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A Dual Media Filter using Zeolite and Mortar for the Efficient Removal of Heavy Metals in Stormwater Runoff

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Abstract: Stormwater runoff from expressways contains high concentrations of various heavy metals. However, heavy metal removal in most current runoff treatment facilities, using infiltration and filtration, is limited and poses substantial risks. Therefore, this study proposes and evaluates a dual media system of mortar and Na-zeolite, which are inexpensive and readily available, using long-term continuous column experiments for the removal of heavy metals. The results showed significant Cu^{2+} removal with Na-zeolites that was improved by the addition of a thin mortar layer, while a sand layer provided negligible improvements. The removal of Cu was further enhanced by increasing mortar layer thickness. The removal of Cu^{2+}, Zn^{2+}, Fe^{3+}, and Ni^{2+} in a mixture was enhanced as the mortar layer's thickness increased, while the contribution of Na-zeolite was significant in 232 h experiments with a fixed empty bed contact time (EBCT) of 1.8 min. Moreover, the media were not saturated with Fe throughout the operation period. These results suggest that the dual media system is cost-effective and efficient in the removal of heavy metals from stormwater runoff via precipitation, filtration, and adsorption with a short EBCT.

Keywords: non-point source pollution; expressway; runoff; heavy metals; adsorption; precipitation; filtration

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Citation: Kim, D.-G.; Ko, S.-O. A Dual Media Filter using Zeolite and Mortar for the Efficient Removal of Heavy Metals in Stormwater Runoff. *Water* **2022**, *14*, 3567. https://doi.org/10.3390/w14213567

Academic Editor: Carmen Teodosiu

Received: 13 October 2022
Accepted: 4 November 2022
Published: 6 November 2022

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1. Introduction

Expressways are highly impervious, resulting in higher loads of pollutants in stormwater runoff than from other non-point sources (NPSs) [1,2]. In particular, the concentration of heavy metals is significantly higher in the runoff from expressways than in those from farmland, residential areas, and commercial areas [2–4]. The reported total concentrations of Al, Cd, Cr, Cu, Fe, Pb, Ni, and Zn in expressway runoff were in the ranges of 4.9–0.15, 400–0.1, 1900–0.056, 9650–1, 162,000–0.334, 13,100–0.5, 19,100–5.5, and 21,060–1 μg/L, respectively, while the dissolved concentrations were 0.16–0.02, 67–1, 8.1–0.03, 21–0.026, 8.1–0.037, up to 18.8, 15.7–1.2, and 416–0.04 μg/L [2–7]. The main sources of heavy metals are vehicles and road surface wear [1–3,8].

NPS pollution reduction facilities that use filtration and infiltration have been designed and installed for the treatment of suspended solids (SS), organic matter, nitrogen, and phosphorus, and their removal efficiencies have been intensively studied and evaluated [9,10]. However, the substantial risks of heavy metals in runoff have not been addressed. In the Korea, an NPS pollution management plan has been established for threducing BOD, total phosphorus, and SS [11].

Infiltration facilities have shown highly variable heavy metal removal efficiencies of 25–60%, but no reliable verification process has been designed [10,12]. In addition, there is a high risk of heavy metal contamination with respect to soil near infiltration facilities. According to a survey of an infiltration facility in Tokyo, Japan, the concentration of heavy metals in soil near the facility was not significantly lower than that of the media applied in the facility [13]. Another study also reported that the soil near an infiltration facility

was seriously contaminated with heavy metals [14]. Therefore, there is an urgent need for developing efficient alternatives for heavy metal removal in stormwater runoff.

It has been suggested that an adsorption–filtration system using engineered media, i.e., adsorbents, could be a better strategy for the effective removal of heavy metals in highway runoff [15,16]. The filtration medium is a critical factor in the effective pollutant reduction when using filtration, adsorption, infiltration, and precipitation [17]. The adsorbents currently studied for heavy metal removal in rainfall runoff include sandy-loam [18], zeolites [19], activated carbon [20,21], construction waste (bricks and small amounts of concrete) [20], granular ferric hydroxide (GFH), manganese dioxide, concrete, crab shells [22], calcite, zeolites, sand, iron filings [23], granulated water treatment sludge [16], activated alumina, porous concrete, activated lignite, dolomite, and iron hydroxide (FerroSorp®) [21].

Based on a literature review of various adsorption/filtration media, a preliminary survey and experiments were conducted to select the optimal media for this study. Several factors including cost, heavy metal removal efficiency, permeability, particle size, and ease of procurement were considered. Sand, GFH, biochar, zeolite, Na-zeolite, and orchid stone were tested, and Na-zeolite was selected as the optimal adsorbent based on the equilibrium adsorption capacity and adsorption kinetics. Na-zeolite is generally prepared by the impregnation of zeolite in NaCl solution to exchange metal cations in zeolite with Na^+ in order to enhance metal ion removal [24]. The improved adsorption of metals by Na-zeolite suggests its use as an intermediate for specific metal doping in zeolite [25]. On the other hand, processing at a higher pH could provide enhanced efficiencies for heavy metal removal via precipitation, followed by filtration/sedimentation/flotation, because most metals form hydroxides above a certain pH [26]. Therefore, the use of an alkali agent, such as calcite and cementitious materials, presents a high potential for heavy metal removal.

In this study, a system consisting of dual adsorption/filtration media was proposed. The upper part of the filtration bed was filled with granular mortar, and the pH of the influent was increased to induce precipitation of dissolved heavy metals. The lower bed was filled with granular Na-zeolite for the adsorption and filtration of dissolved and precipitated heavy metals. A series of column experiments was performed to verify the performance and to investigate the effects of influencing factors such as the ratio of mortar to Na-zeolite layers, empty bed contact time (EBCT), and co-existing heavy metals.

