Performance of Reactive Slag Filter for High Concentration Phosphorous Removal from Aqueous Solutions

K.H. Kang*, H.G. Kim**, T.J. Park** and I.G. Byun*

* Institute for Environmental Technology and Industry, Pusan National University, 2 Busandaehak-ro 63beon-gil, Busan, Rep. of Korea, 46241 (*kangkh21@pusan.ac.kr; big815@pusan.ac.kr*)
** Department of Environmental Engineering, Pusan National University, 2 Busandaehak-ro 63beon-gil, Busan, Rep. of Korea, 46241 (*hyanggi12@pusan.ac.kr; taejoo@pusan.ac.kr*)

Abstract

Steel slag generated from the steel making process contains many divalent cations, such as calcium ions, which adsorb phosphorus. Phosphorus causes eutrophication in rivers and lakes; therefore, the removal of phosphorus has become a major issue. In this study, a reactive steel slag filter was developed from steel slag and carbon nanotubes (CNTs). Steel slag was coated with CNT using ultrasonication, dipping, and drying methods. To test phosphorus removal in the aqueous phase by the reactive slag filter, steel slag coated with acid functionalized CNT was used. The CNT-coated steel slag filter was soaked in 300 mL of a KH_2PO_4 solution. The CNT-coated steel slag filter was characterized by testing it in KH_2PO_4 solutions at various concentrations (25, 125, and 250 mg PO_4-P/L) and different amounts of slag (25, 50, 100, and 150 g). The experiments were performed in batch type, at room temperature for 4 d. The CNT-coated steel slag filter has better potential in phosphorus removal. The removal rate increased with increasing amount of slag filter and decreasing initial KH_2PO_4 concentration. The final pH was below 9.5 indicating that the CNT-coated steel slag filter neutralized the pH. The adsorption isotherm indicated that the Freundlich model provides a better fit to the experimental data of CNT-coated steel slag filter than the Langmuir model. The K and n/1 value were 421.6 and 0.33, respectively. The results indicate that the CNT-coated steel slag filter has great adsorption efficiency and capacity. This is the first case of using CNT-coated slag for pollutant removal. Overall, the development of a CNT-coated steel slag filter is a good candidate for the treatment of wastewater systems and reducing non-point pollution sources.

Keywords

Phosphorus removal; slag filter; steel slag; carbon nanotube; coating; adsorption isotherm

INTRODUCTION

The increases in population and rapid industrial development have caused many environmental problems, such as water pollution. Accordingly, many wastewater treatment processes have been developed. In Korea, the management of water pollution has been focused on point pollution sources, such as municipal and industrial wastewater (Choi and Shin 2002). On the other hand, the management of nonpoint pollution sources is still insufficient; the pollutants due to wastewater out flows, agricultural and storm water runoff affect the water environment and ecosystem. Nonpoint pollution sources include non-degradable organic matter as well as nitrogen and phosphorus (Sharpley et al. 1994). In particular, total phosphorus concentrations higher than 100 mg/L in rivers and lakes provide nutrient enrichment (Oguz 2005), and even very low phosphorus concentrations cause algal blooming. Therefore, it is possible to prevent eutrophication by removing phosphorus. Several attempts have been made to remove phosphorus, such as chemical precipitation, adsorption and biological methods. On the other hand, there are some problems, such as chemical stability, treatment conditions and cost (Kim et al. 2008). For these reasons, the use of natural and industrial by-product materials, such as zeolite, limestone, dolomite, and steel slag have been tested (Vohla et al. 2011). Among them, studies using steel slag materials, e.g., basic oxygen furnace slag (BOF-slag), electric arc furnace slag (EAF-slag), and converter slag, which is a by-product of the steel industry, have focused on phosphorus removal because of their high affinity for phosphorus binding (Yang et al. 2009; Barca et al. 2012). Steel slag contains divalent cations, such as calcium, ferrous and aluminum, making it a potential substrate for phosphorus removal. Phosphorus, which exists in

