



Performance of carbon nanotube-coated steel slag filter media for the removal of phosphorus and heavy metal in stormwater

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ABSTRACT

Phosphorus and heavy metals in nonpoint pollutant sources cause significant problems in water systems, with a 22%–40% loading of the total pollutants in the four major rivers in Korea. No standard exists for phosphorus and heavy metals in device-type, nonpoint pollution abatement facilities in South Korea. Therefore, this study assessed the application of steel slag as a filter medium in these facilities. To increase its reactivity, the surface of slag was coated with carbon nanotubes (CNTs). The adsorption capacity of the CNT-coated slag was 1.36 and 1.83 times higher for phosphate and zinc, respectively, than that of the uncoated slag according to the adsorption isotherm. In addition, the adsorption of phosphate and zinc through both uncoated and CNT-coated slag followed pseudo-first order kinetics. In the cylindrical column test, during a 100-rainfall repetition test, the removal efficiency of phosphate, zinc, and copper were 66.3%, 78.1%, and 68.3%, respectively, by the uncoated slag, and 78.0%, 85.1%, and 70.0%, respectively, by the CNT-coated slag. These results show that CNT-coated steel slag is an attractive filter medium for the removal of phosphorus and heavy metals in a nonpoint pollution abatement system that reduces the overall operating cost by increasing the replacement cycle.

Keywords: Nonpoint pollution abatement system; Steel slag; Carbon nanotubes; Phosphate and metal removal

1. Introduction

Nonpoint sources include pollutants found in accumulated stormwater runoff on an urban surface or land, and contains pathogens, organic matter, nutrients, heavy metals, and sediment [1]. These nonpoint pollution sources from stormwater runoff can deteriorate the water quality [2]. Thus far, the management of water quality has focused mostly on the treatment of point sources, such as sewage, industrial, and livestock wastewater treatment facilities in South Korea [3]. In particular, in South Korea, the pollution load in the four major rivers (Han, Nakdong, Geum, and Yeongsan River) caused by nonpoint sources accounts for

approximately 22%–40% of the total pollution load [4]. Unlike traditional point sources, which are easily identifiable and measurable, nonpoint sources are difficult to quantify; they are highly variable and very often difficult to separate from the background water quality [5]. Furthermore, these sources are difficult to manage and control due to the complicated transfer and transformation of nonpoint pollutants and the unpredictable flow into the water system [6]. Among the pollutants, the total suspended solid (TSS) is a common component of nonpoint pollutants and is a parameter of the stormwater runoff quality [7]. During rainfall, this TSS is accompanied by organic and inorganic matter, which is carried to the water system [8]. In particular, this TSS

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shows that the first flush phenomenon is significantly high with stormwater runoff containing organic matter and total nitrogen (T-N) [9].

The nonpoint-pollution abatement facility is divided into a natural type, such as an infiltration system and a constructed wetland, and a device type facility, such as the vortex and filtration type. In South Korea, passive facilities are difficult to use owing to the limited land area [10]. For this reason, device-type facilities using filter media that can be installed in small spaces and have a high pollutant reduction speed need to be applied [11].

In addition to TSS, dissolved phosphorus and heavy metals from stormwater runoff influence the water quality, even at low concentrations, with high flows and volumes of stormwater that can result in considerable pollutant loads [12]. Phosphorus is discharged to urban stormwater from sediments, gasoline, and tires, and heavy metals can be leached from the sediment with an environmental change [1,13]. In South Korea, the installation criterion for a filtration-device type nonpoint pollution abatement system using filter media requires more than 80% SS removal [14], but there is no removal standard for phosphorus and heavy metals. On the other hand, as the load of phosphorus and heavy metals in stormwater runoff into the water system increases gradually, it is expected that the installation criteria of nonpoint pollution abatement facilities will be strengthened. Therefore, it is important to develop filter media that can remove phosphorus and heavy metals in stormwater runoff for application to a filtration-device type nonpoint pollution abatement facility.

In a filtration-device type facility, the replacement cost of the filter media accounts for the majority of the total operating cost [15]; relatively inexpensive filter media with a long replacement cycle are needed. For these reasons, studies have focused on using natural materials or industrial by-products, such as stones, soils, shales, fly ash, coals, zeolite or steel slag, to remove phosphorus and heavy metals [16]. Among them, steel slag is a good adsorbent that contains a large amount of CaO, which dissociates into Ca^{2+} and OH^- in aqueous solution, reacts with phosphate and toxic metal ions, and removes them in Ca-phosphate and metal-OH form [17,18]. In addition, carbon nanotubes (CNTs), which are known as adsorbents for reducing water contaminants, such as heavy metals, organic matter, and bacteria [19], were used to increase the reactivity of steel slag. CNTs have adsorption sites on the inner and outer layer surfaces [20]. The adsorption capacity for phosphorus and heavy metal by the slag is expected to be increased by coating the surface of slag with CNTs. Studies have also reported the use of CNTs as a toxic metal adsorbent through chemical oxidation and functionalization [21].

Recently, some studies have reported the risk of CNTs. CNTs are cytotoxic to the microbial community, mammalian cells, and food chain of human beings. On the other hand, the impact of CNTs depends on the amount of CNTs released into the environment from a particular water environment plant [22]. In addition, Su and Lu [23] reported that the weight loss of CNTs is lower than that other media in water treatment applications. The low replenishment of the material makes it possible to reduce the high investment cost of CNTs. The release of CNTs from a CNT-doping filter might not be a concern regarding the environment and ecosystem.

The specific objectives of this study are as follows: (1) evaluate the removal characteristics of phosphorus (using phosphate as the P-source in this study) and heavy metals by uncoated and CNT-coated reactive steel slag in a batch and continuous cylindrical type reactor; (2) evaluate phosphorus and heavy metal removal at a linear velocity of 15–20 m/h, which is the standard for the installation of a filtration-device type nonpoint pollution abatement facility; and (3) examine the possibility of phosphorus and heavy metal removal for long periods without the replacement of filter media by analyzing the rainfall events in Busan, South Korea.

2. Materials and methods

2.1. Preparation and modification of the media

The steel slag used in this study was slow cooled basic oxygen furnace slag obtained from 'H' company, Gwangyang, South Korea. The slag used had a particle size of 4–7 mm and a uniformity coefficient (d_{60}/d_{10}) of 2.1. Among the chemical components of steel slag used in this study, the CaO content (44.3%) was higher than those of any other components. Table 1 lists the physical and chemical properties of the steel slag used in this study. The CNTs used as the slag coating reagents were commercially available multi-walled CNTs (MWCNTs, Hanhwa Chemical Co., South Korea). Prior to use, the raw MWCNTs were treated thermally in an oven at 350°C for 1 h to remove any amorphous carbon [24], and then with a mixture of sulfuric acid and nitric acid (v/v, 3:1) to introduce oxygen groups. The mixture was then sonicated for 3 h at 70°C in an ultrasonic bath and vacuum-filtered through a PTFE membrane filter with a pore size of 0.2 μm . The filtered CNTs were washed with distilled water until pH 6.8. A CNT-coating on the slag surface was prepared by dipping into a CNT solution, probe sonicating for 1 h, removing the solution, and drying at 110°C in an oven. The processes were repeated three times to increase the CNT loading.