It is believed that the proposed system would provide a novel alternative for the efficient removal of heavy metals in stormwater runoff within a short contact period via a combination of precipitation, filtration, and adsorption. Moreover, the system can be cost-effective because the media are readily available and cheap, with well-known properties. In addition, this study focused on long-term continuous tests for a better evaluation of the system for field applications, which is different from previous studies [17–21].

2. Materials and Methods

2.1. Materials

Sodium chloride (NaCl), copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), zinc(II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 3H_2O$), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Merck KGaA (Darmstadt, Germany). All were of analytical grade and used as received. Distilled, deionized water (DDW) was obtained using an Aquapuri 551 system (Younglin, Anyang, Korea).

Na-zeolite was prepared by mixing 5 g of zeolite (Rex Materials Co., Ltd., Pohang, Korea) with 1 L of 1 M NaCl aqueous solution, washing with DDW, and drying at 105–110 °C for 24 h [27]. Mortar was prepared by mixing cement, sand, and water at a ratio of 5:2:1 (*w*:*w*:*w*). After curing, the mortar was crushed and sieved using standard #8 and #12 sieves (1.70–2.36 mm). Joomoonjin sand (Joomoonjin Silica Sand Co., Ltd., Gangneung, Korea), generally adopted for the sand filtration of runoff in Korea, was tested as a control material.

2.2. Continuous Experiments

2.2.1. Removal of Cu^{2+} by Various Types of Filter Media

Cu^{2+} was selected as a representative heavy metal in expressway runoff [20,22]. An aqueous solution of 100 mg/L Cu^{2+} was prepared using DDW and $Cu(NO_3)_2 \cdot 3H_2O$, and the pH was adjusted to 5.0 using 0.1 N HCl and 0.1 N NaOH. Meanwhile, it should be noted that the total SS (TSS) is also an important indicator of anthropogenic pollutants in stormwater runoff [28,29]. In addition, a significant fraction of the heavy metals in stormwater runoff exists as particulate form, and can be removed via TSS removal, i.e., filtration and sedimentation [2–7]. It also indicates that the TSS removal is also indicative of the metals in solid form. However, the dissolved metals are not readily removed via TSS removal; therefore, additional or separate treatments are necessary for removing them.

Glass columns with a length of 40 cm and an inner diameter of 1.5 cm were filled with sand or Na-zeolite (Figure 1A) corresponding to an EBCT of 1.8 min. This EBCT corresponds to a linear velocity of 20 m/h, which previously was determined by the evaluation of stormwater filtration devices of Korea [30]. The Cu^{2+} solution was injected onto columns at a flow rate of 8 mL/minute using a metered pump (JWS 100, JeniWell, Korea). The effluent from the columns was collected at a predetermined time interval until the concentration of Cu^{2+} in the effluent was equal to that of the influent. An additional experiment was performed using mortar/Na-zeolite dual media in which a mortar layer of depth producing an EBCT of 0.2 min was placed over the Na-zeolite layer to achieve a total EBCT of 2.0 min. Detailed experimental conditions are provided in Table 1.

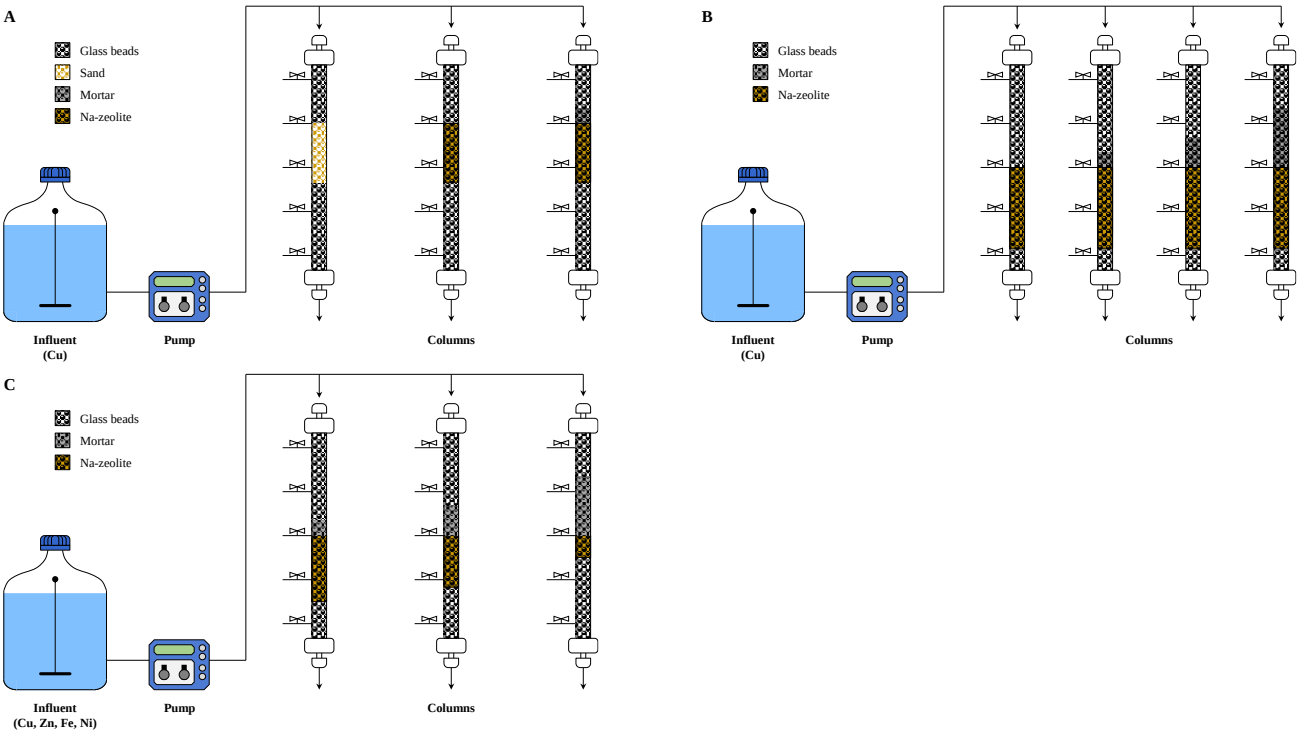


Figure 1. Schematics of the experimental setup for (**A**) the removal of Cu^{2+} using sand, Na-zeolite, or mortar/Na-zeolite; (**B**) the removal of Cu^{2+} using mortar/Na-zeolite with different depths of mortar; and (**C**) the removal of a metal mixture using mortar/Na-zeolite with different ratios of mortar and Na-zeolite depths.