PO_4^{3-} form in solution, is removed by precipitation with Ca^{2+}, Fe^{3+}, and Al^{3+} ion elute from steel slag. On the other hand, the use of steel slag has a problem that CaO, which accounts for more than 40% of steel slag, is ionized in water and dissociates to Ca^{2+} and OH^-, causes an increase in pH (Chazarenc et al. 2010; Riley and Mayes 2015). Accordingly, additional treatments are required to neutralize the water during phosphorus removal using steel slag. Therefore, in this study, carbon nanotubes (CNTs) were used to solve this problem. Since the discovery of CNTs, they have been applied in the biological, chemical, environmental, medical or other industries. In particular, they have great potential to adsorb organic or inorganic chemicals, dioxins, VOCs, heavy metals, etc. (Rao et al. 2007). The adsorption potential of CNTs is affected by the CNT functional group. CNTs contains functional groups, such as hydroxyl, carbonyl, and carboxyl, added by oxidation or heat treatment, which increase its 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 allow the CNT surface to have a negative charge in solution, resulting in the electrostatic attraction of the divalent ion to the negative surfaces of the CNTs, which enhances the adsorption of divalent ions on CNTs (Ren et al. 2011). When the solution pH is high, the negative charge of the CNT surface provides electrostatic interactions with the cation and neutralizes the solution. 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 and precipitation capacity and optimal conditions for efficient phosphorus removal.

METHODS

Materials

Steel slag used in this study was obtained from 'P' steel company (Gwangyang, South Korea) and separated into particle sizes between 2-6 mm using sieve. **Table 1** lists the components of steel slag produced from 'P' steel company (Lee and Jang 2004). Commercially available MWCNTs (Hanwha Chemical Co., South Korea) were selected as the slag coating reagent. KH_2PO_4 solutions of various concentrations were used as the virtual phosphorus containing wastewater.

Table 1. Chemical composition of the steel slag obtained from 'P' steel company

Composition	Steel slag (%)
CaO	40.1
SiO_2	14.4
Fe_2O_3	10.8
MgO	7.2
MnO	3.1
Al_2O_3	2.1
TiO_2	0.8

Methods

Preparations of CNT-coated steel slag and phosphorus solution. A 1 g sample of raw CNT was heated to 350℃ for 30 min to remove the amorphous carbon (Lu and Chiu 2006). After the heat treatment, the raw CNT was placed into 100 ml nitric-sulfuric acid (HNO_3:H_2SO_4, 9:1 (v/v)). The

CNT-acid solution was then shaken in an ultrasonic cleaning bath (model JAC-5020, Kodo Co., South Korea) for 1 h. Subsequently, the CNTs were centrifuged to obtain functionalized CNT 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 70% ethanol solution as a CNT dispersion solution with sodium dedocylbenzene sulfonate (SDBS) as a surfactant (Xie et al. 2012). The concentration was 0.5% CNT and 1% SDBS (w/v). The dispersion process was performed by bath sonication for 3 h. Finally, the sieved slag was dipped into CNT ink, removed, and dried at 150℃. The dipping-drying process was repeated three or four times to increase the CNT loading. The phosphorus-containing wastewater used in this study was prepared using KH_2PO_4 solution, and the pHs were adjusted by 1 N HCl and 1 N NaOH solution.

Operations. The batch operation was carried out in batch-type jar tester (model C-JT-H, Changsin Scientific Co., South Korea) in 500 mL beakers (with 300 mL working volume). First, a study to determine the dissolution of calcium ions was carried out using distilled water and 100 g steel slag at different pH (5, 6, 7, 8, 9, 10, and 11) without phosphorus for 4 d. To characterize and optimize the experimental conditions for phosphorus removal, the batch-type jar test was performed at different K_2HPO_4 concentrations (0.1, 0.5, and 1 g/L) and CNT-coated steel slag weight (25, 50, 100, and 150 g) for 4 d. The temperature and agitation speed were 25℃ and 120 rpm, respectively. Uncoated steel slag was used as the control. During the experiments, the pH, Ca^{2+} and PO_4-P concentration of the samples taken from the beakers were measured.

