

Performance of carbon nanotube-coated steel slag for high concentrations of phosphorus from pig manure

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Abstract. The study objective was to evaluate the enhanced removal of high concentrations of phosphorus from synthetic wastewater (solely phosphorus-containing) and real wastewater (pig manure) by using carbon nanotube (CNT)-coated steel slag. Generally, phosphorus removal by steel slag is attributed to Ca^{2+} eluted from the slag. However, in this study, CNT was used to control the excess release of Ca^{2+} from steel slag and increase the phosphorus removal. The phosphorus removal rate by the uncoated steel slag was lower than that of the CNT-coated steel slag, even though the Ca^{2+} concentrations were higher in the solution containing the uncoated steel slag. Therefore, the phosphorus removal could be attributed to both precipitation with Ca^{2+} eluted from steel slag in aqueous solution and adsorption onto the surface of the CNT-coated steel slag. Furthermore, the protons released from the CNT surface by exchanging with divalent cations acted to reduce the pH increase of the solution, which is attributed to the OH^- eluted from the steel slag. The adsorption isotherm and kinetics of the CNT-coated steel slags followed the Freundlich isotherm and pseudo-second-order model, respectively. The maximum adsorption capacity of the uncoated and CNT-coated steel slags was 6.127 and 9.268 mg P g⁻¹ slag, respectively. In addition, phosphorus from pig manure was more effectively removed by the CNT-coated steel slag than by the uncoated slag. Over 24 hours, the $\text{PO}_4\text{-P}$ removal in pig manure was 12.3% higher by the CNT-coated slag. This CNT-coated steel slag can be used to remove both phosphorus and metals and has potential applications in high phosphorus-containing wastewater like pig manure.

Keywords: pig manure; high concentration of phosphorus; phosphorus removal; steel slag; carbon nanotube; adsorption isotherm; adsorption kinetics

1. Introduction

In Korea, livestock manures such as pig manures have been used as fertilizers that are promoted by the ‘Act on the Management and Use of Livestock Excreta’ (KMOE 2018) and ‘Act on the Promotion of the Development, Use and Diffusion of New and Renewable Energy’ (MOTIE 2017). Therefore, during the farming season, these livestock manures are often used as liquid fertilizer or compost. However, in the off-season, livestock manures are not recycled as fertilizers and therefore require additional treatment. In particular, pig manure contains a high concentration of phosphorus. Wastewater with high concentrations of phosphorus causes nonpoint pollution during rainfall and degrades water ecosystems, which necessitates the development of eco-friendly and economical phosphorus treatment methods.

The various attempts to remove phosphorus have included physicochemical methods like adsorption onto activated carbon and chemical precipitation and biological

methods. However, associated problems have included chemical instability, difficult treatment conditions and high cost (Kim *et al.* 2008). Therefore, the use of natural and industrial by-products, such as dolomite, limestone, sepiolite, steel slag and zeolite, has been tested (Vohla *et al.* 2011, Yin *et al.* 2011). Among them, steel slag materials, e.g., basic oxygen furnace slag (BOF-slag), electric arc furnace slag (EAF-slag), and converter slag, which are by-products of the steel industry, have been used in wastewater treatment as cheap adsorbents to replace granular activated carbon due to their sorptive characteristics (Cha *et al.* 2006). Steel slag has traditionally been used for aggregate recycling for civil engineering and fertilizer for soil improvement (Motz and Geiseler 2001). Studies using steel slag have focused on phosphorus removal because of its high affinity for phosphorus binding (Yang *et al.* 2009, Barca *et al.* 2012). Steel slag elutes divalent cations, such as calcium, ferrous and aluminum in aqueous solution, making it a potential substrate for phosphorus removal from wastewater by adsorption and precipitation. Thus, phosphorus in the form of aqueous phosphate ion (PO_4^{3-}) is removed by precipitation with Ca^{2+} , Fe^{3+} , and Al^{3+} ions eluted from steel slag. Another mechanism of phosphate removal by steel slag is ligand exchange, in which the

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phosphate adsorption forms phosphate-silicon and phosphate-aluminum complexes (Xue *et al.* 2009).

The use of steel slag suffers from the problem that CaO, which accounts for more than 40% of steel slag, is ionized in water and dissociates to Ca^{2+} and OH^- , which increases the pH (Chazarenc *et al.* 2010, Riley and Mayes 2015). The phosphorus removal system that produces hydroxyapatite (HAP) using Ca^{2+} and OH^- is the most stable and effective process for minimizing the sludge (Kim and Lim 2008). However, the pH increase necessitates additional treatments to neutralize the water during phosphorus removal using steel slag. Therefore, in this study, carbon nanotubes (CNTs) were used to solve this problem and increase the adsorption capacity. CNTs have been applied in biological, chemical, environmental, medical and other industries. In particular, they have great potential to adsorb organic or inorganic chemicals, dioxins, VOCs, heavy metals, etc. CNTs have advantages for the adsorption of organic and inorganic components due to their large surface area and electronic properties (Gupta and Saleh 2013). Their adsorption potential is also affected by the CNT functional group. CNTs contain functional groups, such as hydroxyl, carbonyl, and carboxyl, which are added by oxidation or heat treatment and which increase the water solubility and enhance the maximum adsorption capacity (Pan and Xing 2008, Upadhyayula *et al.* 2009). Some studies used chemicals, such as HNO_3 , H_2O_2 , H_2SO_4 , and KMnO_4 , for CNT functionalization. These functional groups give the CNT surface a negative charge in solution, resulting in the electrostatic attraction of the divalent cation to the negative surfaces of the CNT, which enhances the adsorption of divalent cations on the CNT (Ren *et al.* 2011). As protons on the carboxylic group of CNT exchange with the divalent cations in the aqueous phase, the solution pH decreases after divalent cations bind onto the CNTs (Rao *et al.* 2007). Furthermore, the presence of adsorption sites on both the inner and outer layer surfaces of the CNT's hollow structure (Rafiei 2015) may increase the adsorption capacity of CNT-coated steel slag when used as an adsorbent.