2.2. Characteristics of phosphate and metal adsorption from aqueous solutions

Batch tests were performed to examine the adsorption isotherms and kinetics of 50.0 ± 1.0 mg/L of phosphate using a KH_2PO_4 and 50.0 ± 1.0 mg/L zinc (dilution of 1,000 mg/L

Table 1
Physicochemical characteristics of the steel slag used in this study

	Item	Value
Physical properties	Porosity (%)	40.1
	Bulk density (g/cm^3)	3.2
	Uniformity coefficient (d_{60}/d_{10})	2.1
Chemical composition (%)	CaO	44.3
	Fe_2O_3	17.5
	SiO_2	13.8
	MgO	6.4
	Al_2O_3	2.1

standard solution) aqueous solution by both uncoated and CNT-coated slag. The tests were performed in a batch-type jar tester (model C-JT-H, Changsin Scientific Co., South Korea) in 300 mL beakers with a 200 mL working volume and a 1.0–5.0 g slag weight, and the concentrations of residual phosphate and zinc in the solution were measured every 3 h. All experiments were performed in triplicate.

The continuous tests were carried out in a 5 cm diameter cylindrical-type reactor made of PVC. The components and concentrations of the virtual stormwater used in this study were obtained from the Korea Environment Institute report [25]. Table 2 lists the stormwater concentration of urban areas [4], highways [26], and residential areas of Busan analyzed in this study. The water contained not only phosphate and zinc but also copper. A component of the residential area stormwater runoff detected in this study was used for the virtual stormwater. The initial concentrations of phosphate, zinc, and copper in the mixed solution were set to 0.4, 0.5, and 0.20 mg/L, respectively. The regulation for the nonpoint pollution abatement facility focused only on SS removal. The concentrations of BOD, COD, and T-N in nonpoint pollutants have a strong correlation with SS and can be removed sufficiently by removing SS in a nonpoint pollution abatement facility generally used in Korea [3]. On the other hand, the problem of dissolved phosphorus and heavy metals in rivers and streams in Korea still occurs. Even at low concentrations, the loads are large enough to contaminate the water system with large amounts [12]. Therefore, artificial stormwater runoff was prepared for the treatment of phosphorus and heavy metal as targets.

The flow rate was set according to the filtration linear velocity (15–20 m/h), standard of nonpoint pollution abatement facility, and virtual stormwater was pumped continuously into the reactor using a peristaltic pump (JWT-600, Jeniewell®, South Korea). The uncoated and CNT-coated slag were filled and connected to the reactor in 25 cm units (containing 1.00 ± 0.04 kg of slag). The samples were collected at 30 min intervals after the first effluent to analyze the removal rates. In addition, based on the rainfall event data of the Korea Metrological Agency [27], for an evaluation of the sustainability and replacement cycle of the slag

filter media, the number of annual rainfall days of more than 5 mm was analyzed from 2007 to 2016 in Busan city, South Korea. According to the rainfall event, the experiments were performed for 120 min and repeated 100 times.

Continuous cylindrical tests were carried out to assess the feasibility of application to a nonpoint pollution abatement facility. In the test, the flow rates were set to 0.490 and 0.654 L/min, according to the suggested linear velocity standard, 15 and 20 m/h, respectively. The cross sectional area was 1.96×10^{-3} m² and the length of filtration was set to 25–100 cm (Fig. 1). According to the “Water Quality and Ecosystem Conservation Act”, this suggests that a nonpoint pollution abatement facility should be able to treat a cumulative rainfall of 5 mm or more with a standard rainfall intensity of 2.5 mm/h [28]. Therefore, to establish the inflow durations, an analysis of the annual precipitation and the number of days of annual rainfall events exceeding 5 mm based on the data for 2007–2016 of Busan Metropolitan city, South Korea, were performed (Fig. 2). The average annual precipitation is approximately $1,510 \pm 436$ mm, and the number of rainfall events of more than 5 mm was approximately 50. Based on these results, the inflow duration was set to 100 to determine if the slag filter media can be used for more than 2 years in a nonpoint pollution abatement facility.

2.3. Analysis

The surface of the uncoated and CNT-coated slag was coated with a platinum layer and observed by field emission scanning electron microscopy (FE-SEM, Supra 25, Carl Zeiss, Oberkochen, Germany).

The concentrations of PO₄-P and metal analysis were performed according to the standard method [29], the molybdenum blue–ascorbic acid method using a UV-visible spectrophotometer (OPTIZEN 2120UV, MECASYS, South Korea) and inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer, USA), respectively, after an aqueous solution had been filtered through a 0.45 μm Advantec® cellulose acetate filter.

The BET surface area was analyzed using a surface analyzer (Quantachrome ASiQwin, Quantachrome instrument, USA).

Table 2
Stormwater runoff concentration according to the land type

Area	Concentration (mg/L)									References
	SS	BOD	COD	T-N /TKN	T-P	Zn	Cu	Pb	Cd	
Urban area	51	3.0	27.0	0.94	0.110	0.04	0.000	0.014	0.001	[24]
Commercial complex	77	21.0	80.0	1.74	0.330	0.156	0.037	0.049	0.003	[24]
Industrial complex	149	24.0	85.0	2.08	0.320	0.671	0.058	0.072	0.005	[24]
Urban load	43	19.4	68.6	6.80	1.400	0.170	– ^a	n.d. ^b	0.060	[25]
Highway	85	13.7	53.4	10.90	0.200	1.117	0.515	1.059	0.156	[26]
Residential area	28	10.9	27.6	5.40	0.024 ^c	0.416 ^c	0.090 ^c	n.d. ^b	n.d. ^b	This study

^aNot measured.

^bNot detected.

^cMeasured after filtering.

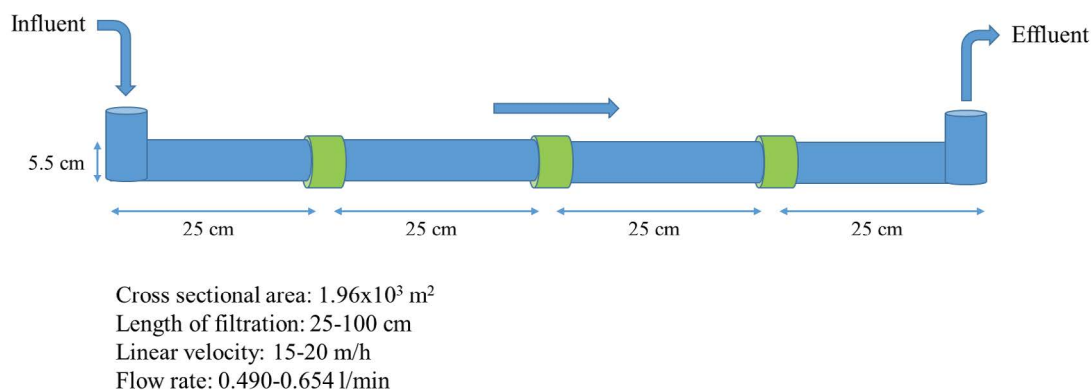


Fig. 1. Schematic diagram of the column test used in this study.

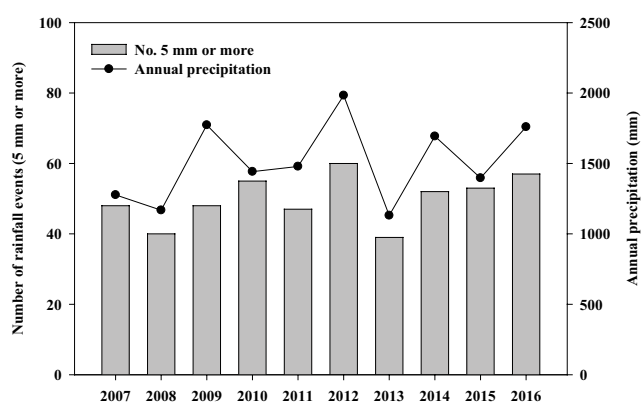


Fig. 2. Annual precipitation and number of days of annual rainfall events that exceeded 5 mm.