Analysis. The pH was measured using a pH meter (model HI 98217, Hanna Instrument, South Korea). PO_4-P analysis was performed according to the molybdo-vanadate spectrophotometric method using a PO_4-P analysis kit (Humas Co., South Korea). The Ca^{2+} ions were analyzed using an atomic absorption spectrophotometric method.

RESULTS AND DISCUSSION

Ca^{2+} elution of steel slag

The pH and elution characteristics of calcium ions from steel slag are important factors for the removal of phosphorus from wastewater contains phosphorus. To examine the elution characteristics of steel slag, the steel slag was placed in distilled water with various pHs and a 1 g/L KH_2PO_4 solution, and the pH and Ca^{2+} release were observed in accordance with the reaction time (**Figure 1** and **Figure 2**). As soon as the steel slag was placed into the distilled water at pH less than 10, the pH increased rapidly to 10.5 within the first five minutes, followed by a gradual increase to 11.2 after 1 h. The pH was maintained at 11.2 to 11.3 for 24 hours, after which it decreased gradually and reached approximately 10.4 after 108 hours. The decrease in pH was attributed to the dissolution of atmospheric CO_2, producing an equilibrium among the proton, carbonate and bicarbonate (Park et al. 2003). In the KH_2PO_4-added solution, the initial pH was 6.8, which increased to 7.5 and 8.0 after 1 and 3 h, respectively, and increased to 9.3 after 108 h. The pH was maintained at a lower value than when distilled water only was used. Kim et al. (2010) reported a similar result using EAF-slag, the pH reached 11 and 8 after 24 h in the distilled water and PO_4-P solution, respectively. The pH increased due to the OH^- released by hydration and dissociation of the components of the steel slag, and the OH^- consumed to generate hydroxyapatite, which decreased the pH in the phosphorus containing solution.

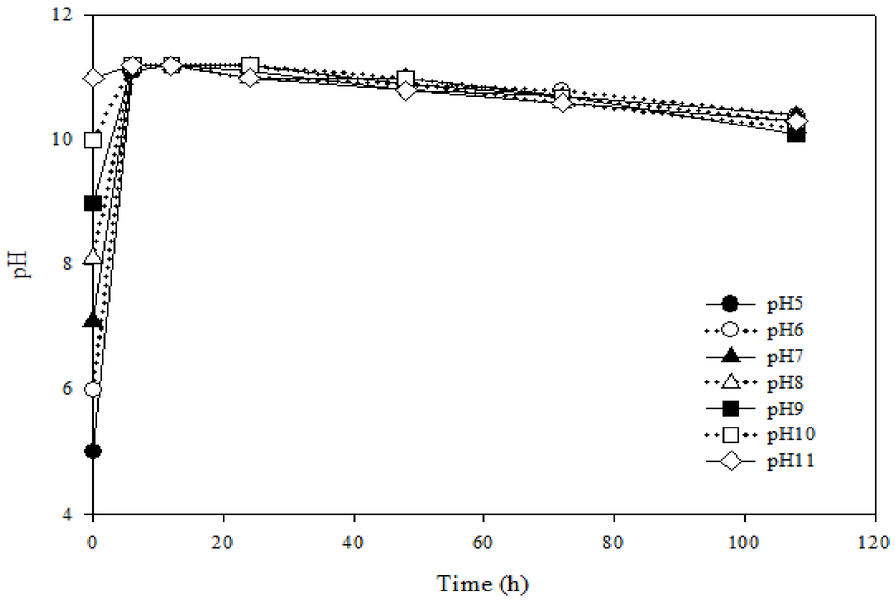

Figure 1. Change in the pH of distilled water with steel slag according to the elution time.