This study evaluated the properties of a reactive CNT-coated steel slag filter to remove phosphorus generated from non-point pollution sources and sewage sludge concentrated in wastewater treatment plants, in terms of the adsorption capacity, kinetics and optimal conditions for efficient phosphorus removal. In addition, the CNT-coated steel slag filter was tested on the removal of phosphorus from pig manure.

2. Materials and methods

2.1 Materials

The steel slag used was obtained from 'H' steel slag processing company (Gwangyang, Jeonnam, South Korea) and separated into particle sizes between 2-6 mm using a sieve. The steel slag used was the same as Park *et al.* (2016) and the chemical composition of the steel slag is listed in Table 1. Commercially available multi-walled CNTs (MWCNTs, Carbon Nano-material Technology Co., South

Table 1 Chemical composition of the steel slag obtained from 'H' company (Park *et al.* 2016)

Composition	CaO	Fe_2O_3	SiO_2	MgO	Al_2O_3
Contents (%)	44.3	17.5	13.8	6.4	2.1

Korea) were selected as the slag coating reagent. Some studies referred that SWCNT (single walled CNT) is more stable in physicochemical properties (Liew *et al.* 2005; Ncibi and Sillanpaa, 2015), but MWCNT has more adsorption capacity (Dehghani *et al.* 2016). Therefore, MWCNT was used in this study due to the availabilities in prices and performances. KH_2PO_4 solutions of various concentrations were used as the synthetic phosphorus-containing wastewater.

2.2 Preparation of the CNT-coated steel slag

One gram of raw CNT was heated to 350°C for 30 min to remove the amorphous carbon (Lu and Chiu 2006), and then added to 200 ml of nitric-sulfuric acid ($\text{HNO}_3:\text{H}_2\text{SO}_4$, 3:1 (v v⁻¹)). After this CNT-acid solution was shaken in an ultrasonic cleaning bath (model JAC-5020, Kodo Co., South Korea) for 1 h, the CNTs were centrifuged to obtain functionalized CNTs at 3000 rpm for 5 min and the supernatant was discarded. To make a CNT-coating ink, the centrifuged CNT pellet was placed into a 94% ethanol solution as a CNT dispersion solution with sodium dedocylbenzene sulfonate (SDBS) as a surfactant (Xie *et al.* 2012) to give a concentration of 0.5% CNT and 1% SDBS (w v⁻¹). The dispersion process was performed by horn sonication (model CV334, Sonics, U.S.) for 3 h. Finally, the sieved slag was dipped into CNT ink, removed, and dried at 150°C . The dipping-drying process was repeated three or four times to increase the CNT loading. The specific surface area of CNT-coated steel slag was $4.39 \text{ m}^2/\text{g}$ slag and it was 1.2 times than the uncoated steel slag ($3.67 \text{ m}^2/\text{g}$ slag).

2.3 Elution of Ca^{2+} and OH^-

To evaluate the elution of calcium and hydroxide ions by CaO, which has the highest content in steel slag, 50 g of the uncoated or CNT-coated slag was added to 300 mL of distilled water in 500 mL vessels, which were then placed on a stirrer set at 25°C , 150 rpm, and the elution of the calcium ions and the pH change were checked over time. The OH^- ion concentration is of course expressed by the pH value.

2.4 Phosphorus removal experiments in synthetic and real wastewater (pig manure)

Batch testing was performed to examine the phosphorus adsorption via isotherm and kinetics experiment. The batch operation was carried out in a batch-type jar tester (model C-JT-H, Changsin Scientific Co., South Korea) in 500 mL vessels (with 300 mL working volume).

The adsorption kinetics and isotherms of phosphorus removal were evaluated via adsorption of different initial

concentrations of PO₄-P (10, 50, 125 and 250 mg L⁻¹) using K₂HPO₄ and uncoated and CNT-coated steel slag weights (0.5, 1.0, 2.5, 5.0, 10.0, 25.0 and 50.0 g) in 500 mL vessels using a jar tester with agitation at 25 °C, 150 rpm and the concentrations of residual phosphorus were measured over time. All experiments were conducted in triplicate.

The removal efficiency (E, %) and adsorption amount (q, mg g⁻¹) were calculated by the following equations.

$$E = (C_0 - C_t) / C_0 * 100 \quad (1)$$

$$q = (C_0 - C_t) * V / m \quad (2)$$

where C₀ is the initial concentration of PO₄-P (mg L⁻¹), C_t the concentration (mg L⁻¹) at time t, q_t the adsorption amount (mg g⁻¹) at adsorption time t(h), V the volume of the K₂HPO₄ solution (L) and m the mass (g) of the slags.