The BET surface area was calculated from the N_2 adsorption isotherms at 77 K based on the nonlocal density functional theory (NL-DFT) model in the Quantachrome ASiQwin 3.01 software package.

3. Results and discussion

3.1. Batch test

The batch tests were preliminary tests to determine the removal and adsorption potential of phosphate and heavy metals by the uncoated and CNT-coated slag. The removal efficiency of phosphate and zinc were evaluated using both uncoated and CNT-coated slag (Fig. 3). Overall, the removal efficiency and adsorption amount per unit mass of phosphate and zinc by the CNT-coated slag were higher than those of the uncoated slag. In addition, the removal efficiency increased with increasing slag mass but the adsorption density (Q_e) decreased. Ozacar and Sengil [30] and Li et al. [31] attributed the decrease in adsorption density with increasing adsorbent mass to the desaturation of adsorption sites during the adsorption reaction or particle interactions, such as aggregation, which reduce the total surface area of the adsorbent and increase the length of the diffusion path. Table 3 and Fig. 4 show the adsorption density of the uncoated and

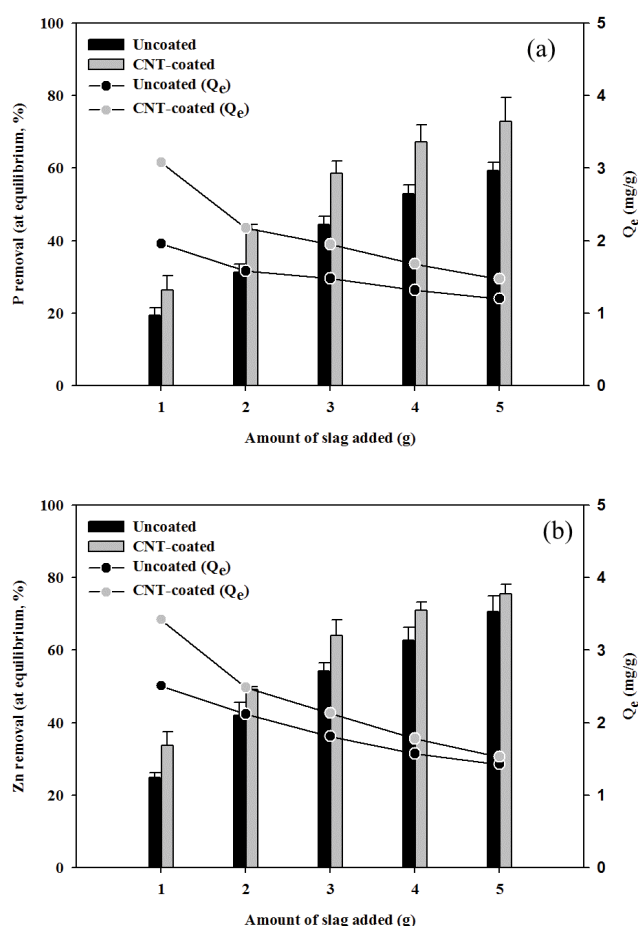


Fig. 3. Effect of the adsorbent (uncoated and CNT-coated slag) mass on phosphate (a) and zinc (b) adsorption ($V = 200 \text{ mL}$; $C_0 = 50 \text{ mg/L}$; adsorbent mass = 1.0, 2.0, 3.0, 4.0 and 5.0 g/200 mL; contact time = time at equilibrium).

CNT-coated slag with the equilibrium concentration of phosphate and zinc. The adsorption density of the uncoated and CNT-coated slag increased with increasing equilibrium concentration of phosphate and zinc.

Table 3
Experimental C_e and Q_e values for adsorption isotherm analysis

Parameter	Slag mass (g)	Uncoated		CNT-coated	
		P	Zn	P	Zn
C_e	1	40.2	37.5	34.6	32.9
	2	34.2	28.8	28.2	25.2
	3	27.8	22.9	20.7	18.0
	4	24.6	18.6	16.4	14.5
	5	20.0	14.4	13.2	11.8
Q_e	1	1.96	2.51	3.08	3.42
	2	1.58	2.12	2.18	2.48
	3	1.48	1.81	1.95	2.13
	4	1.27	1.57	1.68	1.78
	5	1.20	1.43	1.47	1.53

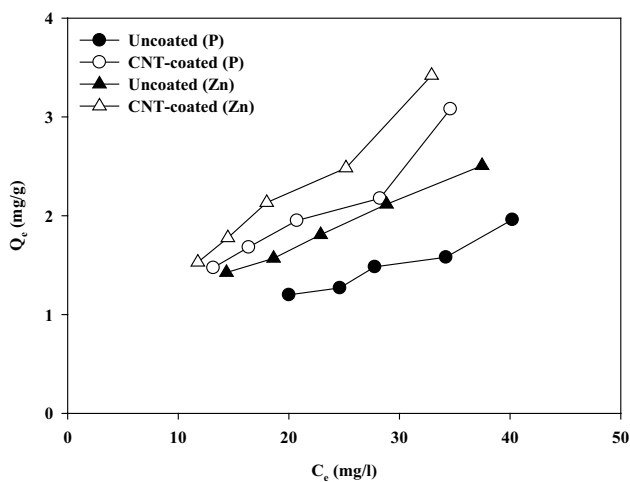


Fig. 4. Adsorption isotherm for phosphate and zinc on the uncoated and CNT-coated slag.

During the batch test, the maximum pH of the aqueous solution at equilibrium reached 9.8 ± 0.4 and 9.1 ± 0.3 in the uncoated- and CNT-coated slag-containing solution, respectively. Therefore, phosphate might have existed in the acidic-phosphate forms ($H_2PO_4^-$ or HPO_4^{2-}), which are dominant in aqueous solutions over the pH range, 4–10, rather than PO_4^{3-} [32]. The acidic-phosphate can be adsorbed by ion exchange between the slag surface and phosphate-mineral

salts, called “chemisorption”, as opposed to Ca-P precipitation [33]. In addition, divalent cations, such as Zn^{2+} , interact with the surface hydroxyl group of slag at the variable-charge sites [34].

Rao et al. [21] reported that the major mechanism of metal removal is the chemical interaction between the metal ions and the surface functional group of CNT. H^+ in the carboxylic group of CNT then exchanges with the divalent metal ion in the aqueous phase and the pH of the solution decreases after the sorption process.

Mahdavi and Akhbari [35] reported phosphate removal by CNTs but the removal efficiency was less than 20%. Some studies reported phosphorus removal by adsorption using surface-modified carbon materials. Graphite oxide (GO) contains ZrO_2 particles that adsorbed phosphate more strongly than untreated GO [36], and iron oxide-introduced activated carbon fiber removed phosphorus by ligand exchange and electrostatic interactions [37]. Furthermore, by $FeSO_4$ modification, the hydrophobic surface of the activated carbon became hydrophilic, so that the ionic materials could be adsorbed, making it suitable for phosphate removal [38,39]. Xiong and Mahmood [40] suggested a cation-bridge mechanism between carbon materials, metal and phosphorus. Carbon materials functionalized with carboxyl and hydroxyl, which were available for chelating metal ions, provided adsorption sites for phosphorus through CNT-COO-M-P formation.