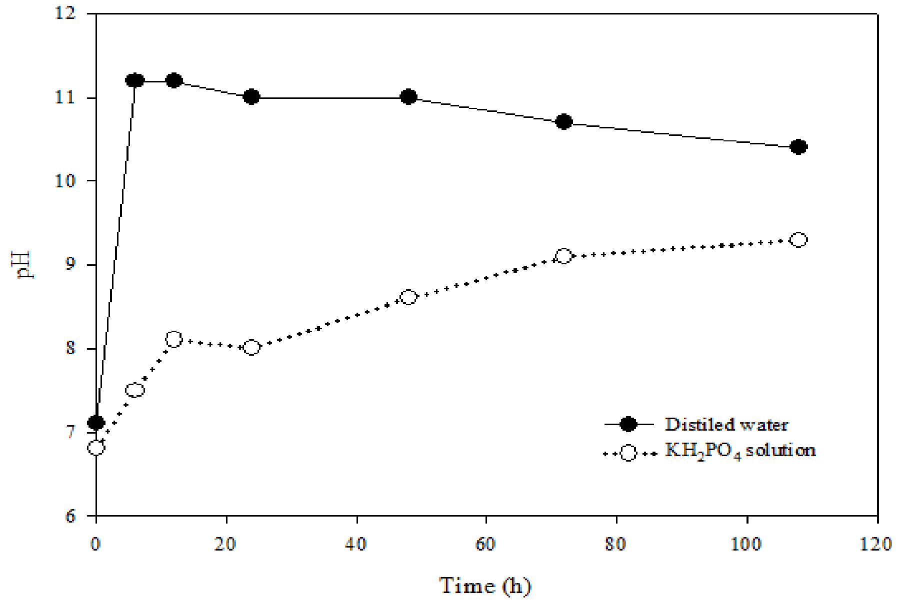

Figure 2. Comparison of the pH change between distilled water and KH_2PO_4 solution with steel slag according to the elution time.

Phosphorus removal characteristics

Phosphorus removal characteristics of CNT-coated steel slag. The removal of phosphorus was tested in a 1 g/L KH_2PO_4 solution with CNT-coated steel slag and uncoated slag. The initial PO_4-P concentration and pH were approximately 250 mg/L and 6.8, respectively. As shown in **Figure 3**, CNT-coated steel slag removed more than 90% of the PO_4-P within 9 h, while the uncoated slag removed 50% of PO_4-P at the same time. In addition, the increase in pH in the CNT-coated slag solution was slower than that of the uncoated slag.

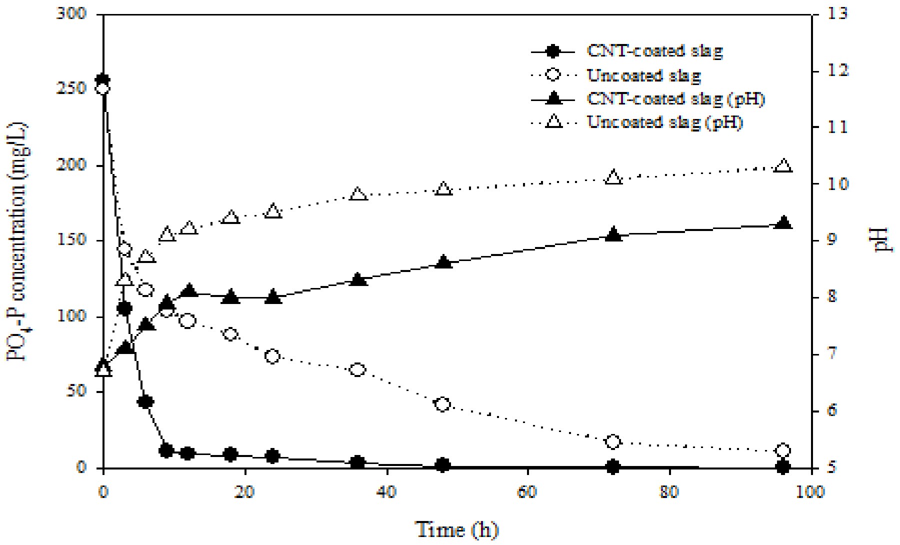

Figure 3. Changes in the PO4-P concentration and pH in the KH_2PO_4 solution with CNT-coated slag and uncoated slag according to the elution time.