In addition, to evaluate the removal properties of the CNT-coated steel slag in real wastewater, pig manure was obtained from 'G' livestock liquid fertilizer production facility. Table 2 lists the characteristics of synthetic wastewater and pig manure used in this study.

2.5 Analysis

The pH was measured using a pH meter (model HI 98217, Hanna Instrument, South Korea). The Ca²⁺ concentrations were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, PerkinElmer, USA) according to atomic absorption spectrophotometric methods. The concentration of PO₄-P was determined according to the standardized (APPA-AWWA-WEF 2005) molybdenum blue-ascorbic acid method using a UV-visible spectrophotometer (OPTIZEN 2120UV, MECASYS, South Korea) after the aqueous solution was filtered through Whatman GF/C filters. The surfaces of the CNT-coated and uncoated steel slags were investigated using a field emission scanning electron microscope (FE-SEM, Supra 25, Carl Zeiss, Oberkochen, Germany). The samples for SEM observation were coated by a platinum layer in advance.

3. Results and discussion

3.1 Ca²⁺ and OH⁻ elution characteristics of the uncoated and CNT-coated steel slags

The elution characteristics of Ca²⁺ and OH⁻ concentrations are important factors for the removal of phosphorus and Ca-P precipitation (Joko 1984). The Ca²⁺ concentration and the OH⁻ concentration, calculated by pH, are closely related to each other and the Ca²⁺ concentration and pH are increased by the dissolution CaO, which forms as Ca(OH)₂ in aqueous solution.

This increase is the first step in the system of phosphorus removal by slag (Blanco *et al.* 2016). Thus, before examining the effect of the CNT-coated steel slag on phosphorus removal, the effect of CNT on the Ca²⁺ and OH⁻ ions was first evaluated.

Table 2 The characteristics of synthetic wastewater and pig manure

Wastewater	Concentration (mg L ⁻¹)						pH
	T-P	PO ₄ -P	COD	T-N	Zn	61 SS	
Synthetic	10, 50,	10, 50,	3.5*	0.005*	-	-	6.8±0.2
	125 and	125 and					
	250	250					
Pig manure	421±22	345±12	27,490±10,060	6,408±919	63±2	5,950±2,250	7.7±0.6

*Data from Busan Water Authority (Beomeosa water purification plant)

For both the uncoated and CNT-coated steel slags, the pH and the elution of Ca²⁺ ions reached equilibrium at 3 and 8 h, respectively, after the beginning of the experiments. As shown in Fig. 1(a), the Ca²⁺ ion concentration of the solution containing the CNT-coated steel slag was lower than that of the solution containing the uncoated slag because the Ca²⁺ ions were considered to have been affected by the CNTs. Before the CNTs were coated onto the steel slag, the CNT surface was functionalized using nitric acid and sulfuric acid to introduce a carboxyl group onto the CNT surface in advance. Ca²⁺ ions can bind negatively charged groups such as the carboxyl group of CNT (Yang *et al.* 2009). The functional group by acidification and/or oxidation improves the ion-exchange capability and promotes the adsorption of divalent cations onto the CNT surface (Atieh *et al.* 2010). Tofighy and Mohammadi (2011) used the same method to soften hard water by removing Ca²⁺ and Mg²⁺ from hard water using acid-functionalized CNT, which has high affinity with hard mineral ions. They noted that both electrostatic and chemical attraction occurred simultaneously. This can also be demonstrated by the cation-π interaction between Ca²⁺ and CNT, which is a noncovalent interaction in which the positively charged cation interacts with the negatively charged π cloud (Mahadevi and Sastry 2012).

In addition, due to the binding between divalent cations such as calcium ions and functionalized CNT, protons (H⁺) are released from the CNT surface, then exchanged with the divalent cations at the CNT surface, and therefore released into the aqueous phase, which neutralizes and prevents any increase in the solution pH. The pH after pH equilibrium in the CNT-coated slag solution remained lower than that in the uncoated slag solution, as shown in Fig. 1(b). The pH was increased to 12.3 and 11.3 at 14 hours in the uncoated and CNT-coated steel slags, respectively, after which it decreased gradually in the uncoated slag solution, but this decrease was delayed till after 16hr in the CNT-coated slag. The decrease in pH in the uncoated slag was attributed to the dissolution of atmospheric CO₂, producing an equilibrium among the proton, carbonate and bicarbonate (Park *et al.* 2003).

The scanning microscope (SEM) images of the uncoated and CNT-coated steel slags are shown in Fig. 2. Unlike the rough surface of the uncoated slag, the CNT-coated slag surface was covered by the dispersed CNT bundles.