Table 1. Experimental conditions for continuous Cu^{2+} removal.

Condition	Sand	Na-Zeolite	Mortar/Na-Zeolite
Depth (cm)	8.2	8.2	1 + 8.2
EBCT (minute)	1.8	1.8	0.2 + 1.8
Mass (g)	33.05	17.84	3.18 + 17.84
Initial Cu^{2+} (mg/L)	100	100	100

Effluent samples were filtered through a 0.45 µm polyvinylidene fluoride (PVDF) filter, and the Cu^{2+} concentration of the filtrate was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, OPTIMA 5300 DV, Perkin-Elmer).

The Thomas model was used to analyze the experimental results (Equation (1)) [31,32]:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{k_T q_e x}{Q} - \frac{k_T C_0 t}{1000}\right)} \quad (1)$$

where C_0 is the influent Cu concentration (mg/L), C_t is the Cu^{2+} concentration of effluent at time t (mg/L), k_T is the Thomas model adsorption rate constant (mL/min·mg), q_e is the equilibrium adsorption amount per unit mass of adsorbent (mg/g), x is the mass of adsorbent (g), and Q is the flow rate (mL/min). The Thomas model is the most widely used model for continuous adsorption, assuming that the adsorption rate depends on a reversible secondary reaction and the Langmuir kinetics of adsorption–desorption [31–33]. The Thomas model was used in this study, although it was expected that heavy metal removal in this study was attributable not only to adsorption but also to precipitation, because the Thomas model has been successfully used for describing column performance with a combination of various mechanisms accompanied with adsorption, such as precipitation in metal removal by iron-oxide-coated gravel [34], oxidation, and complexation, i.e., in the metal removal by humic-acid-coated sand [35], and ion exchanges [31,36].

2.2.2. Removal of Cu^{2+} in Mortar/Na-Zeolite Dual Filter Media

For the mortar/Na-zeolite dual media, Cu^{2+} adsorption was examined by changing the depth of the mortar layer to 2, 4, or 8 cm, corresponding to an EBCT of 0.31, 0.62, and 1.25 min, respectively. The depth of Na-zeolite was fixed at 11 cm (Table 2, Figure 1B). The experiments were carried out as described in Section 2.2.1 but with an influent flowrate of 10 mL/min to keep the EBCT of the Na-zeolite layer at 1.8 min.

Table 2. Experimental conditions of mortar/Na-zeolite dual media according to EBCT.

Condition		Mortar/Na-Zeolite, 0/1.8 Min	Mortar/NaCl-Zeolite, 0.31/1.8 Min	Mortar/NaCl-Zeolite, 0.62/1.8 Min	Mortar/NaCl-Zeolite, 1.25/1.8 Min
Depth (cm)	Mortar	0	2	4	8
	Na-zeolite	11	11	11	11
	Total	11	13	15	19
EBCT (minute)	Mortar	0	0.3	0.6	1.3
	Na-zeolite	1.8	1.8	1.8	1.8
	Total	1.8	2.1	2.4	3.1
Mass (g)	Mortar	0	6.07	12.08	20.83
	Na-zeolite	17.84	17.84	17.84	17.84
	Total	17.84	23.91	29.92	38.67

2.2.3. Removal of Heavy Metals Mixture by Mortar/Na-Zeolite Dual Media

Considering the frequency and concentrations of metals in expressway stormwater runoff reported previously, a mixture of 1 mg/L each of Cu^{2+}, Zn^{2+}, Fe^{3+}, and Ni^{2+} in

an aqueous solution was used for the evaluation of metal removal [1–7,37]. A procedure using metals at higher concentrations was proposed for a quick evaluation of heavy metal removal in runoffs [22]. However, it seems reasonable to perform experiments under low concentrations of metals, although they require much longer periods. Adsorption at a high metal concentration would be faster than that at low concentrations because the rate of adsorption is generally governed by the difference in adsorbate amounts between the adsorbent and solution [38]. It should be noted that the concentration of metals in this study may not be representative because it varies significantly. The ratio of the event's mean concentration (EMC) of Fe^{3+}, Ni^{2+}, and Zn^{2+} in stormwater runoffs to that of Cu^{2+} was 2.80–635.71, 0.85–5.61, and 1.20–148.57, respectively [2–7]. Therefore, the results in this study can be addressed as the metal's relative feasibility towards precipitation and adsorption. In addition, an experimental study must be performed for the application of the system in this study for a specific case.

The effects of the ratio of mortar to Na-zeolite layers were investigated to determine the optimum configuration. Therefore, the thicknesses of the mortar and Na-zeolite layers were adjusted to 2/9 cm, 4/7 cm, and 8/3 cm, which correspond to an EBCT of 0.33/1.47, 0.65/1.15, and 1.31/0.49 min, respectively, while maintaining a total EBCT of 1.8 min [30] (Table 3, Figure 1C).

Table 3. Mixed heavy metal removal test conditions with mortar/Na-zeolite dual media according to the ratio of media.