Effects of the amounts of CNT-coated steel slag on phosphorus removal. The phosphorus removal characteristics of the CNT-coated steel slag amounts were examined. As shown in **Figure 4**, the PO_4-P removal efficiency was proportional to the amount of CNT-coated steel slag. In particular, approximately 99% PO4-P was removed in 18 h in a KH_2PH_4 solution with 150 g CNT-coated steel slag. As the phosphorus was removed, the pH was finally increased to 9.5. Unlike the use of uncoated steel slag, the final pHs were no more than 9.5; it took 44, 28, 16, and 7 h to remove 90% of the PO_4-P using 25, 50, 100, and 150 g CNT-coated steel slag, respectively. **Table 2** lists the final pH and PO_4-P removal according to the input CNT-coated steel slag for 12 and 24 h.

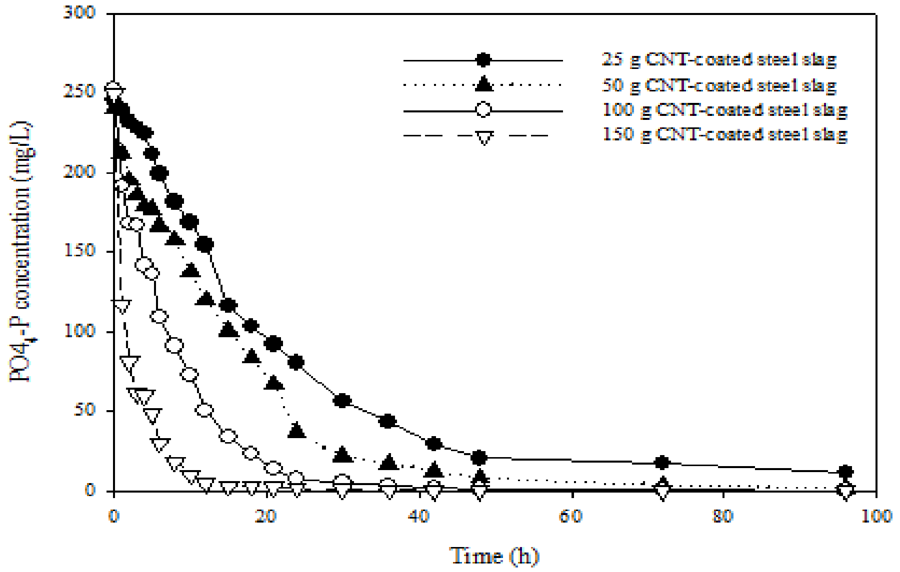

Figure 4. Kinetics of the PO_4-P concentration at different amounts of CNT-coated steel slag (C_0 = 250 mg PO_4-P/L).

Table 2. PO_4-P removal efficiency according to input CNT-coated steel slag for 12 and 24 h

CNT-coated steel slag (g)	Final pH	PO_4-P removal efficiency (%)	
		12 h	24 h
25	9.0	37.1	67.4
50	8.8	50.3	84.7
100	9.4	80.1	97.2
150	9.5	98.2	99.5

Effect of initial PO_4-P concentration on phosphorus removal. **Figure 5** shows the influence of the initial concentration of PO_4-P on phosphorus removal. A 50 g sample of CNT-coated steel slag was placed into a 100, 500, and 1000 mg/L KH_2PO_4 solution and their initial PO_4-P concentration and pH were 25 and 7.5 (100 mg/L KH_2PO_4), 127 and 6.9 (500 mg/L KH_2PO_4), and 240 and 6.4 (1000 mg/L KH_2PO_4), respectively. Valsami-Jones (2001) reported that phosphorus removal depends on the pH, Ca^{2+}, and initial PO_4-P concentration. When starting with lower initial PO_4-P concentrations, PO_4-P removal was performed within a short period; it took 14, 20, and 28 h to remove 90% of the PO_4-P using the initial PO_4-P concentration of 25, 127, and 240 mg/L, respectively. All the final pHs were not more than 9.5 after all the reactions were complete. The oxidized and functionalized CNT appear to prevent the increase in pH by neutralizing the solution. The solution pH decreased when protons in the carboxylic group of CNT exchange with the divalent cation in the aqueous phase (Rao et al. 2007).