To describe the adsorption mechanisms of phosphate and zinc by the uncoated and CNT-coated slag, the Langmuir and Freundlich adsorption models were used to fit the experimental data [41,42].

Langmuir:

$$Q_e = \frac{Q_m C_e}{1 + K_L C_e} \quad (1)$$

Freundlich:

$$Q_e = K \times C_e^{1/n} \quad (2)$$

where Q_e (mg/g) and C_e (mg/L) are the amounts of phosphate and zinc adsorbed (adsorbate mass per unit mass sorbent) and the equilibrium aqueous phosphate and zinc concentration, respectively. Q_m (mg/g) and K_L (L/mg) are the Langmuir constants, and K (mg/g) and n are the Freundlich constants. Table 4 lists the calculated parameters for the Langmuir and Freundlich constants. In this study, the uncoated and CNT-coated slag fitted the Freundlich and Langmuir isotherm, respectively, as indicated by the R^2 value. When the

Table 4
Calculated isotherm constants for phosphate and zinc adsorption on both the uncoated and CNT-coated slag

	Langmuir constants			Freundlich constant		
	Q_m (mg/g)	K_L (L/mg)	R^2	K (mg/g)	n	R^2
Uncoated (phosphate)	4.26	2.80	0.9223	0.15	1.46	0.9352
CNT-coated (phosphate)	5.79	1.18	0.9400	0.24	1.44	0.9301
Uncoated (zinc)	4.44	1.61	0.9702	0.28	1.65	0.9890
CNT-coated (zinc)	8.13	0.78	0.9820	0.24	1.34	0.9787

adsorption isotherm shows a better fit to the Freundlich equation, phosphorus and heavy metals are adsorbed on the surface of the slag in the form of Ca–P and M–OH [43]. On the other hand, when the adsorption isotherm shows a better fit to the Langmuir model, it assumes surface homogeneity of the active sites for the adsorbents. The active sites have equal affinity to the molecules of the adsorbate [41].

The maximum adsorption capacity (Q_m) calculated by the Langmuir equation suggests that the CNT-coated slag (phosphate, 5.79; zinc, 8.13 mg/g) has higher capacity than the uncoated one (phosphate, 4.26; zinc, 4.44 mg/g).

Vohla et al. [44] reported that the adsorption capacity from the adsorption isotherm equation is likely to be relatively overestimated. These results are higher than the experimental values. The experimental Q_m data were 3.08 and 3.42 mg/g for phosphate and zinc, respectively, by the CNT-coated slag, and 1.96 and 2.51 mg/g for phosphate and zinc, respectively, by the uncoated slag.

The increase in adsorption capacity in CNT-coated steel slag is due to CNTs, which gave the slag a higher specific surface area (CNT-coated slag, 4.39; uncoated slag 3.67 m²/g), pore size (CNT-coated slag, 0.545; uncoated slag 0.455 nm), and pore volume (CNT-coated slag, 0.0120; uncoated slag 0.0083 cm³/g). Carbon nanomaterials, such as CNTs, fullerenes, graphene, and graphite, have been applied to various environmental fields because of their highly porous structure, large specific surface area, and strong interactions with pollutants [19,45]. Fig. 5 presents SEM images and an EDS scan of the uncoated and CNT-coated steel slag. Changes in the surface structure of steel slag were observed after the CNT-coating. The surface of CNT-coated slag was covered with CNTs and became smooth compared with uncoated slag. The compositions of carbon and oxygen were increased because the slag was coated after oxygen had been introduced onto the CNTs through a functionalization process.

Studies of phosphate and metal adsorption kinetics have contributed to an understanding of the overall process and mechanism of phosphate and metal removal by steel slag [46]. To determine the kinetics of phosphorus removal by uncoated and CNT-coated slag, the changes in the adsorption capacity (Q_t) were examined as a function of the contact time. Fig. 6 shows the relationship between the adsorption capacities and contact time for the removal of phosphate and zinc. The adsorption of zinc was slightly more pronounced than the adsorption of phosphate in both slags. In addition, CNT-coated slag adsorbed more pollutants during the same period.

To examine the kinetics of adsorption by the uncoated and CNT-coated slag, the pseudo-first and pseudo-second order kinetic models were applied to determine the constants, which are expressed as follows:

Pseudo-first order:

$$\ln(Q_e - Q_t) = \ln Q_e - \frac{k_1 t}{2.303} \quad (3)$$

Pseudo-second order:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

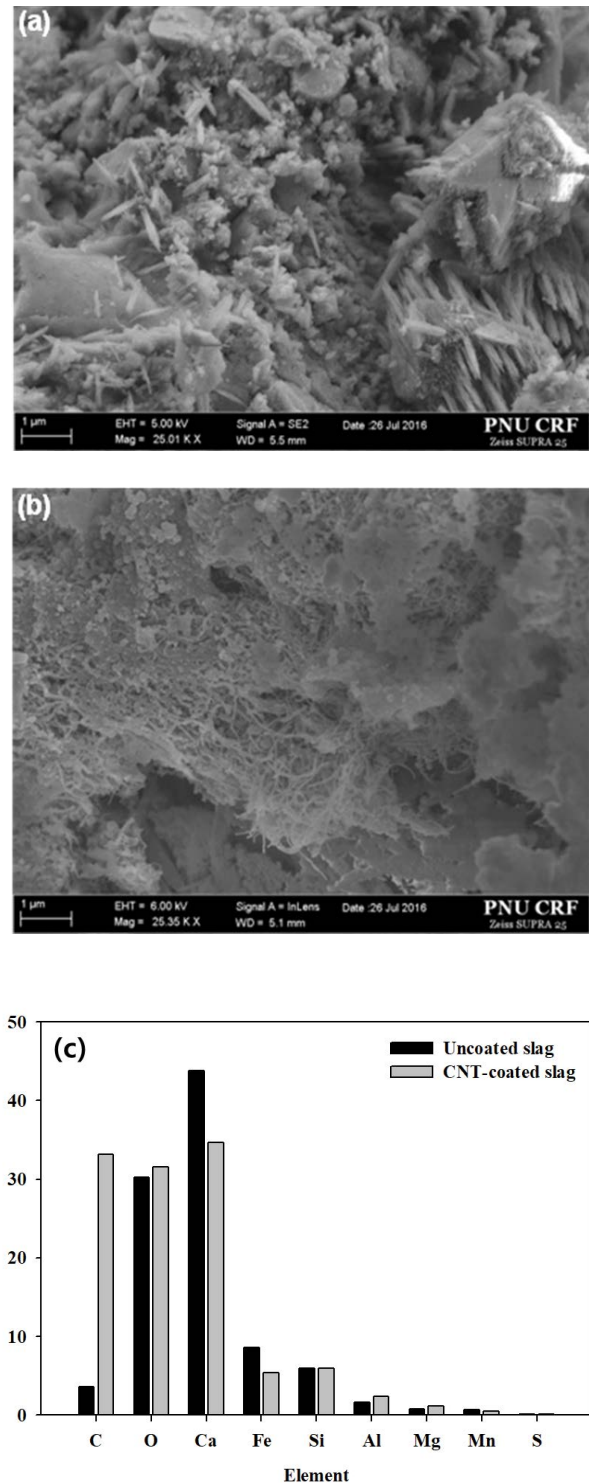


Fig. 5. SEM images of uncoated (a) and CNT-coated steel slag (b) and EDS scan (c).

where Q_e (mg/g) and Q_t (mg/g) represent the amount of phosphate and zinc at equilibrium and at time t (h), respectively, and k_1 (h⁻¹) and k_2 (g/mg h) are the rate constants of the pseudo-first order and pseudo-second order adsorption, respectively.