Condition		**Mortar/Na-Zeolite, 0.33/1.47 Min**	**Mortar/Na-Zeolite, 0.65/1.15 Min**	**Mortar/Na-Zeolite, 1.31/0.49 Min**
Depth (cm)	Mortar	2	4	8
	Na-zeolite	9	7	3
	Total	11	11	11
EBCT (min)	Mortar	0.33	0.65	1.31
	Na-zeolite	1.47	1.15	0.49
	Total	1.80	1.80	1.80
Mass (g)	Mortar	13.7	10.6	4.6
	Na-zeolite	6.0	11.9	23.8
	Total	19.6	22.5	28.4

During the column experiments with an influent flowrate of 10 mL/min for 232 h, the effluent at the sampling port at the bottom of the mortar and Na-zeolite layers was collected for analyzing the metals using ICP-AES, as described in Section 2.2.1.

3. Results

3.1. Effects of Filter Media on Cu^{2+} Removal

Figure 2 and Table 4 show breakthrough curves of Cu^{2+} and the Thomas model constants for Cu^{2+} removal with Na-zeolite and mortar/Na-zeolite. When the sand filter was used, the Cu^{2+} concentration of the effluent rapidly increased and was similar to that of the influent after 30 min of operation. In the effluent from the column using Na-zeolite, Cu^{2+} was not detected until 150 min of operation time, and the concentration increased to 8, 54.7, and 90.0 mg/L at 210, 360, and 750 min, respectively. In the effluent from dual mortar/Na-zeolite media, Cu was not detected until 180 min of operation, and the concentration increased to 6.8, 55.3, and 90.0 mg/L at 240, 510, and 870 min, respectively.

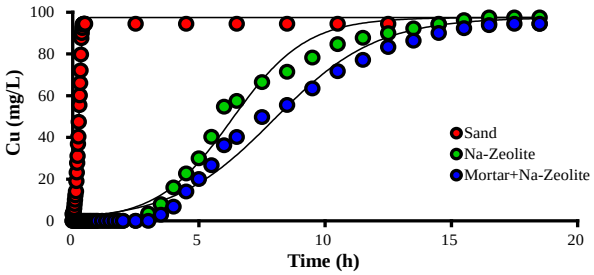


Figure 2. Variation over time of the concentration of Cu^{2+} ions in the effluent collected after different media layer, in mg/L; the working temperature is 20.5 °C.

Table 4. Adsorption constants for Cu^{2+} removal by sand, Na-zeolite and mortar (Cu 100 mg/L).

	Sand	Na-Zeolite	Mortar/Na-Zeolite
k_T ($\times 10^{-5}$ L/min·mg)	278.6	11.7	8.5
q_e (mg/g)	0.35	16.57	17.78
r^2	0.995	0.988	0.986
q_L (g/L)	0.79	20.40	22.99

The q_e calculated by the Thomas model was 0.35, 16.57, and 17.78 mg/g for sand, Na-zeolite, and mortar/Na-zeolite, respectively, while the equilibrium adsorption amount per volume of media layer (q_L) was 0.79, 20.40, and 22.99 g/L. These data indicate the negligible removal of Cu^{2+} by sand, significant removal by Na-zeolite, and substantially improved removal by the addition of a layer of alkaline materials, i.e., mortar.

The k_T calculated by the Thomas model was 167.2, 7.0, and 5.1 mL/min·mg for sand, Na-zeolite, and mortar/Na-zeolite, respectively. Since the Thomas model assumes that the driving force of adsorptions is the difference between adsorbate concentrations on the adsorbent's surface and in the solution, k_T increases as the adsorbate concentrations in solution increase, i.e., at smaller adsorption amounts [38], as shown in Table 4.

3.2. Effects of Mortar Amount on the Cu^{2+} Removal in Dual Media

Figure 3 and Table 5 show the breakthrough curves of Cu^{2+} and the Thomas model constants of the mortar/Na-zeolite dual media with different amounts of mortar. When the EBCT of the mortar layer increased to 0, 0.31, 0.62, and 1.25 min, the Cu^{2+} concentration in the effluent was 16, 5.02, 1.9, and 0.0 mg/L, respectively, at 240 min of operation, while the time for near 50% saturation was 360 (48.9 mg/L), 450 (50.4 mg/L), 690 (48.8 mg/L), and 1410 min (48.9 mg/L).

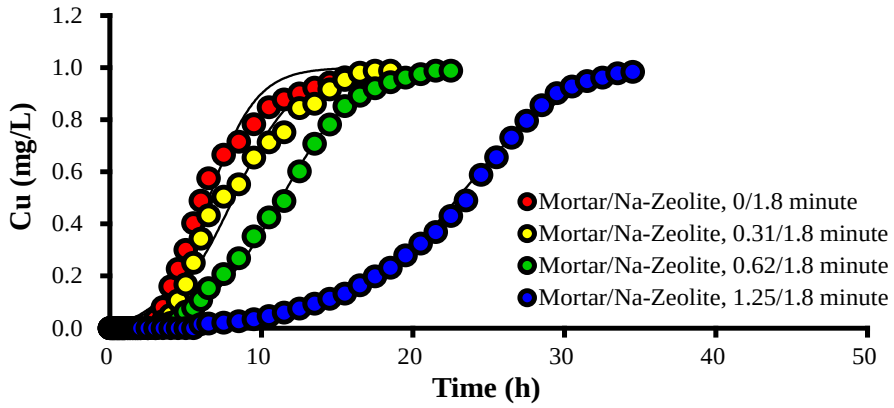


Figure 3. Variations over time in the concentration of Cu^{2+} ions in the effluent collected after the dual layer, in mg/L, for different ratios of EBCTs; the working temperature is 20.5 °C.

Table 5. Adsorption constants for Cu^{2+} removal with mortar/Na-zeolite dual media according to EBCT.