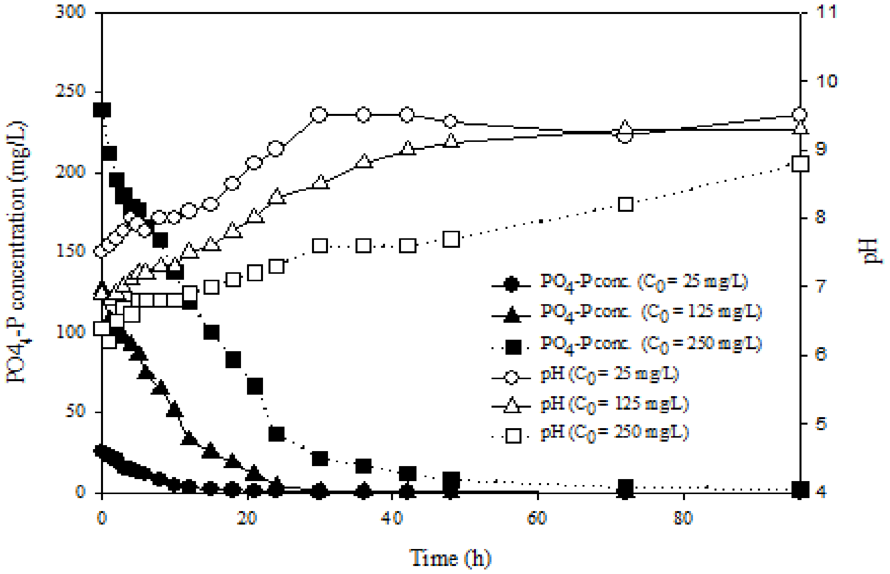

Figure 5. Kinetics of the PO_4-P concentration and changes in pH at various initial PO_4-P concentrations (CNT-coated steel slag input = 50 g).

Adsorption isotherm. The Freundlich and Langmuir adsorption isotherm model were applied to study the adsorption capacity of the CNT-coated steel slag for phosphorus removal. **Figures 6** and **7** show the phosphorus adsorption capacity according to the Freundlich and Langmuir model. The Freundlich (**Eq .1**) and Langmuir (**Eq. 2**) model is expressed as follows (Reynolds and Richards 1996):

$x/m = X = KC_e^{1/n}$ (1)

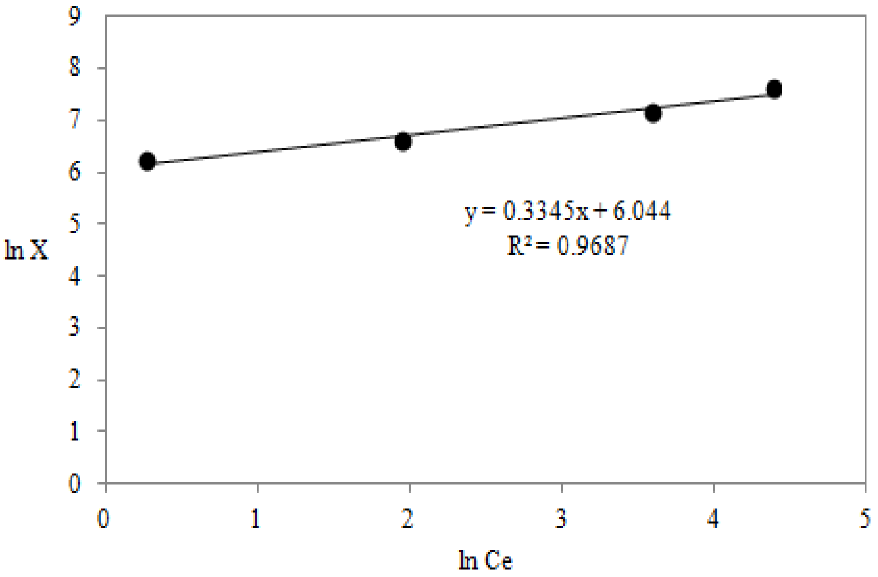

Figure 6. Relationship between ln X and ln C_e based on the Freundlich isotherm equation for CNT-coated steel slag at 25℃.

where x/m (X) is the amount of PO_4-P adsorbed per CNT-coated steel slag (mg/g), C_e is the concentration of the PO_4-P solution at equilibrium, K is the Freundlich isotherm constant (L/mg), and 1/n is intensity of adsorption (Hussain et al. 2011).