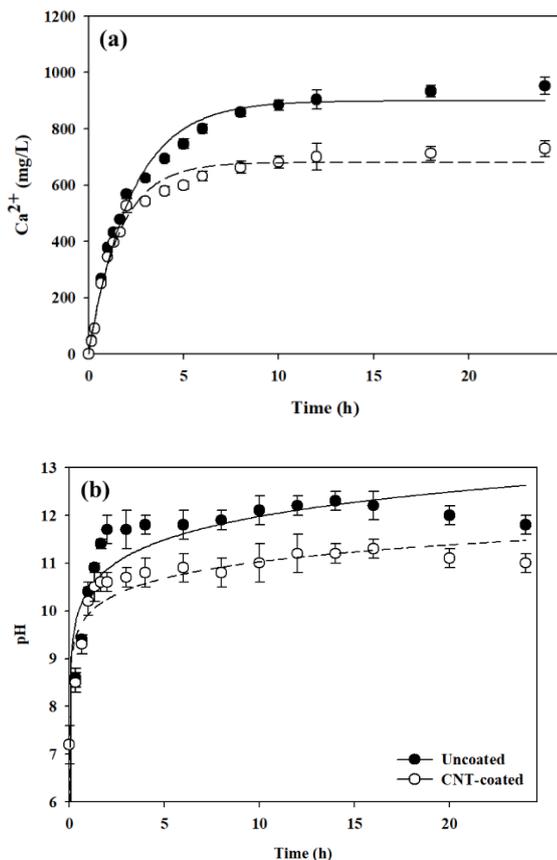


Fig. 1 Elution of Ca²⁺ (a) and pH (b) of the uncoated and CNT-coated steel slags in distilled water according to time

3.2 Phosphorus removal characteristics of the uncoated and CNT-coated slags in synthetic wastewater

The removal of phosphorus was tested in a 1 g L⁻¹ KH₂PO₄ solution with the uncoated and CNT-coated steel slags. The initial PO₄-P concentration and pH were approximately 250±2 mg L⁻¹ and 6.8±0.1, respectively. As shown in Fig. 3(a), PO₄-P removal processes attained equilibrium for both the uncoated and CNT-coated steel slags at 12 hours. After 24 hours, 75.8 and 87.8% of PO₄-P was removed by the uncoated and CNT-coated steel slags, respectively. Furthermore, the final pH of the solution containing the uncoated steel slag was higher than that of the solution containing the CNT-coated steel slag.

Lu *et al.* (2008) reported that the initial removal of phosphate occurred rapidly due to the precipitation with dissolved Ca²⁺ ion by steel slag. The present study showed that the PO₄-P removal efficiency by the uncoated steel slag was lower than that by the CNT-coated steel slag, even though the uncoated steel slag elutes more Ca²⁺ ions in aqueous solution.

During the phosphorus removal process, the pH increase differed from that described in Fig. 3(b). Bowden *et al.* (2009) stated that calcium-phosphate precipitation occurred spontaneously and that the mechanism is the dominant phosphate removal process at pH above 8 and the phosphorus adsorption to metal oxide surface of steel slag

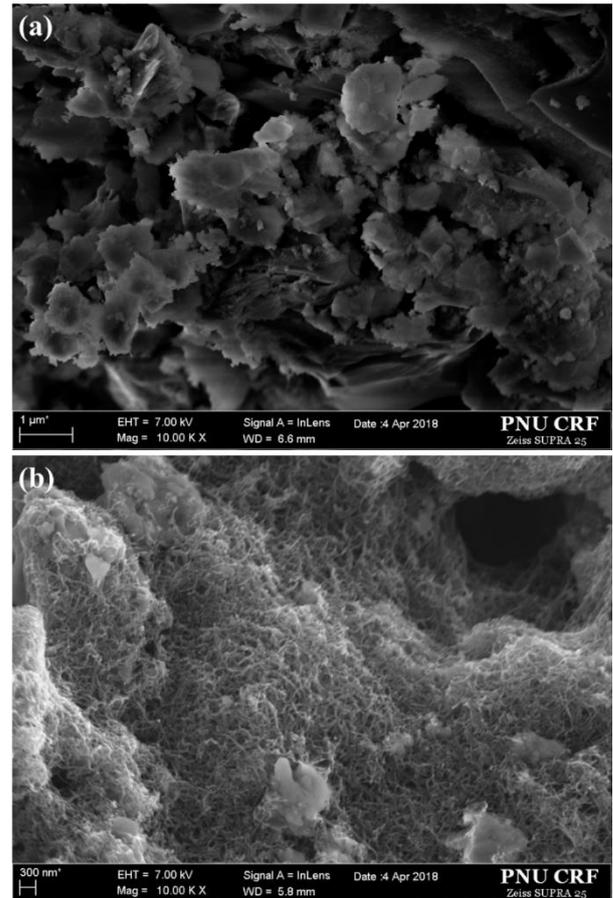


Fig. 2 FE-SEM images of the uncoated (a) and CNT-coated (b) steel slags

at pH under 7.5. In the present study, phosphorus removal by the uncoated steel slag was dominated by Ca-P precipitation due to rapid pH increase over 8 in the initial period. However, it is considered that the both mechanisms of Ca-P precipitation and surface adsorption worked for the removal of phosphorus in case of the CNT-coated steel slag due to relatively slow pH increase in the initial period.