	Mortar/NaCl-Zeolite, 0/1.8 Min	**Mortar/NaCl-Zeolite, 0.31/1.8 Min**	**Mortar/NaCl-Zeolite, 0.62/1.8 Min**	**Mortar/NaCl-Zeolite, 1.25/1.8 Min**
k_T (L/min·mg)	0.106	0.082	0.069	0.047
q_e (mg/g)	22.0	20.5	22.7	35.6
r^2	0.986	0.984	0.998	0.998
q_t (mg)	392.6	490.5	679.6	1378.1
q_L (g/L)	27.1	28.8	34.8	56.2

The q_e values were 16.74, 16.01, 17.79, and 27.91 mg/g when the EBCT of the mortar layer was 0, 0.31, 0.62, and 1.25 min, respectively. Since the specific gravity of the mortar was higher than that of the zeolite, q_e did not show a dramatic increase. However, q_L and the total mass of removed Cu^{2+} (q_t) increased significantly as the mortar layer's thickness increased. On the other hand, the k_T value decreased as the EBCT of the mortar layer increased, indicating that Cu adsorptions improved with increasing mortar layer depths. These data confirm that Cu^{2+} removal can be significantly enhanced by increasing alkali supplies.

3.3. Removal of Heavy Metals Mixture by Mortar/Na-Zeolite Dual Media

3.3.1. Removal of Heavy Metals Mixture in Mortar Layer

Column experiments were performed with different ratios of mortar and Na-zeolite, and breakthrough curves of each metal in the effluent of the mortar layer are presented in Figure 4, along with Thomas model constants (Table 6).

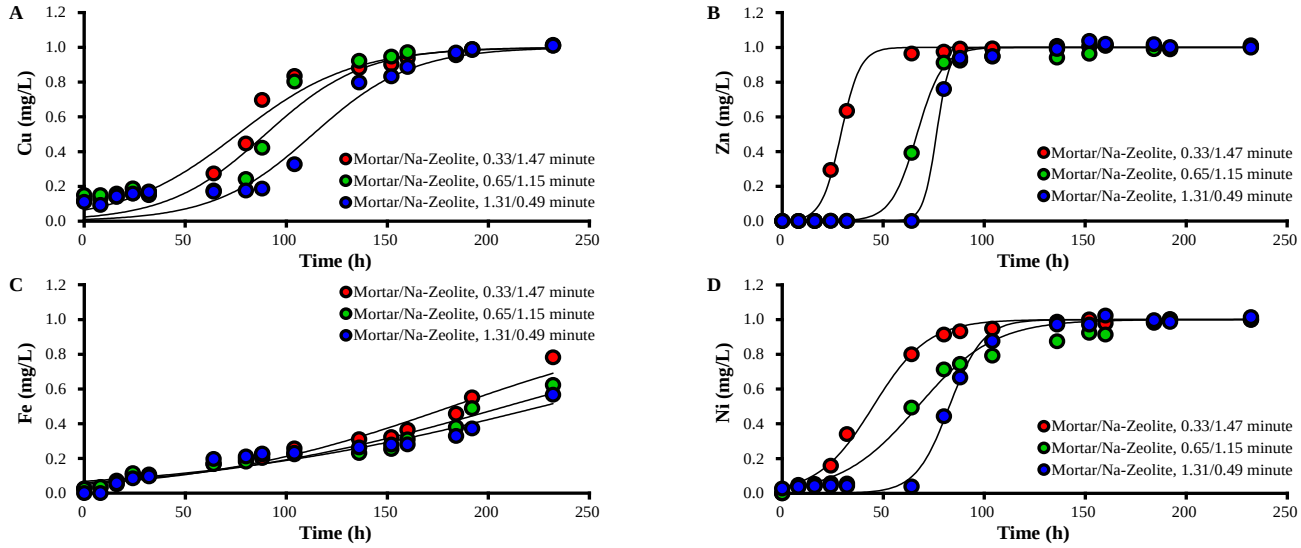


Figure 4. Variations over time in the concentration of (**A**) Cu^{2+}, (**B**) Zn^{2+}, (**C**) Fe^{3+}, and (**D**) Ni^{2+} ions in the effluent collected after the mortar layer from the dual system, in mg/L, for different ratios of EBCTs; the working temperature is 20.5 °C.

The concentrations of heavy metals in the effluent of the mortar layer decreased as the layer depth increased (Figure 4). For EBCTs of mortar/Na-zeolite of 0.33/1.47, 0.65/1.15, and 1.31/0.49 min, the 50% breakthrough times for Zn were 24–32, 64–80, and 72–80 h; those for Ni were 16–32, 40–64, and 72–88 h; those for Cu were 80–88, 93–112, and 112–136 h; those for Fe were 160–192, 208, and 208–232 h, respectively. These data indicate that heavy metals are effectively removed by the mortar. The increased q_t and q_L of each metal correspond to the increased EBCT of the mortar layer.

Table 6. Adsorption constants for heavy metals collected from the mortar layer.

		Mortar/Na-Zeolite, 0.33/1.47 Min	Mortar/Na-Zeolite, 0.65/1.15 Min	Mortar/Na-Zeolite, 1.31/0.49 Min
Cu^{2+}	k_T (L/min·mg)	0.589	0.689	0.680
	q_e (mg/g)	8.758	5.174	3.265
	r^2	0.974	0.940	0.956
	q_t (mg)	45.5	53.8	67.9
	q_L (g/L)	12.9	7.6	4.8
Zn^{2+}	k_T (L/min·mg)	3.505	2.599	5.141
	q_e (mg/g)	3.354	3.849	2.204
	r^2	0.997	0.997	0.998
	q_t (mg)	17.4	40.0	45.8
	q_L (g/L)	4.9	5.7	3.2
Fe^{3+}	k_T (L/min·mg)	0.267	0.220	0.192
	q_e (mg/g)	20.995	12.046	6.539
	r^2	0.961	0.942	0.905
	q_t (mg)	109.2	125.3	136.0
	q_L (g/L)	30.9	17.7	9.6
Ni^{2+}	k_T (L/min·mg)	1.225	0.885	2.013
	q_e (mg/g)	5.189	3.922	2.385
	r^2	0.995	0.984	0.994
	q_t (mg)	27.0	40.8	49.6
	q_L (g/L)	7.6	5.8	3.5

Among the heavy metals in this study, q_t and q_L in the mortar layer were observed in the order of Fe > Cu > Zn ≒ Ni, while k_T was Zn ≒ Ni > Zn > Fe regardless of the amount of mortar, which indicates that the removal of a metal by alkali supplies was enhanced with increasing pH, where the metal forms precipitates. Fe^{3+} forms $Fe_2O_3 \cdot nH_2O$, Fe_3O_4, and $Fe(OH)_2$; Cu^{2+} forms CuO_2 and $Cu(OH)_2$; Zn^{2+} forms ZnO; Ni^{2+} forms NiO_2 and $No(OH)_2$ at pH 3.5, 4, 7.5, and 9, respectively [39].

