed “singular system” and that containing both Cu(II) and Zn(II) is termed “binary system”. Experimental solutions containing Cl⁻ or SO₄²⁻ were prepared from CaCl₂ and Na₂SO₄. The pH of the experimental solution was adjusted to a required value before the experiment using 0.1 M NaOH and 0.1 M HCl.

Each adsorbent–adsorbate mixture sample (termed hereafter as “experimental sample”) for the batch experiments was prepared by adding a selected amount (e.g., 5 g for the kinetic studies) of sand or IOCS to 100 mL experimental solution. The experimental samples were shaken at 120 rpm in an orbital shaker maintained at 25°C \pm 1°C during the required adsorption times, and were filtered through 0.45 μ m membrane filters for the heavy metal analysis using inductively coupled plasma mass spectrometry (ICP-MS 7500ce, Agilent Technologies, CA, USA).

To examine the effects of coexisting anions, kinetic studies were conducted at Cl⁻ = 0, 50, and 100 mg/L, and

$\text{SO}_4^{2-} = 0, 25, \text{ and } 50 \text{ mg/L}$. These concentration ranges of Cl^- and SO_4^{2-} were determined based on the typical concentration ranges observed in the urban stormwater runoff [27]. In particular, effects of Cl^- on the adsorption were of great interest because Cl^- primarily originates from deicing agents such as NaCl and CaCl_2 applied to the road. For each set of the kinetic studies, seven experimental samples of $\text{pH} = 7$ were used with the adsorption times of 0, 15, 30, 60, 120, 180 and 240 min, respectively.

Batch equilibrium experiments were performed to compare the adsorption capacity between sand and IOCS, and to investigate the effects of pH and coexistence of Cu(II) and Zn(II) on the adsorption capacity. The effects of pH were investigated using the singular experimental solutions at the initial $\text{pH} = 6, 7, \text{ and } 8$, which were determined based on the typical pH range of urban stormwater runoff [33]. The effects of coexistence of Zn(II) and Cu(II) were investigated using the binary experimental solutions at $\text{pH} = 7$. An adsorption time of 240 min was used as an equilibrium time, which was determined from the kinetic study. For each set of the batch experiment, six experimental samples containing 0.5, 1, 2, 5, 10, and 15 g of sand or IOCS were used.

2.4. Analysis of experimental data

Solid phase concentrations of the heavy metals from the batch experiments were calculated using the following equation.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where q_t is the solid phase heavy metal concentration after an adsorption time, t ($\mu\text{g/g}$), C_0 and C_t are the heavy metal concentrations in the solution at $t = 0$ and $t = t$, V is the volume of the solution (L), and m is the dry weight of the adsorbent (g).

Data from the kinetic study were fitted to the pseudo-second-order kinetic model, which showed better fitting results than the pseudo-first-order kinetic, Elovich kinetic, and intra-particle diffusion models. The pseudo-second-order kinetic model is expressed as [34].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where k_2 is the second order rate coefficient ($\mu\text{g/g min}$) and q_e is the solid phase heavy metal concentration at equilibrium ($\mu\text{g/g}$). Eq. (2) was rearranged for the linear data fitting as follows.

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

In Eq. (3), $k_2 q_e^2$ is defined as the initial removal rate, h ($\mu\text{g/g min}$). Values of h , k_2 and q_e can be obtained from the linear data fitting.

Data from the equilibrium experiments were fitted to the Freundlich isotherm model, which showed

overall better fitting results than the Langmuir isotherm model. The Freundlich isotherm model is expressed as [35]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where C_e is the heavy metal concentration in the solution at equilibrium ($\mu\text{g/L}$). The Freundlich parameters, K_F ($\mu\text{g/g}$) and $1/n$ are associated with the adsorption capacity and adsorption intensity, respectively, and can be obtained from the linear correlation between $\log q_e$ and $\log C_e$.

2.5. Heavy metal speciation modeling

Speciation of Cu(II) and Zn(II) in water was modeled using a chemical equilibrium modeling software, MINEQL+ (Environmental Research Software, Hallowell, ME, USA). An open system with a constant atmospheric CO_2 pressure of $10^{-3.5}$ atm was assumed and speciation calculations were performed at a pH range of 4 – 10. The speciation modeling was performed with and without Cl^- and SO_4^{2-} with maximum concentrations used in the batch experiments.