Based on the adsorption kinetics, the contact time, amount of substrate, and hydraulic retention time can be determined for a pilot- and full-scale treatment system [47]. Table 5 lists the adsorption kinetic parameters

for phosphate and zinc by the uncoated and CNT-coated slag. Based on the R^2 value, the adsorption of phosphate and zinc adsorption by both the uncoated and CNT-coated slag are expressed suitably by pseudo-first order kinetics.

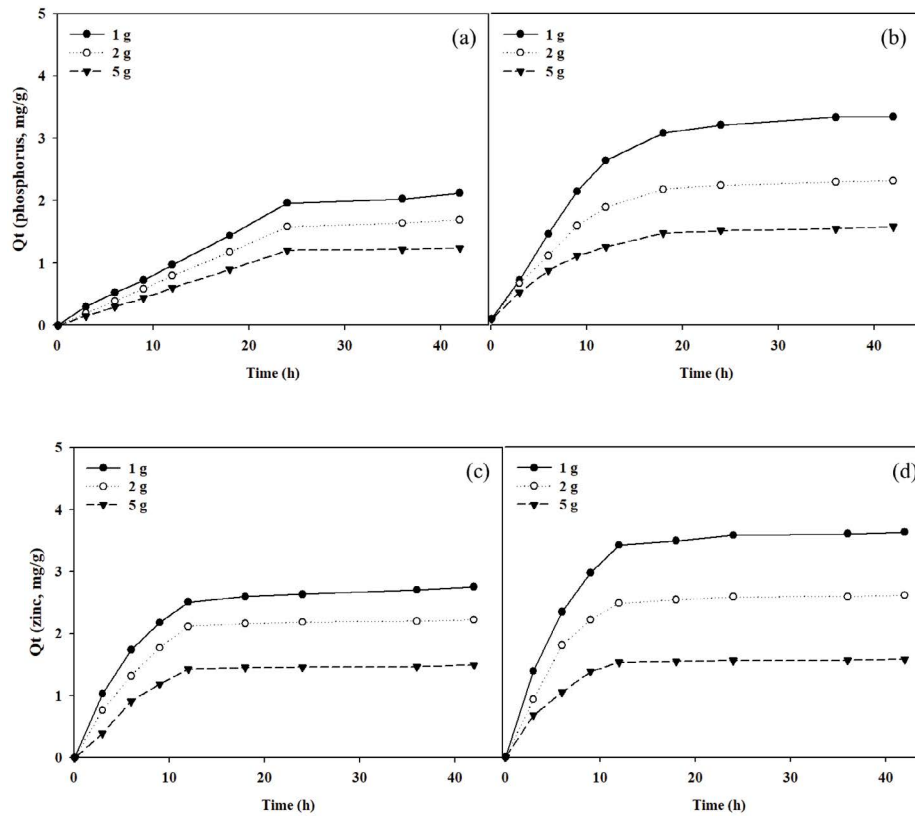


Fig. 6. Effect of the contact time on the adsorption of phosphorus and zinc on an uncoated slag ((a) and (c)) and CNT-coated steel slag ((b) and (d)) containing solution.

Table 5

Estimated pseudo-first order and pseudo-second order adsorption rate constants and experimental values for phosphate and zinc on different slag masses in uncoated and CNT-coated steel slag

	Slag mass (g)	q_e (exp, mg/g)	Pseudo-first order			Pseudo-second order		
			k_1 (h^{-1})	q_e^a (mg/g)	R^2	k_2 (g/mg·h)	q_e^a (mg/g)	R^2
Uncoated slag (phosphate)	1	1.96	0.17	2.13	0.96	0.02	2.91	0.40
	2	1.58	0.17	1.75	0.96	0.01	2.76	0.28
	5	1.20	0.17	1.34	0.95	0.02	2.10	0.28
CNT-coated slag (phosphate)	1	3.08	0.37	3.59	0.96	0.03	4.10	0.65
	2	2.18	0.38	2.44	0.97	0.08	2.61	0.81
	5	1.47	0.37	1.51	0.99	0.20	1.67	0.88
Uncoated slag (zinc)	1	2.50	0.51	2.70	0.98	0.14	2.78	0.85
	2	2.12	0.46	2.30	0.98	0.13	2.40	0.77
	5	1.43	0.46	1.62	0.97	0.11	1.80	0.58
CNT-coated slag (zinc)	1	3.42	0.52	3.72	0.98	0.10	3.81	0.84
	2	2.48	0.58	2.83	0.98	0.12	2.86	0.81
	5	1.53	0.58	1.72	0.96	0.26	1.69	0.87

^aCalculated value.

In addition, all the equilibrium adsorption capacities (Q_e) calculated by the pseudo-first order model were closer to the experimental data. These results suggest that the adsorption mechanism was controlled by the external diffusion of adsorbate, which is controlled mainly by the external surface area, particle density, solution concentration, and agitation speed [48,49].

3.2. Cylindrical column test

The removal efficiencies of phosphate, zinc, and copper increased with increasing filtration length in the entire process, as shown in Fig. 7. In addition, when the linear velocity was 15 m/h, the removal efficiency was higher than that with a linear velocity of 20 m/h. An increase in linear velocity decreases the contact time between the slag and wastewater, resulting in a decrease in removal efficiency [50]. Similarly, a longer filtration length resulted in a longer contact time between slag and wastewater, and a concomitant increase in removal efficiency.

Fig. 8 shows the results of the 100-rainfall repetition continuous-cylindrical column test with the uncoated and CNT-coated slag. The influent concentrations of phosphate, zinc, and copper were 0.47 ± 0.05 , 0.63 ± 0.06 , and 0.23 ± 0.02 mg/L, respectively, and the filtration length and linear velocity were 100 cm and 20 m/h, respectively. The influent flow rate was 0.65 mL/min, and the hydraulic residence time to pass through the reactor was approximately 3 min.

The cylindrical column test revealed a different aspect compared with the batch test. Adam et al. [51] reported that a small imitating system could not explain the full-scale experiment. Vohla et al. [44] also showed that column studies need to predict the possible removal capacity in a real system. For these reasons, a 100-rainfall repetition column test was carried out to examine the phosphate, zinc, and copper removal efficiency as well as the sustainability between the two types of slags. During 60-rainfall repetitions from the beginning of the experiments, the removal rates of phosphate, zinc, and copper by the uncoated slag and CNT-coated slag were similar: 72.4%, 80.8%, and 67.7%, respectively, by the uncoated slag; and 78.6%, 85.4%, and 69.5%, respectively, by the CNT-coated slag. The phosphate and zinc removal rates decreased after 61 and 75 repetitions using the uncoated slag, respectively, but decreased after 90 repetitions using the CNT-coated slag. In addition, there was no significant change in the removal of copper from both the uncoated CNT-coated slag and copper-coated slag. Copper first reaches equilibrium and the zinc and phosphorus are then removed. This is because when copper and zinc are present together in aqueous solutions, the affinity with the adsorbent is higher when copper is removed using slag or CNTs than zinc in a multi-element system [34]. In addition, the adsorption of Cu occurs at a relatively lower pH than Zn [52].