3.3.2. Removal of Heavy Metals Mixture in the Entire Layers of Mortar/Na-Zeolite

The breakthrough and saturation times of each metal in the effluent of mortar/Na-zeolite dual media were prolonged with increasing mortar layer thickness (Table 5, Figure 5). The 50% breakthrough times of Zn^{2+} were 80, 80–88, and 88–96 h; those of Ni^{2+} was 64–72, 88–104, and 88 h; those of Cu^{2+} were 88–65, 112–136, and 136–152 h at a mortar/Na-zeolite EBCT ratio of 0.33/1.47, 0.33/1.47, and 0.33/1.47 min, respectively. However, Fe^{3+} did not achieve 50% breakthrough even after 232 h. These data indicate that heavy metal removal in the dual media improved due to alkali elution from the mortar layer.

The values of q_t and q_L of each metal increased as the mortar layer's thickness increased (Table 7). The q_t of Cu^{2+} was 58.5, 69.3, and 79.6 mg; that of Zn^{2+} was 47.9, 49.5, and 57.1 mg; that of Fe^{3+} was 161.6, 141.4, and 167.3 mg; and that of Ni^{2+} was 46.5, 50.6, and 52.2 mg when the EBCT ratio was 0.33/1.47, 0.65/1.15, and 1.31/0.49 min, respectively. The respective q_L of Cu^{2+} was 3.0, 3.6, and 4.1 mg/L; that of Zn^{2+} was 2.5, 2.5, and 2.9 mg/L; that of Fe^{3+} was 8.3, 7.3, and 8.6 mg/L; and that of Ni^{2+} was 2.4, 2.6, and 2.7 mg/L. In addition, q_t and q_L for the dual media changed in the order of $Fe^{3+} > Cu^{2+} > Zn^{2+} \fallingdotseq Ni^{2+}$, regardless of the EBCT, as in the mortar layer, suggesting the importance of the mortar layer.

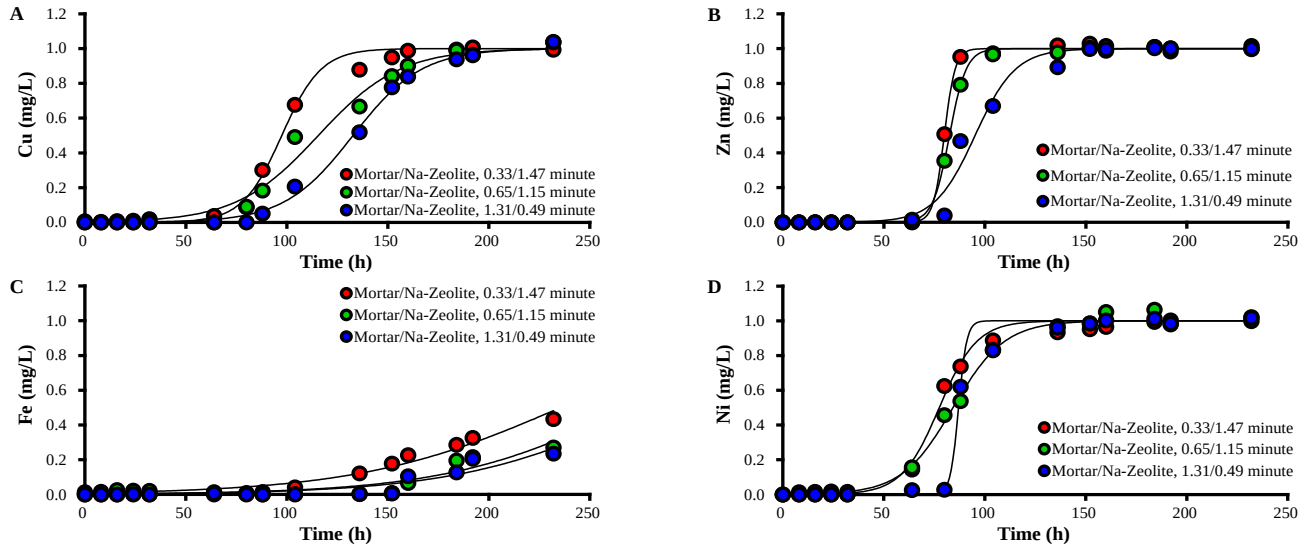


Figure 5. Variations over time in the concentrations of (**A**) Cu^{2+}, (**B**) Zn^{2+}, (**C**) Fe^{3+}, and (**D**) Ni^{2+} ions in the effluent collected after the Na-zeolite layer from the dual system, in mg/L, for different ratios of EBCTs; the working temperature is 20.5 °C.

Table 7. Adsorption constants for heavy metals collected from the mortar/Na-zeolite dual layer.