3. Results and discussion

3.1. Characteristics of sand and IOCS

The Fe content of IOCS was $0.62 \pm 0.07 \text{ mg-Fe/g-sand}$, which was less than those reported in previous studies ranging from 1.6 to 6.2 mg-Fe/g-sand [25,36,37]. Conditions of pH and temperature during the coating procedure and the grain size of the sand can affect the amount of Fe coated on the sand [36]. The lower Fe content of IOCS compared to previous studies might be because this study used a relatively lower coating temperature (150°C – 550°C in previous studies) to reduce the production energy, and multiple washing procedures taken after the coating to avoid potential Fe release during the experiments.

The BET specific surface areas (S_{BET}) of sand and IOCS were 0.20, and 0.27 m^2/g , respectively, indicating that the iron oxide coating could increase the surface area potentially available for heavy metal adsorption. As shown in Fig. 1, iron oxide coating could also increase pH_{PZC} of the media (3.0 for sand and 6.0 for IOCS). However, S_{BET} and pH_{PZC} of the IOCS prepared in this study were relatively low compared to previous studies reporting 2.6–7.0 m^2/g for S_{BET} [22,25,36–38] and 7.4–9.8 for pH_{PZC} [19,22,25,38,39], due to the relatively low Fe content.

Relatively low Fe content, S_{BET} and pH_{PZC} of the prepared IOCS compared to the previous studies were due to the relatively low coating temperature and vigorous washing procedure, which might compromise the adsorption performance of the IOCS. However, the lower coating temperature and vigorous washing procedure during the IOCS production should be more appropriate for the field application by reducing the production cost and secondary pollution due to Fe detachment during the operation.

3.2. Adsorption kinetics of sand and IOCS

Adsorption kinetics of Cu(II) and Zn(II) were compared between sand and IOCS in Fig. 2. In all cases, the adsorption

equilibrium was reached within 120 min, and over 90% of the maximum adsorption capacity for Cu(II) or Zn(II) was reached within 30 min for IOCS. IOCS showed greater and faster adsorption for both Cu(II) and Zn(II) than sand while Cu(II) adsorption was more efficient than Zn(II) for both sand and IOCS: The maximum adsorption efficiencies of Cu(II) and Zn(II) on the sand were 92.8% and 71.8%, respectively, and those on IOCS were 99.8% and 96.2%, respectively. In particular, Zn(II) adsorption was greatly improved by coating iron oxides on sand (greater than a 20% increase in the adsorption efficiency).

The time-varying sorption data were well fitted to the pseudo-second-order kinetic model with R^2 values greater than 0.99 (Table 1). As shown in Table 1, significant improvements were observed after coating iron oxides on the sand in adsorption rates (k_2), adsorption capacity (q_e), and initial adsorption (h), with a particularly significant increase in those parameters for Zn(II).

3.3. Effect of pH and coexistence

Table 2 shows the parameters of the Freundlich isotherm model obtained from the batch experiments for IOCS. The adsorption capacity (K_f) of Cu(II) increased as pH increased between pH 6 and 8: The value of K_f increased significantly at pH 6–7, and slowly at pH 7–8. The lower adsorption capacity at lower pH values can be partly due

to the higher competition between Cu^{2+} and H^+ over the available negative sites of IOCS for adsorption [40]. Note that the value of pH_{PZC} of IOCS was about 6, implying that the IOCS surface should be dominantly negatively charged in the studied pH range. Furthermore, precipitation of $\text{Cu}(\text{OH})_2(\text{s})$ at a $\text{pH} > 6.8$ (Fig. 3) might contribute to the significant increase in the liquid phase Cu(II) removal at pH 6–7 [41]. In contrast, no significant difference or trend in the value of K_f was observed for Zn(II) in the studied pH range. As shown in Fig. 3, Zn(II) is dominantly present as Zn^{2+} ion at $\text{pH} < 8.2$, suggesting that electrostatic interactions and complexation on the IOCS surface can primarily contribute to the Zn(II) removal from the solution [25,42]. Zn(II) does not precipitate in the studied pH range (Fig. 3), which might partly explain the little difference in the adsorption capacity among the three pH conditions, and the lower removal efficiency compared to Cu(II).

Freundlich parameters obtained for the singular and binary experimental solutions were summarized in Table 3. The adsorption capacities of those heavy metals were lower in the binary system than in the singular system due to the competition between Cu(II) and Zn(II) [22,38]: the value of K_f for Cu(II) and Zn(II) decreased by 45.7% and 38.4%, respectively in the binary system as opposed to the singular system. Cu(II) consistently showed a greater adsorption efficiency than Zn(II) in both singular and binary systems.