Table 6 lists the average influent and effluent concentrations and removal rates for the 100-rainfall experiment. The

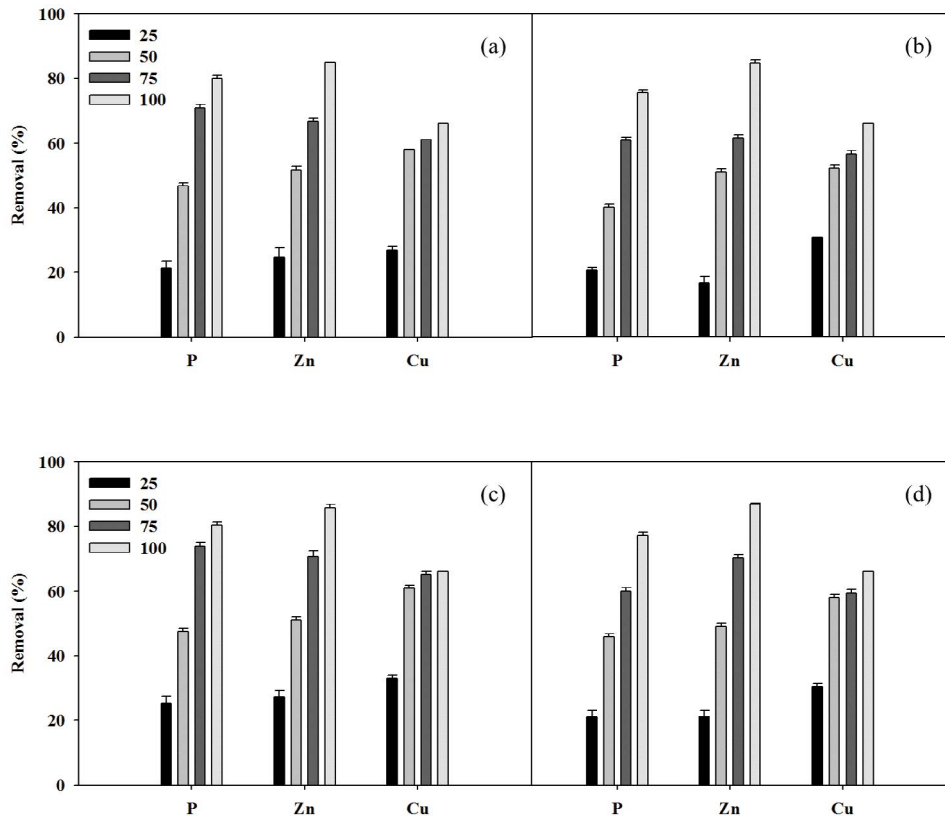


Fig. 7. Comparison of the removal efficiency of phosphate, zinc, and copper according to the length (25, 50, 75, and 100 cm) of the reactor and linear velocity (a) uncoated at 15 m/h; (b) uncoated at 20 m/h; (c) CNT-coated at 15 m/h; (d) CNT-coated at 20 m/h.

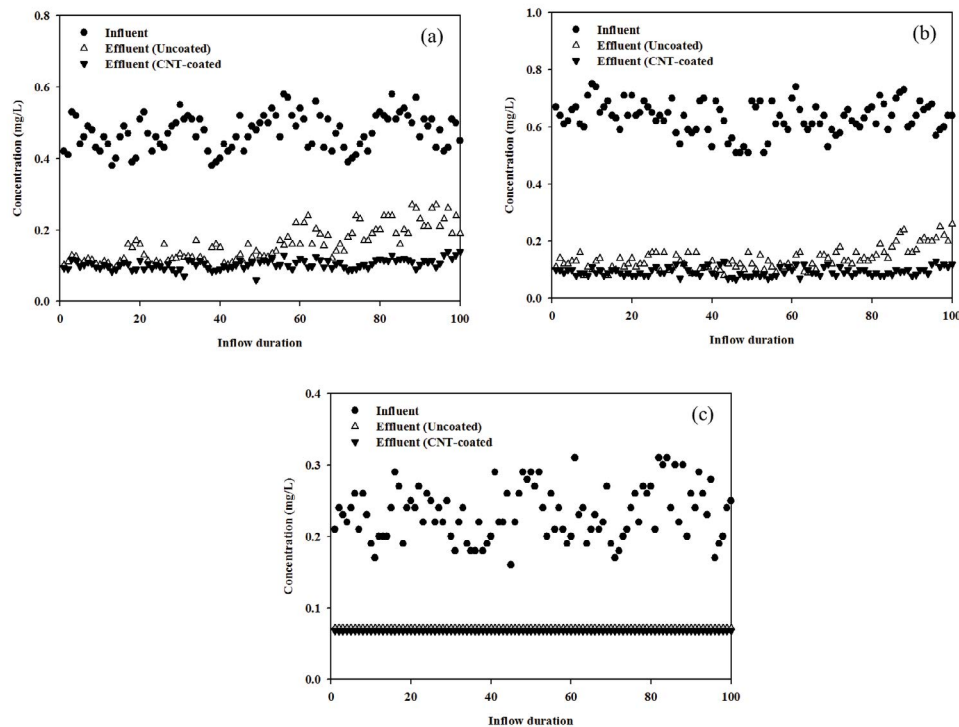


Fig. 8. Comparison of the removal of phosphate (a), zinc (b) and copper (c) by the uncoated and CNT-coated slag (length = 100 cm; $C_0 = 0.47 \pm 0.05$ (phosphate), 0.63 ± 0.06 (zinc) and 0.23 ± 0.02 (copper) mg/L; adsorbent mass = 4 kg; hydraulic residence time = 3.0 ± 0.1 min).

Table 6

Average influent and effluent concentration, removal rate, adsorption amount, and adsorption capacity of phosphate, zinc, and copper by the uncoated and CNT-coated slag in a 100-time column test

Component	Slag	Influent (mg/L)	Effluent		Adsorption capacity (mg/g)
			Concentration (mg/L)	Removal (%)	
Phosphate	Uncoated	0.47 ± 0.05	0.17 ± 0.02	66.3 ± 1.0	0.60
	CNT-coated		0.10 ± 0.01	78.0 ± 0.3	0.73
Zinc	Uncoated	0.63 ± 0.06	0.21 ± 0.02	78.1 ± 0.6	0.83
	CNT-coated		0.10 ± 0.01	85.1 ± 0.3	1.05
Copper	Uncoated	0.23 ± 0.02	0.07 ± 0.01	68.3 ± 0.5	0.32
	CNT-coated		0.07 ± 0.01	70.0 ± 0.5	0.32

removal rates of phosphate, zinc, and copper were 66.3%, 78.1%, and 68.3%, respectively, using the uncoated slag, and 78.0%, 85.1%, and 70.0%, respectively, using the CNT-coated slag. The amount of phosphate, zinc, and copper adsorbed was 0.600, 0.805, and 0.315 mg/g slag, respectively, by the uncoated slag, and 0.726, 1.046 and 0.323 mg/g slag by the CNT-coated slag, respectively. In addition, as the column study indicates, the removal efficiency of the CNT-coated slag was constant, whereas that of the uncoated slag decreased gradually. The CNT-coated slag is expected to be more advantageous than the uncoated slag when the flow rate and pollutant load of the influent are high.

During the column test, the pH of the effluent was 8.9 ± 0.3 and 8.4 ± 0.4 for the uncoated and CNT-coated slag,

respectively. This is because the short residence time was not enough to elute a large amount of Ca^{2+} and OH^- .