The high phosphorus adsorption by the CNT-coated steel slag can also be illustrated by the CNT-induced enlarged surface area of the steel slag that increases the contact efficiency with phosphorus in aqueous solution (Su *et al.* 2013). Although the main mechanism of phosphorus removal by steel slag is chemical adsorption and precipitation, oxidized-pretreated and/or divalent cation-modified carbon materials like activated carbon, graphene and CNT can remove phosphorus by adsorption from the electrostatic attraction (Mahdavi and Akhzari 2016). Xiong and Mahmood (2010) 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, such as Al³⁺, Fe³⁺ and Ca²⁺, provide adsorbing sites for phosphorus as R-COO-M-P formation.

Some studies reported the phosphorus removal by adsorption using surface-modified carbon materials. Zirconia-functionalized graphite oxide (GO) contains ZrO₂ particles that adsorbed phosphate more strongly than

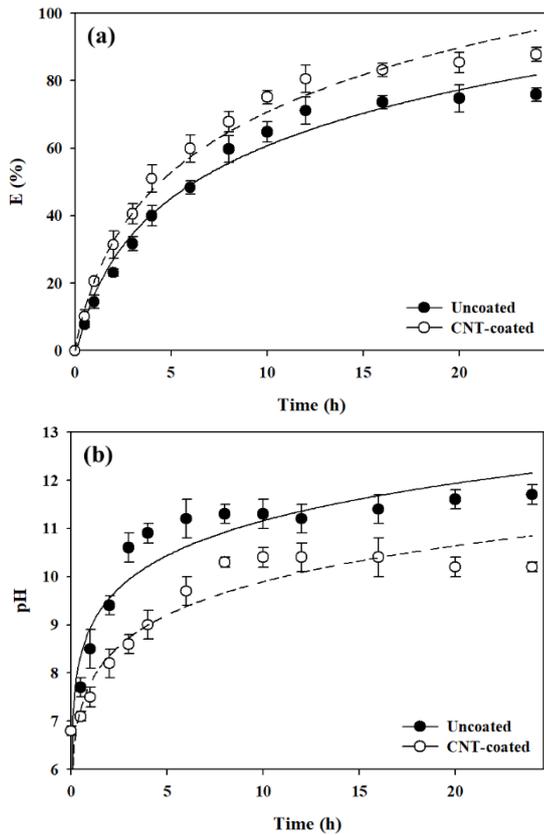


Fig. 3 Changes in the PO₄-P removal efficiency (E%) (a) and pH (b) in the KH₂PO₄ solution with the CNT-coated and uncoated steel slags according to the elution time

untreated GO (Zong *et al.* 2013), and ionic oxide-doped, activated carbon fiber removed phosphorus by ligand exchange and electrostatic interaction (Zhou *et al.* 2012). Further, the hydrophobic surface of the activated carbon became hydrophilic by FeSO₄ modification, so that the ionic materials could be adsorbed in a process suitable for phosphate removal (Lee *et al.* 2015, Tran *et al.* 2015). In the present study, the phosphorus removal by CNT alone was not considerable (data are not shown). Although CNT has low potential to remove phosphorus, the coating of the steel slag surface by acid-functionalized and cation-interacted CNT is thought to have increased the surface area and thereby raised the adsorption efficiency and capacity for phosphorus removal.

The final pH was 11.7 and 10.2 in the solutions containing the uncoated and CNT-coated steel slags, respectively. The amounts of slag and phosphorus solution affect the equilibrium pH of the solution after adsorption experiments (Park *et al.* 2016). In addition, protons are exchanged with the divalent ions on the CNT surface, and hence released into the aqueous phase, which prevents any sharp increase in the solution pH.

3.3 Phosphorus adsorption isotherms of the uncoated and CNT-coated steel slags

The adsorption isotherm represents the relationship between the adsorption capacity of the steel slag and the

equilibrium concentration of phosphate in the solution (Niu *et al.* 2017). Equilibrium studies using Freundlich and Langmuir adsorption isotherm models were performed to examine the adsorption capacity of the uncoated and CNT-coated steel slags at different adsorbent doses in the phosphorus solution. The Freundlich model is a semi-empirical equation that assumes a heterogeneous surface and is based on the distribution of a single solute between the solid phase and aqueous phase at equilibrium (Ng *et al.* 2002, Ozacar 2003), while the Langmuir model assumes a homogeneous distribution of active sites on the adsorbent surface (Gong *et al.* 2009).

$$\text{Freundlich equation : } q_e = KC_e^{1/n} \quad (3)$$

$$\text{Langmuir equation : } q_e = q_m C_e / (1 + K_L C_e) \quad (4)$$

Where C_e (mg L⁻¹) is the concentration of the phosphorus solution at equilibrium, q_e (mg g⁻¹) is the corresponding adsorption capacity, K (mg g⁻¹) and n are the Freundlich constants and q_m (mg g⁻¹) and K_L (L mg⁻¹) are Langmuir constants related to the maximum adsorption capacity and energy or net enthalpy of adsorption, respectively.

Fig. 4 shows the Freundlich and Langmuir adsorption isotherms of phosphorus on the uncoated and CNT-coated steel slags. The adsorption constants and correlation coefficient (R^2) for the two isotherm models were calculated by linear regression and are summarized in Table 3. The R^2 values obtained from the Freundlich and Langmuir models were 0.982 and 0.981 in the uncoated slag and 0.999 and 0.988 in the CNT-coated slag, respectively. This indicates that the adsorption of phosphorus in the uncoated slag followed both the Freundlich and Langmuir model, whereas that in the CNT-coated slag was fitted well to the Freundlich isotherm. In the uncoated slag, when the amount of adsorbent was small, the adsorption of phosphorus was competitive and more suited to the Langmuir isotherm, but was more suited to the Freundlich isotherm when the amount of adsorbent was large (Na *et al.* 2011). In contrast, the CNT-coated slag case followed the Freundlich equation regardless of the amount of adsorbent, indicating that the phosphorus in aqueous solution was removed by multi-layer adsorption with the heterogeneous surface of adsorbents (Lian *et al.* 2009).