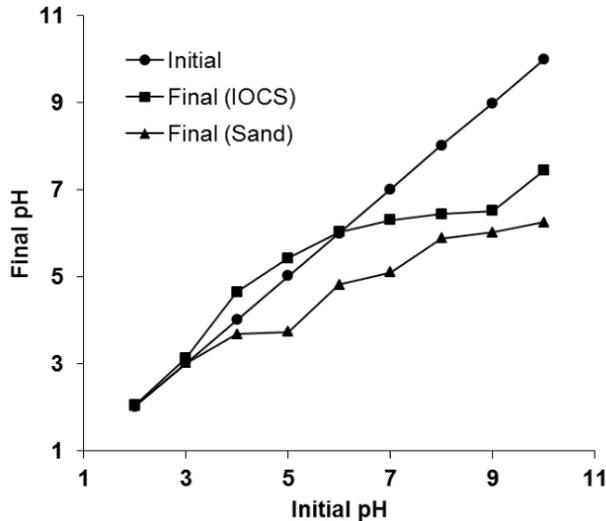


Fig. 1. Determination of pH_{PZC} for sand and IOCS by the salt addition method.

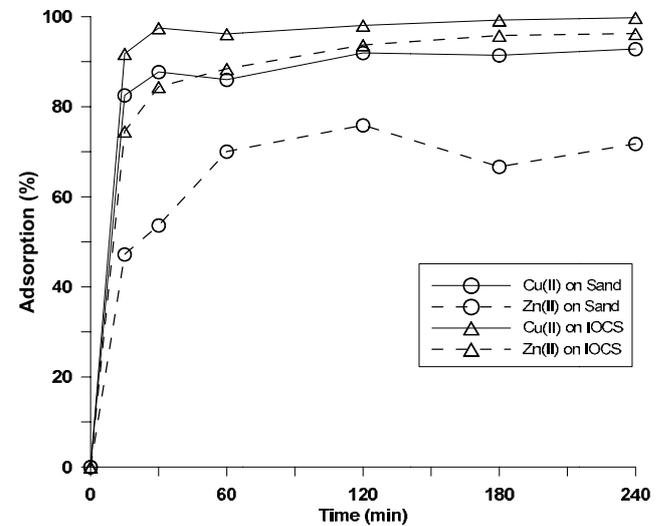


Fig. 2. Adsorption of Cu(II) and Zn(II) on sand and IOCS with respect to time.

Table 1
Kinetic parameters for adsorption of Cu(II) and Zn(II) on sand and IOCS

Adsorbent	Adsorbate	k_2 (g/ $\mu\text{g min}$)	q_e ($\mu\text{g/g}$)	h ($\mu\text{g/g min}$)	R^2
Sand	Cu(II)	2.25×10^{-2}	15.1	5.18	0.999
	Zn(II)	1.52×10^{-2}	10.4	1.65	0.993
IOCS	Cu(II)	3.47×10^{-2}	16.6	9.59	0.999
	Zn(II)	1.24×10^{-2}	14.7	2.68	0.999