$x/m = X = abC_e/(1+bC_e)$ (2)

where a and b are the surface homogeneity and surface heterogeneity, respectively.

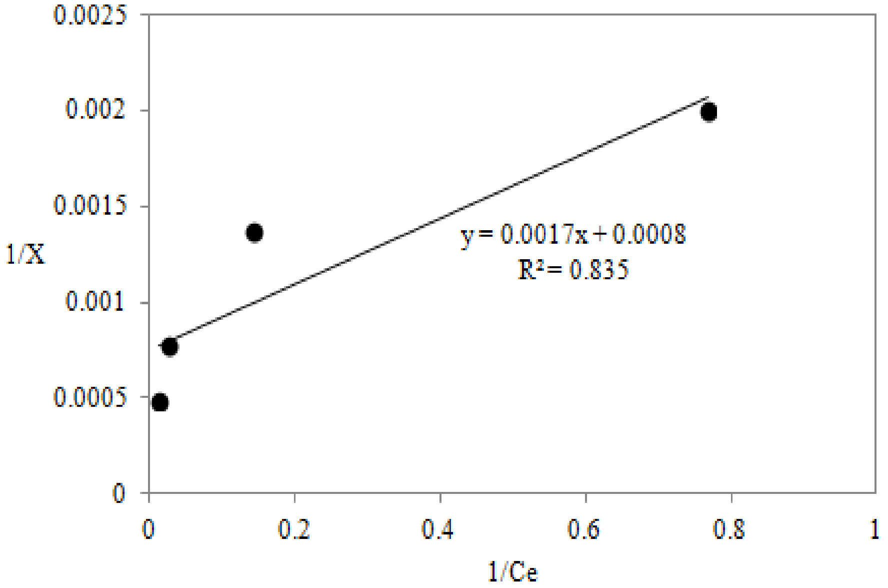

Figure 7. Relationship between 1/X and $1/C_e$ based on the Langmuir isotherm equation for CNT-coated steel slag at 25℃.

Table 3 summarizes the estimated adsorption constants with the corresponding correlation coefficient (R^2). In this study, the R^2 value obtained from the Freundlich and Langmuir model was 0.97 and 0.83, respectively. This indicates that the Freundlich model is better in fitting the experimental data than the Langmuir model (Zhou et al. 2012). In the Freundlich model, 1/n and K values indicate the adsorption efficiency and capacity, respectively. The 1/n value represents the adsorption efficiency. When it is less than 2.0, the adsorption efficiency is relatively good, whereas, when the K value is higher, the absorbent has higher capacity. The K value in this study was higher than that reported for other materials (e.g. K value of shale, 69.2; Ironstone, 29.7; EAF-slag, 29.3) (Tang et al. 2009; Kim et al. 2010); this is expected to be used as a great absorbent.

Table 3. Freundlich and Langmuir isotherm constant in CNT-coated steel slag

Freundlich isotherm constant		Langmuir isotherm constant	
K (mg/g)	421.6	a (mg/g)	1250
1/n	0.33	b (L/mg)	0.47
R^2	0.97	R^2	0.83

CONCLUSIONS

This study evaluated the phosphorus removal efficiency and characteristics of a CNT-coated slag filter. Steel slag is a by-product of steel processing and contains CaO, Fe_2O_3, and Al_2O_3, which can remove phosphorus by reacting with PO_4-P. On the other hand, when the slag component dissolves in water, it causes an increase in pH because of OH^-, making it necessary to neutralize the effluent pH. On the other hand, acid-functionalized CNTs solved this problem by the protons released by exchanging with divalent cations (e.g. Ca^{2+}). The CNT-coated steel slag has great potential to remove phosphorus from aqueous solutions. The slag removed phosphorus because of its excellent absorption capacity. The Freundlich adsorption isotherm equation confirmed the phosphorus adsorption efficiency and capacity of the CNT-coated steel slag. Functionalized CNT is also known as an adsorbent for heavy metals. The CNT-coated steel slag can be applied to both phosphorus and heavy metals and is a great candidate for a wastewater treatment system.

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