Table 7 summarizes the results of continuous flow experiments using steel slag performed in various studies. For comparison, the retention time, pollutant concentration, and effluent pH given in each study are listed and the results of the present study are also attached. Among these studies, Wang et al. [53] performed phosphorus removal using EAF-slag with a short retention time (1 min) and influent phosphorus concentration 4.2 mg/L in runoff interception trenches. The average removal rate of phosphorus was approximately 20%. The study was conducted to test the effectiveness of the trench filter system, with 1 tonne of slag.

Table 7
Slag-using continuous flow experiments

Type of slag	Retention time	Target pollutant	Concentration (mg/L)		Effluent pH	Reference
			Influent	Effluent		
BOF slag	24 h	P	10.09	0.35	10.8	[17]
BOF slag	3.2 d	P	11.8	0.7	8.9	[33]
EAF slag	13.7 h	P	8.9	0.02	11.0	[52]
EAF slag	1 min	P	4.17	3.22	7.9	[53]
BOF slag (uncoated)	3 min	P	0.4	0.17	8.9	This study
		Zn	0.5	0.21		
		Cu	0.2	0.07		
CNT-coated slag	3 min	P	0.4	0.10	8.4	This study
		Zn	0.5	0.10		
		Cu	0.2	0.07		

BOF slag: basic oxygen furnace slag; EAF slag: electric arc furnace slag; P: phosphate or phosphorus.

Although this study was carried out to remove pollutants at low concentration in stormwater runoff, the pollutants had been removed more efficiently than other studies, even at low residence times. In addition, the continuous flow experiments using slag focused mainly on the removal of phosphate, and there has been no removal experiment of mixtures of both phosphate and heavy metals in aqueous solution, as in the present study. This study showed that phosphate and heavy metals can be treated simultaneously in a nonpoint pollution abatement facility using slag. In addition, it was shown that the removal efficiency and durability can be increased by the CNT-coating on the slag surface.

According to the maximum capacity by the adsorption isotherms obtained from the batch test and the results of the column test, it is expected that the CNT-coated slag can take a long replacement cycle and help reduce the overall operating cost.

Although the developed slag is useful for phosphorus and metal removal, there are several design considerations for full-scale nonpoint pollution abatement facilities to apply the developed slag. The BOD, COD, and T-N components in the actual rainfall runoff correlated with the SS [3]. They can be removed satisfactorily by removing the SS, but clogging of the nonpoint pollution abatement facility by SS might be a problem. In addition, Massoudieh and Ginn [54] reported that colloidal particles could act as vehicles that transport the adsorbed metals to the effluent. Therefore, it is necessary to consider relevant pre- or post-treatment methods, such as coagulating or backwashing, depending on the environment of the location to be installed and the stormwater runoff condition.

4. Conclusion

This study examined the removal characteristics of phosphorus (phosphate) and heavy metal (zinc and copper) using two types of steel slag (uncoated and CNT-coated slag) for applications in a filtration-device type nonpoint pollution abatement facility. The CNT-coated slag was a highly effective medium to remove phosphate and metal from aqueous solution according to the adsorption isotherm in a

batch study. The phosphate and zinc adsorption capacities of the CNT-coated steel slag were 1.36 and 1.83 times higher than that of the uncoated slag, respectively. The 100-rainfall cylindrical column tests confirmed the efficiency and sustainability of the steel slag filter to remove phosphate and metal in a filtration-device type nonpoint pollution abatement facility according to the installation criteria of South Korea. Moreover, CNT-coated slag is expected to increase the filter replacement cycle and reduce the overall operating cost of a nonpoint pollution abatement facility.

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References

- [1] N. Okochi, D. McMartin, A laboratory study of the treatability of synthetic stormwater under varying conditions using electric arc furnace steel slag, *Water*, 4 (2012) 321–344.
- [2] J. Lee, K. Bang, Characterization of urban stormwater runoff, *Water Res.*, 34 (2000) 1773–1780.
- [3] S. Kim, S. Shin, Y. Jeon, C. Won, Washoff characteristics of nonpoint source pollutants and estimation of unit loads in suburban industrial complex areas runoff, *J. Environ. Impact Assess.*, 21 (2012) 315–325.
- [4] H. Lee, S. Lee, Runoff characteristics of stormwater in small city urban area, *J. Korean Soc. Environ. Eng.*, 31 (2009) 193–202.
- [5] V. Novotny, *Nonpoint Pollution and Urban Stormwater Management*, Technomic Publishing Company, Inc., Lancaster, 1995.
- [6] R. Aryal, H. Furumai, F. Nakajima, M. Boller, Dynamic behavior of fractional suspended solids and particle-bound polycyclic aromatic hydrocarbons in highway runoff, *Water Res.*, 39 (2005) 5126–5134.
- [7] C. Hsieh, A. Davis, B. Needelman, Bioretention column studies of phosphorus removal from urban stormwater runoff, *Water Environ. Res.*, 79 (2007) 177–184.
- [8] R. Aryal, S. Vigneswaran, J. Kandasamy, R. Naidu, Urban stormwater quality and treatment, *Korean J. Chem. Eng.*, 27 (2010) 1343–1359.
- [9] H. Chi, G. Shin, Selection of best management practices for urban watershed corresponding to the runoff characteristics from nonpoint pollution source, *J. Environ. Sci. Int.*, 25 (2016) 31–40.