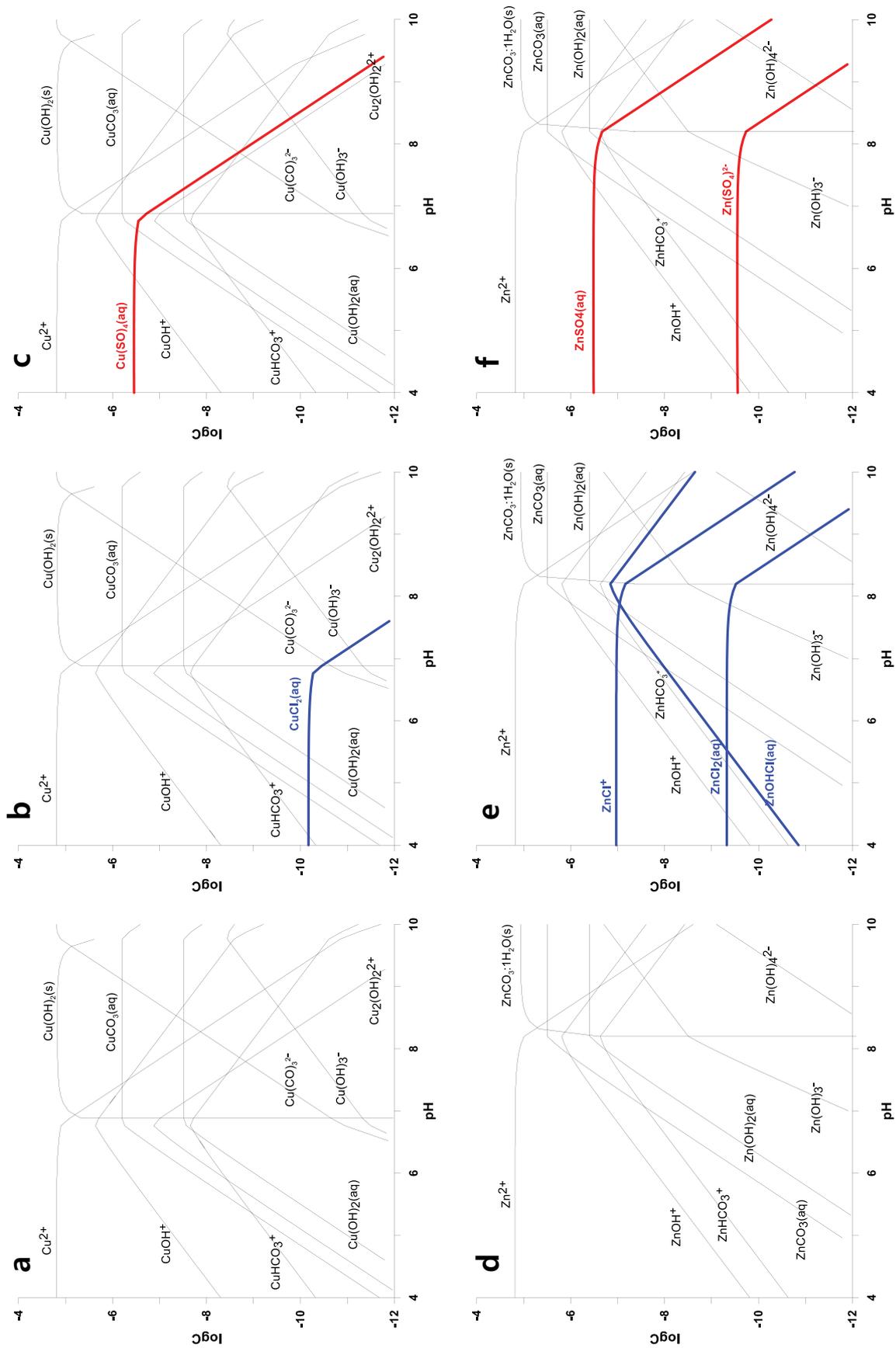


Fig. 3. Speciation of (a) Cu(II) and (b) Zn(II) in the solution (total Cu(II) or Zn(II) concentration = 1,000 µg/L) modeled by MINEQL+; (a) Cu(II), (b) Cu(II) with 100 mg/L of total Cl^- ; (c) Cu(II) with 50 mg/L of total SO_4^{2-} ; (d) Zn(II), (e) Zn(II) with 100 mg/L of total Cl^- , and (f) Zn(II) with 50 mg/L of total SO_4^{2-} . Blue and red curves indicate Cu(II) or Zn(II) complexes formed with Cl^- and SO_4^{2-} , respectively.

Table 2
Freundlich parameters for adsorption of Cu(II) and Zn(II) on IOCS at different initial pH in the singular system

Adsorbate	pH	K_f ($\mu\text{g/g}$)	$1/n$	R^2
Cu(II)	6	2.773	0.429	0.737
	7	4.966	0.322	0.961
	8	5.395	0.324	0.868
Zn(II)	6	2.336	0.399	0.958
	7	2.412	0.367	0.877
	8	2.062	0.399	0.910

Table 3
Freundlich parameters for adsorption of Cu(II) and Zn(II) on IOCS at pH = 7

Experimental solution	Adsorbate	K_f ($\mu\text{g/g}$)	$1/n$	R^2
Singular system ^a	Cu(II)	4.966	0.322	0.961
	Zn(II)	2.419	0.367	0.877
Binary system ^b	Cu(II)	2.692	0.475	0.908
	Zn(II)	1.490	0.334	0.937

^aExperimental solution containing either Cu(II) or Zn(II);

^bExperimental solution containing both Cu(II) and Zn(II).