In the Freundlich model, $1/n$ and K values indicate the adsorption efficiency and capacity, respectively. A value of n higher than 1.0 indicates relatively good adsorption efficiency and favorable adsorption, and a higher K value indicates that the adsorbent has higher capacity (Xiong and Mahmood 2010). In addition, the maximum adsorption capacity was calculated from the Langmuir equation. In the present results, the maximum phosphorus adsorption was increased 1.4-fold from 6.127 mg g⁻¹ for the uncoated slag to 9.268 mg g⁻¹ for the CNT-coated slag. The slag used in this study was the same as the BOFS-A slag (adsorption capacity of 2.320 mg g⁻¹) previously reported by Park *et al.* (2016). Park *et al.* (2017) postulated that the physicochemical properties of even the same material may vary under different conditions.

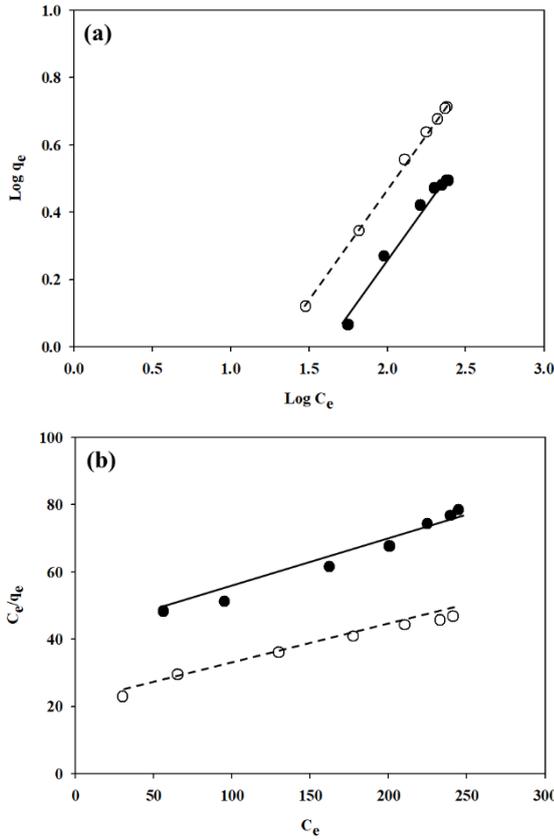


Fig. 4 Freundlich (a) and Langmuir (b) adsorption isotherms of phosphorus in aqueous solution. The closed and opened circles indicate the uncoated and CNT-coated steel slags, and the linear solid and dash lines indicate the fit-curve of the uncoated and CNT-coated steel slags, respectively

Table 3 Freundlich and Langmuir isotherm constants in the uncoated and CNT-coated steel slags

	Freundlich isotherm constant		Langmuir isotherm constant	
	K	1/n	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)
Uncoated slag	0.086	1.511	6.127	0.004
	0.982		0.981	
CNT-coated slag	0.140	1.515	9.268	0.005
	0.999		0.988	

3.4 Phosphorus adsorption kinetics of the uncoated and CNT-coated steel slags

Studies on phosphorus adsorption kinetics contribute to the understanding of the overall process and mechanism of phosphorus removal by steel slag (Han *et al.* 2015). In order to elucidate the kinetics of phosphorus removal by the uncoated and CNT-coated slags, the changes of phosphorus concentration were measured at different initial phosphorus concentrations according to the contact time. Fig. 5 shows the relationship between adsorption capacities and contact time for the removal of phosphorus. All curves show similar characteristics in that the adsorption rates of phosphorus

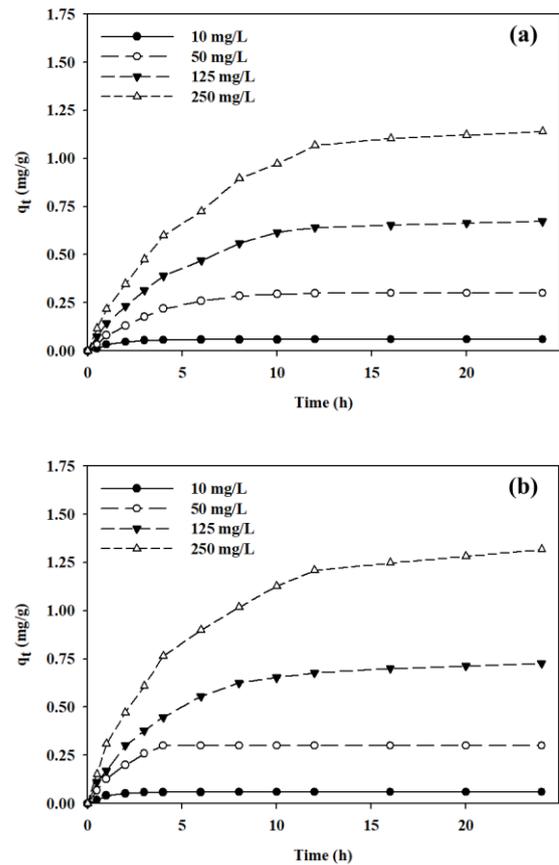


Fig. 5 Effect of contact time on the adsorption of phosphorus on the uncoated (a) and CNT-coated (b) steel slag solutions