- [10] G. Choi, J. Park, D. Kang, J. Yu, I. Byun, H. Shin, T. Lee, T. Park, Study on the performances and microbial community in the biofilm process for treating nonpoint source pollutants, *J. Korean Soc. Environ. Eng.*, 30 (2008) 1021–1027.
- [11] S. Kim, E. Gwon, S. Park, S. Joh, C. Lim, S. Kang, Identification of operating parameters in auto-discharging filter system for treatment of urban storm water, *J. Korean Soc. Water Wastewater*, 24 (2010) 377–386.
- [12] N. Okochi, D. McMartin, Laboratory investigations of stormwater remediation via slag: effect of metals on phosphorus removal, *J. Hazard. Mater.*, 187 (2011) 250–257.
- [13] S.K. Pitcher, R.C.T. Slade, N.I. Ward, Heavy metal removal from motorway stormwater using zeolite, *Sci. Total Environ.*, 334–335 (2004) 161–166.
- [14] Korean Ministry of Environment (KMOE), Installation and Management of Nonpoint Pollution Control Facilities, Operation Manuals, 2016.
- [15] J. Lee, K. Bang, Performance evaluation of backwash hydrodynamic separator filter for treatment of micro particles, *J. Kor. Soc. Environ. Eng.*, 34 (2012) 694–701.
- [16] C. Barca, C. Gerente, D. Meyer, F. Chazarenc, Y. Andres, Phosphorus removal from synthetic and real wastewater using steel slags produced in Europe, *Water Res.*, 46 (2012) 2376–2384.
- [17] C. Barca, D. Meyer, M. Liira, P. Drissen, Y. Comeau, Y. Andres, F. Chazarenc, Steel slag filters to upgrade phosphorus removal in small wastewater treatment plants: removal mechanisms and performance, *Ecol. Eng.*, 68 (2014) 214–222.
- [18] D. Kim, M. Shin, H. Choi, C. Seo, K. Baek, Removal mechanisms of copper using steel-making slag: adsorption and precipitation, *Desalination*, 223 (2008) 283–289.
- [19] V.K. Gupta, T.A. Saleh, Sorption of pollutants by porous carbon, carbon nanotubes and fullerene – an overview, *Environ. Sci. Pollut. Res.*, 20 (2013) 2828–2843.
- [20] S. Rafiei, Foundation of Nanotechnology, Vol. 3, Mechanics of Carbon Nanotubes, Apple Academic Press Inc., Oakville, Ontario, 2015.
- [21] G.P. Rao, C. Lu, F. Su, Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review, *Sep. Purif. Technol.*, 58 (2007) 224–231.
- [22] V.K.K. Upadhyayula, S. Deng, M.C. Mitchell, G.B. Smith, Application of carbon nanotube technology for removal of contaminants in drinking water: a review, *Sci. Total Environ.*, 408 (2009) 1–13.
- [23] F. Su, C. Lu, Adsorption kinetics, thermodynamics, and desorption of natural dissolved organic matter by multi walled carbon nanotubes, *J. Environ. Sci. Health., Part A*, 42 (2007) 1543–1552.
- [24] C. Lu, H. Chiu, Chemical modification of multiwalled carbon nanotubes for sorption of Zn^{2+} from aqueous solution, *Chem. Eng. J.*, 139 (2009) 462–468.
- [25] J. Choi, C. Shin, Management of Nonpoint Pollution by Reducing Storm Runoff, Korea Environment Institute, Seoul, 2002.
- [26] H.M. Park, Y.J. Kim, S.O. Ko, Characteristics of particle size distribution and heavy metal concentration in pavement road runoff, *Int. J. Highway Eng.*, 11 (2009) 141–149.
- [27] Korea Metrological Agency, National Weather Information, <http://www.weather.go.kr>.
- [28] Korea Ministry of Government Legislation, “Water Quality and Ecosystem Conservation Act”.
- [29] APPA-AWWA-WEF, Standard Method for the Examination of Water and Wastewater, 21st Ed., American Public Health Association, Washington D.C., 2005.
- [30] M. Ozacar, I.A. Sengil, Adsorption of metal complex dyes from aqueous solutions by pine sawdust, *Bioresour. Technol.*, 96 (2005) 791–795.
- [31] K. Li, Z. Zheng, X. Huang, G. Zhao, J. Feng, J. Zhang, Equilibrium, kinetic and thermodynamic studies on the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fibre, *J. Hazard. Mater.*, 166 (2009) 213–220.
- [32] G. Ma, S. Salahub, C. Montemagno, S. Abraham, Highly active magnesium oxide nano materials for the removal of arsenates and phosphates from aqueous solution, *Nano-structures Nano-objects*, 13 (2018) 74–81.
- [33] J. Park, J.J. Wang, S. Kim, J. Cho, S. Kang, R.D. Delaune, D. Seo, Phosphate removal in constructed wetland with rapid cooled basic oxygen furnace slag, *Chem. Eng. J.*, 327 (2017) 713–724.
- [34] Y. Xue, H. Hou, Z. Shujing, Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag, *J. Hazard. Mater.*, 162 (2009) 391–401.
- [35] S. Mahdavi, D. Akhbari, The removal of phosphate from aqueous solution using two nano-structures: copper oxide and carbon tubes, *Clean Technol. Environ. Policy*, 18 (2016) 817–827.
- [36] E. Zong, D. Wei, H. Wan, S. Zheng, Z. Xu, D. Zhu, Adsorptive removal of phosphate ions from aqueous solution using zirconia-functionalized graphite oxide, *Chem. Eng. J.*, 221 (2013) 193–203.
- [37] Q. Zhou, X. Wang, J. Liu, L. Zhang, Phosphorus removal from wastewater using nano-particles of hydrated ferric oxide doped activated carbon fiber prepared by Sol-Gel method, *Chem. Eng. J.*, 200–202 (2012) 619–626.
- [38] S. Lee, C. Kim, D. Paik, Evaluation of phosphorus adsorption characteristic with surface modified activated carbon, *J. Korean Soc. Urban Environ.*, 15 (2015) 189–197.
- [39] D. Tran, S. Kabiri, L. Wang, D. Losic, Engineered graphene-nanoparticle aerogel composites for efficient removal of phosphate from water, *J. Mater. Chem. A*, 3 (2015) 6844–6852.
- [40] J. Xiong, Q. Mahmood, Adsorptive removal of phosphate from aqueous media by peat, *Desalination*, 259 (2010) 59–64.
- [41] G. Gong, S. Ye, Y. Tian, Q. Wang, J. Ni, Y. Chen, Preparations of a new sorbent with hydrated lime and blast furnace slag for phosphorus removal from aqueous solution, *J. Hazard. Mater.*, 166 (2009) 714–719.
- [42] V.K. Jha, Y. Kameshima, A. Nakajima, K. Okada, Utilization of steel-making slag for the uptake ammonium and phosphate ions from aqueous solution, *J. Hazard. Mater.*, 156 (2008) 156–162.
- [43] J. Park, S. Kim, R.D. Delaune, B. Kang, S. Kang, J. Cho, Y. Ok, D. Seo, Enhancement of phosphorus removal with near-neutral pH utilizing steel and ferronickel slags for application of constructed wetlands, *Ecol. Eng.*, 95 (2016) 612–621.
- [44] C. Vohla, M. Koiv, H.J. Bavor, F. Chazarenc, U. Mander, Filter materials for phosphorus removal from wastewater in treatment wetlands – a review, *Ecol. Eng.*, 37 (2011) 70–89.
- [45] X. Ren, C. Chen, M. Nagatsu, X. Wang, Carbon nanotubes as adsorbents in environmental pollution management: a review, *Chem. Eng. J.*, 170 (2011) 395–410.
- [46] C. Han, Z. Wang, H. Yang, X. Xue, Removal kinetics of phosphorus from synthetic wastewater using basic oxygen furnace slag, *J. Environ. Sci.*, 30 (2015) 21–29.
- [47] N. Moelants, I.Y. Smets, J.F. van Impe, The potential of an iron substrate for phosphorus removal in decentralized wastewater treatment systems, *Sep. Purif. Technol.*, 77 (2011) 40–45.
- [48] C. Na, H. Park, Applicability of theoretical adsorption models for studies on adsorption properties of adsorbents (II), *J. Korean Soc. Environ. Eng.*, 33 (2011) 804–811.
- [49] A.S. Ozcan, A. Ozcan, Adsorption of acid dyes from aqueous solution onto acid-activated bentonite, *J. Colloid Interface Sci.*, 276 (2004) 39–46.
- [50] I.A. Katsoyiannis, A.I. Zouboulis, Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials, *Water Res.*, 36 (2002) 5141–5155.
- [51] K. Adam, A.K. Sovik, T. Krogstad, Sorption of phosphorous to Filtrate-PTM - the effect of different scales, *Water Res.*, 40 (2006) 1143–1154.
- [52] J. Ikhsan, B.B. Johnson, J.D. Wells, A comparative study of the adsorption of transition metals on kaolinite, *J. Colloid Interface Sci.*, 217 (1999) 403–410.
- [53] Z. Wang, G.E. Bell, C.J. Penn, J.Q. Moss, M.E. Payton, Phosphorus reduction in turfgrass runoff using a steel slag trench filter system, *Crop Sci.*, 54 (2014) 1859–1867.
- [54] A. Massoudieh, T.R. Ginn, Modeling colloid-enhanced contaminant transport in stormwater infiltration basin best management practices, *Vadose Zone J.*, 7 (2008) 1261–1268.