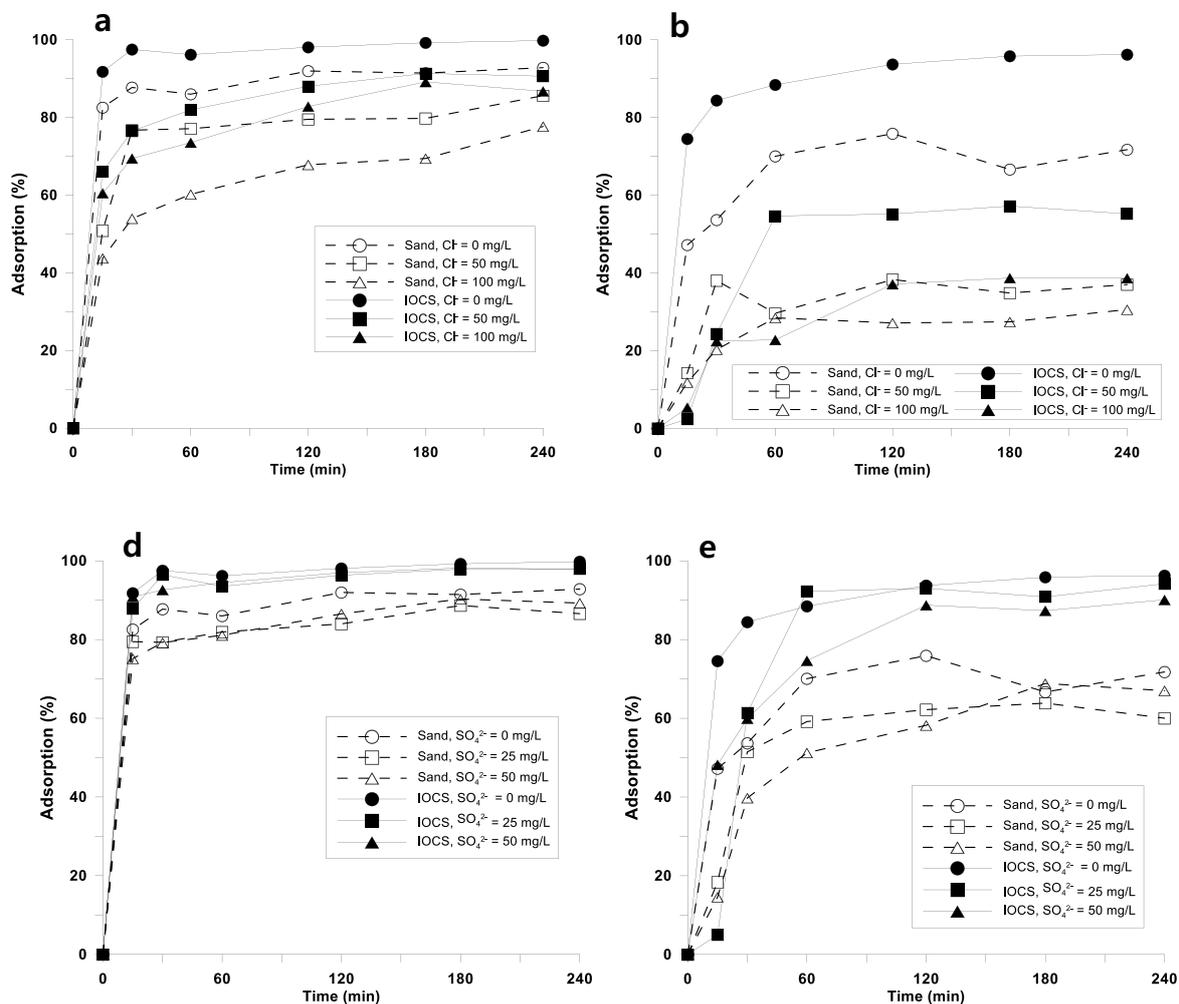


Fig. 4. Adsorption kinetics of heavy metals on sand and IOCS with varying concentrations of chloride and sulfate ions (adsorbent dose = 5 g/100 mL): (a) Cu(II) with Cl⁻, (b) Zn(II) with Cl⁻, (c) Cu(II) with SO₄²⁻, and (d) Zn(II) with SO₄²⁻.