		Mortar/Na-Zeolite, 0.33/1.47 Min	Mortar/Na-Zeolite, 0.65/1.15 Min	Mortar/Na-Zeolite, 1.31/0.49 Min
Cu^{2+}	k_T (L/min·mg)	1.709	0.823	0.982
	q_e (mg/g)	3.461	3.556	3.224
	r^2	0.994	0.988	0.997
	q_t (mg)	58.5	69.3	79.6
	q_L (g/L)	3.0	3.6	4.1
Zn^{2+}	k_T (L/min·mg)	6.195	4.034	1.665
	q_e (mg/g)	2.837	2.538	2.311
	r^2	0.999	1.000	0.984
	q_t (mg)	47.9	49.5	57.1
	q_L (g/L)	2.5	2.5	2.9
Fe^{3+}	k_T (L/min·mg)	0.367	0.331	0.359
	q_e (mg/g)	8.287	8.365	6.775
	r^2	0.846	0.960	0.860
	q_t (mg)	161.6	141.4	167.3
	q_L (g/L)	8.3	7.3	8.6
Ni^{2+}	k_T (L/min·mg)	1.793	1.311	8.269
	q_e (mg/g)	2.750	2.594	2.114
	r^2	0.994	0.996	0.990
	q_t (mg)	46.5	50.6	52.2
	q_L (g/L)	2.4	2.6	2.7

The total mass of each metal removed per unit mass of the dual media (q_e) (Table 7) was higher than that reported in previous column studies using metals mixtures, suggesting the excellence of the dual media. The removed amount of Pd^{2+}, Cu^{2+}, and Zn^{2+} was 0.21–0.57, 0.43–1.12, and 1.56–4.42 mg/g when mineral-based technical filter media were used and when their initial concentrations were 50, 100, and 400 µg/L, respectively [40]. The adsorption capacity of Cd^{2+} of calcite, zeolite, and iron filings was 0.48, 2.00, and 2.0 mg/g, respectively; that of Cu^{2+} was 0.49, 0.49, and 0.48 mg/g, respectively; that of Pb^{2+} was 4.66, 0.14, and 4.48 mg/g, respectively; that of Ni^{2+} was 1.22, 2.60, and 4.44 mg/g, respectively; that of Cr^{2+} was 0.016, 0.026, and 0.270 mg/g, respectively; and that of Zn was 5.0, 3.3, and 5.0 mg/g, respectively [41]. When the concentration of Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+},

and Zn^{2+} in the influent was 0.625, 2.5, 2.5, 2.5, and 5.0 mg/L, respectively, the removed amount was approximately <0.5, 1.5–3.0, 0.5–1.5, 1.5–3.5, and 2.0–3.5 mg/g, respectively, for alumina; <0.1, 1.0–2.5, <1.0, 1.5–2.0, and 0.5–2.0 mg/g, respectively for granular activated carbon (GAC); <0.25, 1.0–2.5, 0.1–1.5, 1.0–2.0, and 2.5–3.0 mg/g, respectively, for lignite; and negligible, <0.1, <0.1, <1.0, and <0.1 mg/g, respectively, for granular ferric hydroxide [21]. The removed amount of Ni^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+} was 0.0048, 0.0034, 0.2984, 0.1024, and 0.1371 mg/g, respectively, for basalt; 0.0103, 0.0114, 0.6517, 0.2133, and 0.3004 mg/g, respectively, for zeolite; and 0.0148, 0.0127, 0.7378, 0.0233, and 0.3056 mg/g, respectively, for the layer consisting of zeolite, GAC, and a titanate nano-fibrous material [42]. In addition, the removal of Ni^{2+}, Zn^{2+}, and Fe^{3+} by an iron-oxide-coated gravel was 0.43, 1.15, and 1.13 mg/g, respectively [34].

On the other hand, k_T did not show a correlation with the mortar/Na-zeolite ratio, which indicates that heavy metal removal in the mortar/Na-zeolite dual media is governed not only by mass transfer, i.e., adsorption, but also by precipitation from the mortar alkali supply and the filtration of precipitates.

3.3.3. Contribution of Each Layer in Mortar/Na-Zeolite Dual Media

Figure 6 shows the amounts of heavy metals removed (q_t in Tables 6 and 7) in the mortar layer and Na-zeolite layer according to ratio of EBCTs of mortar and Na-zeolite layers. The q_t values in the mortar layer were significantly larger than those in the Na-zeolite layer, except for Zn^{2+} at 0.33/1.47 min, indicating the major role of the mortar layer. The mass fraction of removed metals in the mortar layer from the dual layer was 77.9%, 77.6%, and 85.3% for Cu^{2+}; 36.4%, 80.9%, and 80.3% for Zn^{2+}; 77.2%, 77.5%, and 81.3% for Fe^{3+}; and 58.0%, 80.7%, and 95.0% for Ni^{2+} at EBCT ratios of 0.33/1.47, 0.65/1.15, and 1.31/0.49 min, respectively.