were the fastest at the beginning of the experiment and the adsorption capacities were influenced by the initial concentration and contact time in both the uncoated and CNT-coated steel slags. The same result was previously reported for both phosphorus removal using modified-activated carbon fiber and heavy metal removal using modified-chitosan (Liu *et al.* 2013, Niu *et al.* 2017). The sufficiency of adsorption sites on the slag surface drives the mass transfer and adsorption at the beginning stage of adsorption, even for high initial phosphorus concentrations.

The adsorption kinetic mechanisms are investigated by fitting the most common model, which is the Lagergren kinetic models (Ho and McKay 1998), and the pseudo-first- and pseudo-second-order models are expressed as follows:

$$\text{Pseudo-first-order model:} \quad (5)$$

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303$$

$$\text{Pseudo-second-order model:} \quad (6)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) represent the amount of phosphorus at equilibrium and at time t (h), respectively, and k_1 (h⁻¹) and k_2 (g mg⁻¹·h⁻¹) represent the adsorption rate constants of pseudo-first-order adsorption and the equilibrium rate constant of pseudo-second-order

Table 4 Comparison of the pseudo-first- and pseudo-second-order adsorption rate constants and experimental values for different initial phosphorus concentrations in the uncoated and CNT-coated steel slags

Slag	C_0 (mg L ⁻¹)	q_e^* (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order		
			k_1 (h ⁻¹)	q_e^{**} (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ ·h ⁻¹)	q_e^{**} (mg g ⁻¹)	R^2
Uncoated slag	10	0.060	3.068	0.534	0.969	15.649	0.065	0.991
	50	0.300	0.665	0.601	0.976	0.833	0.367	0.982
	125	0.679	0.539	0.829	0.988	0.344	0.772	0.995
	250	1.153	0.086	0.836	0.992	0.156	1.350	0.994
CNT-coated slag	10	0.060	2.640	0.256	0.996	30.689	0.063	0.997
	50	0.300	1.070	0.505	0.986	3.101	0.322	0.994
	125	0.750	0.483	0.841	0.976	0.377	0.878	0.998
	250	1.356	0.072	0.871	0.986	0.161	1.529	0.999

*Experimental value

**Calculated value

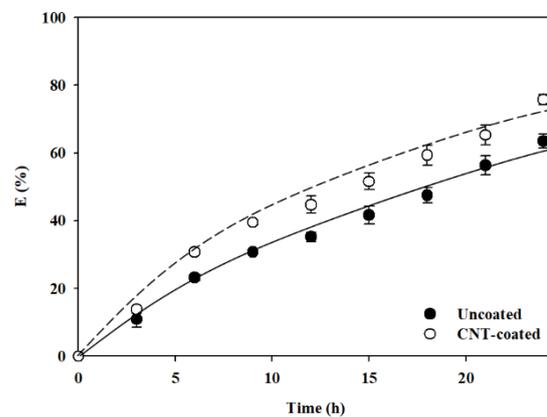
adsorption, respectively. The validity of these models is supported by their ability to predict behaviors across a range of studies and show the rate-limiting elements (Yu *et al.* 2015).

Table 4 shows the kinetic parameters for the adsorption of phosphorus by the uncoated and CNT-coated steel slags. Comparing the R^2 value, the pseudo-second-order model better explains the adsorption mechanism than the pseudo-first-order model in both the uncoated and CNT-coated steel slags. Comparison of the experimental and calculated q_e values also revealed that the pseudo-second-order model is closer than the pseudo-first-order model. These results suggested that chemisorption was the rate-limiting step for the adsorption of phosphorus onto both the uncoated and CNT-coated steel slags, and that the reaction rate is proportional to the number of active sites present on both the uncoated and CNT-coated steel slags (Park *et al.* 2017).

3.5 Phosphorus removal in pig manure

Using the results obtained from the synthetic wastewater, the removal efficiency of the uncoated and CNT-coated steel slags was evaluated to determine phosphorus removal from real wastewater (pig manure). Unlike synthetic wastewater, pig manure contains not only phosphorus also COD, T-N, SS and heavy metals, as well as other contaminants. The phosphorus removal efficiency of both steel slags tended to differ from that of synthetic wastewater. The previous results of Fig. 3(a) and Table 4 satisfied the pseudo-second order in both slags.

However, as shown in Fig. 6, the phosphorus removal in the pig manure presented an almost linear trend, which was attributed to the variety of aqueous components contained. As the affinity of these other components with the adsorbent is higher than that of phosphorus, the phosphorus removal efficiency in real wastewater is lower than that of single-component wastewater (Kang *et al.* 2019). In a multi-element system, the adsorption rate of the components adsorbed on the slag depends on the degree of affinity with the adsorbent (Xue *et al.* 2009). Therefore, unlike synthetic wastewater, the removal of PO₄-P is linear in pig manure because the other components such as metals

Fig. 6 Changes in the PO₄-P concentration in the pig manure by the uncoated and CNT-coated steel slags

in pig manure affect the phosphorus adsorption affinity of the CNT-coated slag.