3.4. Effects of chloride and sulfate

Fig. 4 shows the effects of Cl⁻ and SO₄²⁻ on the adsorption of Cu(II) and Zn(II). The adsorption efficiencies of sand and IOCS decreased proportionally to the concentrations of Cl⁻ or SO₄²⁻, with greater decreases with Cl⁻ than with SO₄²⁻. Overall IOCS was less affected by those coexisting ions than

sand, suggesting that IOCS can be a better filter material than sand for urban stormwater treatment.

The adsorption efficiency of Zn(II) was more significantly affected by the coexisting ions than that of Cu(II). For example, adsorption capacity (q_e at the adsorbent dose = 5 g/100 mL) of Zn(II) decreased by 60% (from 96.6% to 38.7%) as the Cl⁻ concentration increased from 0 to

100 mg/L while that of Cu(II) decreased by only 16% (from 92.8% to 77.7%) for the same condition. Previous studies have reported that coexisting anions such as Cl^- and SO_4^{2-} can reduce the adsorption efficiency of heavy metals because of the formation of heavy metal complexes with those anions [28,43]. However, the concentrations of Cl^- and SO_4^{2-} investigated in the present work were not sufficiently high to measurably affect the adsorption efficiency by heavy metal complexation. As shown in Figs. 3b, c, e, f, negligibly small fractions of heavy metal complexes with Cl^- and SO_4^{2-} can be formed between at 4–10 (<1% for heavy metal- Cl^- complexes and <2.5% for heavy metal- SO_4^{2-} complexes). Therefore the decrease of the heavy metal adsorption efficiency might be primarily due to the competition between the heavy metals and other cations such as Ca^{2+} and Na^+ [28], which were contained in the experimental solutions created from CaCl_2 and Na_2SO_4 . We presumed that the greater apparent impacts of Cl^- than SO_4^{2-} might be mainly due to the fact that divalent cations such as Ca^{2+} can compete more efficiently for cation exchange sites of the adsorbent than monovalent cations such as Na^+ [44].

4. Conclusions

In this study, we investigated the adsorption efficiencies of Cu(II) and Zn(II) on sand and IOCS, which were considered as potential filter media for treating urban stormwater runoff. A series of batch experiments were conducted to examine the effects of chloride and sulfate ions, pH and coexistence of the heavy metals on the adsorption efficiencies of Cu(II) and Zn(II) on sand and IOCS. From this study, the following conclusions were made:

- Coating of iron oxides on sand could increase the specific surface area and positively charged sites on the surface of the adsorbent, potentially increasing the adsorption capacity of heavy metals. Surface area and point of zero charge were $0.20 \text{ m}^2/\text{g}$ and 3.0 for sand, and $0.27 \text{ m}^2/\text{g}$ and 6.0 for IOCS.
- Cu(II) was more efficiently removed than Zn(II) using sand or IOCS. Adsorption capacity of Cu(II) on IOCS increased as pH increased from 6 to 8, with a sharp increase from pH 6 to 7. Precipitation of Cu(II) at pH > 6.8 might result in the significant increase in the liquid phase Cu(II) removal. Little change in the adsorption capacity of Zn(II) on IOCS was observed.
- Coexistence of Cu(II) and Zn(II) decreased their adsorption efficiencies by IOCS. Cu(II) and Zn(II) decreased by 45.7% and 38.4%, respectively in the binary system as opposed to the singular system. Cu(II) consistently showed a greater adsorption efficiency than Zn(II) in both singular and binary systems.
- IOCS showed overall greater and more stable adsorption of Cu(II) and Zn(II) than sand under varying conditions of Cl^- and SO_4^{2-} concentrations. Adsorption efficiencies of sand and IOCS decreased as the concentrations of Cl^- and SO_4^{2-} increased with smaller effects on IOCS than on sand. Competitions of the heavy metal ions with other cations such as Ca^{2+} and Na^+ , the counter-ions for Cl^- and SO_4^{2-} , were likely the main cause of the decreased adsorption.

The results of this study suggest that the use of IOCS for urban stormwater treatment can be potentially beneficial because it can provide stable and efficient removal of heavy metals contained in the stormwater runoff under varying chemical conditions. Furthermore, IOCS can be a good alternative to the regular sand filter media in treating urban stormwater because the high adsorption performance of IOCS can reduce the size or extend the lifetime of the stormwater treatment facility.

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