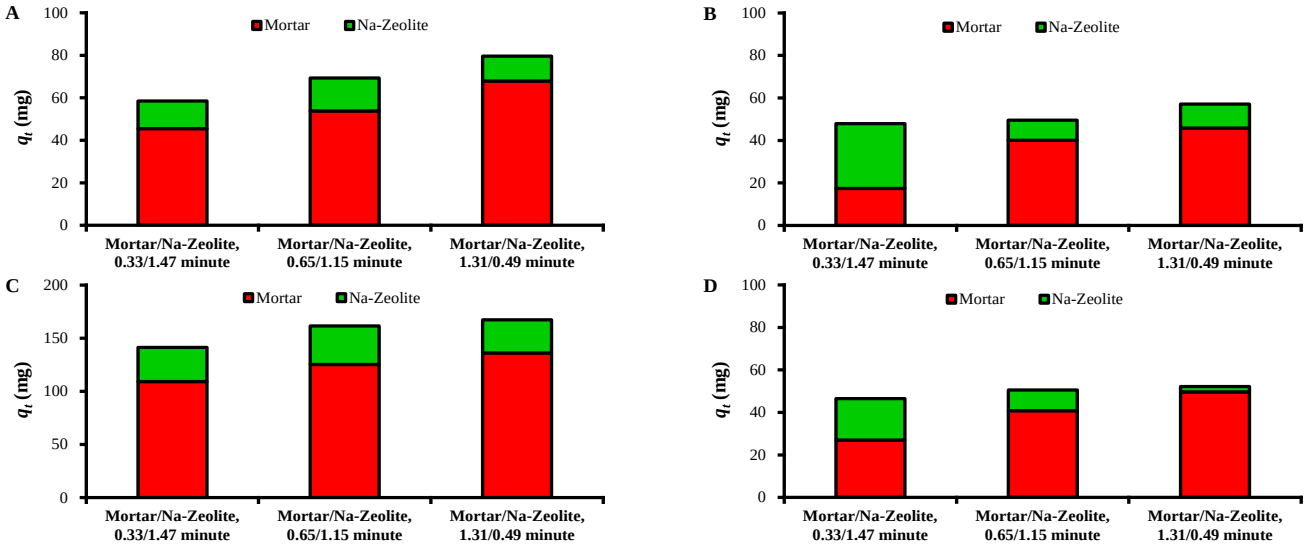


Figure 6. Removed amounts of (**A**) Cu^{2+}, (**B**) Zn^{2+}, (**C**) Fe^{3+}, and (**D**) Ni^{2+} in each layer of mortar/Na-zeolite dual media for different ratios of EBCTs.

The q_t values of Ni^{2+} and Zn^{2+} in the mortar layer increased significantly with the increasing EBCT of the mortar layer. However, the increase was less significant for Cu^{2+} and Fe than the other metals, which is attributable to easier precipitation of Cu^{2+} and Fe^{3+} under low alkalinity, i.e., a thin EBCT mortar layer, resulting in better removal in the mortar layer than for Zn^{2+} and Ni^{2+} [39].

The q_t of Ni^{2+} in the Na-zeolite layer decreased with the decreasing EBCT of the layer (Figure 6D), suggesting a contribution of the layer to Ni removal. The q_t of Zn^{2+} was larger at 0.33/1.47 min than at 0.65/1.15 and 1.31/0.49 min. The q_t values of Zn^{2+} and Ni^{2+} for the Na-zeolite layer were comparable to or significantly larger than those of Cu^{2+} and Fe at

0.33/1.47 min. This finding may be ascribed to the higher concentrations of Zn^{2+} and Ni^{2+} in the influent of the layer than those of Cu^{2+} and Fe^{3+} because adsorption is governed by the difference of adsorbate amounts on the adsorbent surface and in the liquid phase [38]. On the other hand, the q_t values of Cu^{2+} and Fe^{3+} for the Na-zeolite layer did not show a correlation with the EBCT of the layer, which can be attributed to lower loads of Cu and Fe on the Na-zeolite layer because of the excellent removal in the mortar layer (Tables 6 and 7).

The q_t values of Fe^{3+} must be higher than those in Tables 6 and 7 because Fe^{3+} concentrations in the effluent did not reach that of the influent (Figures 4 and 5).

4. Conclusions

In this study, a dual media system of mortar and Na-zeolite was investigated via continuous column experiments for the efficient removal of heavy metals in expressway stormwater runoff. First, the potential of the dual media system was evaluated. Sand, which is used widely as a filtration medium in conventional NPS pollution reduction, showed negligible Cu^{2+} removal, while the q_e of Na-zeolite increased to as high as 16.57 mg/g at an EBCT of 1.8 min (linear velocity of 20 m/h). The addition of a thin mortar layer over the Na-zeolite layer resulted in a substantial improvement in Cu^{2+} removal, suggesting the high potential of the dual mortar and Na-zeolite media. By adding mortar layers corresponding to EBCTs of 0, 0.31, 0.62, and 1.25 min to the Na-zeolite layer, at a Cu^{2+} concentration of 100 mg/L, the q_e values were 22.0, 20.5, 22.7, and 35.6 mg/g, respectively, confirming the significant role of the mortar layer.

The removal of a mixture of heavy metals commonly found in runoff at significant levels was subjected to the dual layer system under various ratios of EBCTs of mortar and Na-zeolite layers. The dual layer system showed excellent performances in the removal of all metals. In particular, the effluent concentration of Fe did not reach that of the influent after operation for 232 h. The removal of metals in the mortar layer and in the dual layers improved with an increasing EBCT of the mortar layer, confirming the important role of the layer. With the increasing EBCT of the mortar layer from 0.33/1.47 to 1.31/0.49 min, the q_L of the dual layer increased from 3.0 to 4.1 g/L for Cu^{2+}, from 2.5 to 2.9 g/L for Zn^{2+}, from 8.3 to 8.6 g/L for Fe^{3+}, and from 2.4 to 2.6 g/L for Ni^{2+}. In addition, the contribution of the mortar layer to the total removal for the dual layer was 77.6–85.3%, 36.4–80.3%, 77.2–81.3%, and 58.0–95.0% for Cu^{2+}, Zn^{2+}, Fe^{3+}, and Ni^{2+}, respectively. However, the removal with Na-zeolite was also significant, indicating a synergistic effect of the layers.

The results in this study strongly suggest that a dual layer system of mortar and Na-zeolite can be an excellent alternative for heavy metal removal from stormwater runoff via the combination of alkaline precipitation, the filtration of precipitates, and adsorption. Moreover, the good performance at a short EBCT suggests that the system is suitable for compact stormwater treatment practices installed where available space is limited; the TSS can be effectively removed simultaneously in the system due to the use of granular media, i.e., mortar and Na-zeolite; moreover, the media in the system are cheap and provide cost-effective removals of pollutants in stormwater runoff. However, it is thought that the effects of real stormwater chemistry affecting the performance and clogging of the media should be investigated for successful field applications.

Author Contributions: Conceptualization and methodology, D.-G.K.; validation and formal analysis, D.-G.K. and S.-O.K.; investigation, resources, data curation, and writing—original draft preparation, D.-G.K.; writing—review and editing, D.-G.K. and S.-O.K.; visualization and supervision, S.-O.K.; project administration, and funding acquisition, S.-O.K. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2022R1A2B5B02001584).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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