The phosphorus from pig manure removed by the CNT-coated steel slag was more effective than that of the uncoated slag. Over 24 hours, the PO₄-P removal in pig manure was 12.3% higher by the CNT-coated slag (Fig. 6).

Furthermore, the reusability of CNT-coated steel slag has been evaluated in the previous study (Kang *et al.* 2019) by 100 replicate experiments for the simultaneous removal of phosphorus and metals in stormwater. The phosphorus and metals removal rates began to decrease after 61 and 75 replicates in case of the uncoated slag, respectively, but the removal rates began to decrease after 90 replicates in case of the CNT-coated steel slag. In addition, no significant releases of the coated CNT from the slag media were observed in the previous study (Kang *et al.* 2019). Therefore, the reusability of the CNT-coated steel slag is also expected but it will be needed to evaluate the specific reusability of the CNT-coated steel slag through the long term continuous operation because this study had been performed in batch reactor.

Table 5 shows the changes of COD, T-N, T-P, PO₄-P and Zn concentrations and pH in pig manure after 12 and 24 h treatment by the uncoated and CNT-coated steel slags. After 12 and 24 h, COD and T-P were not significantly

Table 5 Change of concentrations of the pig manure components after 12 and 24 h treatment by the uncoated and CNT-coated steel slags

	Time	Concentration (mg L ⁻¹)					pH
		COD _{cr}	T-N	T-P	PO ₄ -P	Zn ²⁺	
Uncoated	Initial	27,490±10,060	6,408±919	421±22	345±12	63±2	7.7±0.6
	12	27,354±6,329	6,362±112	283±8	223±7	31±4	8.2±0.4
	24	27,306±7,821	6,256±53	193±2	126±5	20±3	8.7±0.3
CNT-coated	12	27,162±8,344	6,330±77	261±7	191±3	26±1	8.2±0.2
	24	27,088±7,714	6,213±68	125±4	84±7	11±2	8.5±0.4

removed by either the uncoated or CNT-coated steel slag. Actually, nitrogen in wastewater can be removed by slag via struvite crystallization with phosphorus (Yim 2010). In addition, Qui *et al.* (2013) reported that ammonia nitrogen was removed by combined steel slag and fly ash media from a micro-polluted stream. T-P concentration was lowered as PO₄-P was removed by the uncoated and CNT-coated steel slags. Zinc was also removed by both the uncoated and CNT-coated steel slags. The removal efficiency of heavy metals was also higher in the CNT-coated steel slag. This is related to the adsorption of the CNT surface through CNT-coating simultaneously with the reaction between OH⁻ and divalent cation heavy metals eluted from slag (Kang *et al.* 2019). In addition, the heavy metals removed by CNT and nanocarbons enable additional adsorption of phosphorus by the aforementioned R-COO-M-P formation.

Unlike synthetic wastewater, pig manure contains other substances such as metals. As the hydroxide ions eluted from the slag were consumed by the reaction with divalent cations (Zn²⁺) in the pig manure, the rate of pH increase was lower than that of the synthetic wastewater. In the synthetic wastewater which only contains phosphorus, the pH rapidly increases because the hydroxide ions eluted from the slag are remain in the aqueous solution without binding to metals.

Metals such as zinc and copper in pig manure tend to be removed by binding to hydroxide ions, so it was found that there was no significant difference in pH between the uncoated and CNT-coated steel slag. However, in CNT-coated steel slag, as H⁺ on functional group of CNT is exchanged with Ca²⁺ eluted from steel slag by electrostatic attraction, the pH is relatively lower than that of the uncoated steel slag after 24 h.

4. Conclusions

This study evaluated the phosphorus removal characteristics of the uncoated and CNT-coated steel slag. The CNT-coated steel slag showed a superior performance for phosphorus removal than the uncoated steel slag. The phosphorus removal by the CNT-coated steel slag was approximately 13.0% higher than that of uncoated one for the synthetic wastewater. The adsorption isotherm of the CNT-coated steel slag followed by pseudo-second-order kinetics revealed the superior adsorption efficiency and

capacity for phosphorus removal. In case of real wastewater (pig manure), the phosphorus removal by the CNT-coated steel slag was also higher with 12.3% than that of the uncoated one. The relatively lower increase of phosphorus removal for the pig manure than the synthetic wastewater may occurred by suspended solid in the pig manure which is a hindrance to the contact between dissolved phosphorus and CNT-coated steel slag. Therefore, it is expected that the increase of the surface area of the CNT-coated steel slag by enlargement of CNT-coated steel slag amount will considerably enhance the removal efficiency of phosphorus and reusability of the CNT-coated steel slag. Furthermore, simultaneously removal of phosphorus and metals is also expected by formation of CNT-COO-M-P bridge in the wastewater treatment using the CNT-coated steel slag. However, as this study had been performed in batch system, it will be needed to evaluate and optimize the phosphorus removal by the CNT-coated steel slag through the long term continuous operation study.

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