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Adsorption of Phosphate and Nitrate Using Modified Spent Coffee Ground and Its Application as an Alternative Nutrient Source for Plant Growth

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Abstract

Phosphate (PO_4^{3-}) and Nitrate (NO_3^-) are two main nutrients that cause water eutrophication. In the other hand, the presence of PO_4^{3-} and NO_3^- is needed for plant growth. The aims of this study are to recycle Spent Coffee Ground (SCG) modified with calcium hydroxide for adsorption PO_4^{3-} and NO_3^-. The optimum adsorption capacity for PO_4^{3-} and NO_3^- is 36.74 mg/L and 20.21 mg/L, respectively. The Freundlich isotherm model was suitable for PO_4^{3-} and NO_3^- adsorption. The kinetic model for adsorption was linear using Pseudo-second order. The application of modified SCG after enrichment with PO_4^{3-} and NO_3^- for plant growth (*Raphanus sativus*) showed optimum growth at a dose of 0.3% with value of germination index was 203%.

Keywords

Spent Coffee Ground, Adsorption, Calsium Hydroxide, Phosphate and Nitrate, Plant Growth

1. Introduction

Water pollution containing high concentration of nutrients such as phosphorus and nitrogen is a serious concern in the environment worldwide, because both are implicated in the eutrophication of receiving water [1]. Phosphorus is released into the aquatic environment through the weathering of rocks and by various human activities [2]. Furthermore, the presence of nitrate ion in drinking water is a potential public health hazard. A high concentration of nitrate

leads to production of nitrosamine, which is related to cancer [3]. On the other hand, phosphorus in the form of phosphate (PO_4^{3-}) and nitrogen in the form of nitrate (NO_3^-) are an important part of the mechanism of plant growth in agricultural sector.

Several physical-chemical and biological methods have been developed to manage the PO_4^{3-} and NO_3^- in water, such as ion exchange, chemical precipitation, adsorption and bacterial assimilation method. Adsorption is one of the techniques for removal anions from aqueous solution, which is comparatively more useful and low cost using easily available materials in wastewater treatment has been widely investigated [4].

Coffee is one of the most popular drinks worldwide, a significant quantity of by-products as well (6 Mt/year). As a consequence, the coffee industry is responsible for producing large amounts of coffee residues. One of the residues of coffee produced is Spent Coffee Ground (SCG) [5]. SCG is one of the biomass that is suitable to be used as an adsorbent because it has porous characteristic on its surface. Therefore, SCG is often used as an adsorbent for removal of heavy metal or dyes [6] [7]. Based on the early research, the adsorption of PO_4^{3-} and NO_3^- using original SCG showed a low adsorption capacity. In this study, we improved the adsorption capacity of SCG treated using calsium hydroxide (hereafter referred to the modified SCG). The addition of calsium hydroxide to carbonization of wood biomass has been shown to adsorb more phosphorus [8]. The evaluation of modified SCG based on initial concentration, effect of pH, adsorbent dosage, isotherm and kinetic model. The final objective of this study is to make SCG as an alternative source of nutrients that contribute to plant growth.

2. Materials and Experimental Methods

2.1. Materials

The samples of SCG in this study were collected from coffee machine at convenience store in Shobara City, Hiroshima, Japan. First, SCG washed using distilled water and dried in the oven for 1 - 2 days at 60˚C. After, it was sifted using test sieve by Tokyo Screen Co., Ltd. with sieving size 425 μm. Then, SCG immersed in 0.04 M calcium hydroxide solution with ratio of 2 g of SCG in 160 mL of calcium hydroxide solution during 24 hours and dried in the oven at 60˚C. The modified SCG washed using distilled water subsequently until pH become 7.5. All chemicals were either reagent on analytical grade and purchased from Kanto Chemical Co. Inc. and Wako pure chemical corporation.

2.2. Experiment

2.2.1. Adsorption Study

Evaluation of adsorption characteristics PO_4^{3-} and NO_3^- in this study was conduct using batch experiments. Stock solution of PO_4^{3-} and NO_3^- (having concentration of 2000 mg/L) were prepared by dissolving 1 mol/L nitric acid and

0.5 mol/L phosphoric acid in distilled water. Some various concentrations (10 - 500 mg/L) were prepared from which working solution. About 0.2 g of adsorbent was added to 16 mL of PO_4^{3-} and NO_3^- solution. The mixture was subsequently placed in temperature controllable magnetic stirrer for the adsorption process begin. The effect of initial pH was adjusted from pH range 1 - 9 by hydrochloric acid and potassium hydroxide solution. The PO_4^{3-} and NO_3^- were determined by standard method (Japan Industrial Standard method JIS KO 102). Adsorption capacity (q) was determined using the following equations:

$$q = (C_o - C_e)V/m \quad (1)$$

where q (mg/g) represents the adsorption capacity, C_e and C_o (mg/L) stand for equilibrium and initial concentrations, respectively, V (L) is volume of the solution and m (g) is the mass of adsorbent.

The effect of adsorbent dosage needed for pot treatment experiment, the aims to determine the best composition of modified SCG in adsorbing PO_4^{3-} and NO_3^-. Various amount of adsorbent (0.1, 0.2, and 0.6 g) conducted to 16 mL PO_4^{3-} and NO_3^- solution.

2.2.2. Desorption Study

Desorption experiments of PO_4^{3-} and NO_3^- were conducted after the completion of the adsorption experiments. After the supernatant was separated with the adsorbent, the adsorbent immersed in 0.1 - 0.5 M sodium hydroxide for 24 hours. The desorption amount and the rate of desorption were calculated as follow:

$$q_{des} = (C_1 \times V)/m \quad (2)$$

$$D(\%) = (q_{des}/q)100\% \quad (3)$$

where D is the rate of desorption, q_{des} (mg/g) is the desorption amount of PO_4^{3-} and NO_3^-, V (L) is the volume of desorption solution, C_1 (mg/L) represents the PO_4^{3-} and NO_3^- concentration of desorption supernatant and m (g) is the mass of adsorbent.

2.2.3. Application for Plant Growth

From the best treatment of adsorbent dosage, 0.1%, 0.2%, and 0.3% of the fertilizer from modified SCG enrichment with PO_4^{3-} and NO_3^- mixed with 150 g of soil in polybag (diameter 8 cm). The plant seeds used were *Raphanus sativus*. Observation of plant height and leaf width was carried out for 10 days.

The acute toxicity of the examined fertilizer was determined based on a plant's germination test. It was made with the fertilizer for modified SCG after adsorption process (0.1%, 0.2%, and 0.3%) mixed distilled water in ration 1:10 and put in a homogenizer for about 1 hour. Then, take the supernatant and put 5 mL in Petri dishes with 5 seed *Raphanus sativus*, which were then incubated in the dark at room temperature (25˚C ± 0.5˚C) for 72 hours. The germination index was calculated from equation GI = $G_e/G_k \times 100$, where G_e and G_k are the numbers of germinated seeds in the experimental and control series [9].

3. Result and Discussion

3.1. Characteristics of the Modified SCG

Figure 1 shows SEM images of original and modified SCG. SEM was used to observe the morphology of the adsorbent. The porosity of the modified SCG was relatively more formed than the original SCG. The addition of calcium hydroxide gives advantage to SCG for adsorb more PO_4^{3-} and NO_3^-.

FTIR was used to analyze the functional groups on the adsorbent before and after modified. The spectra are shown in Figure 2, both of original and modified SCG have peak between 3600 and 3200 cm^{-1} is related to the hydroxyl groups of O-H stretching vibration. The hydroxyl groups causes an increase in the

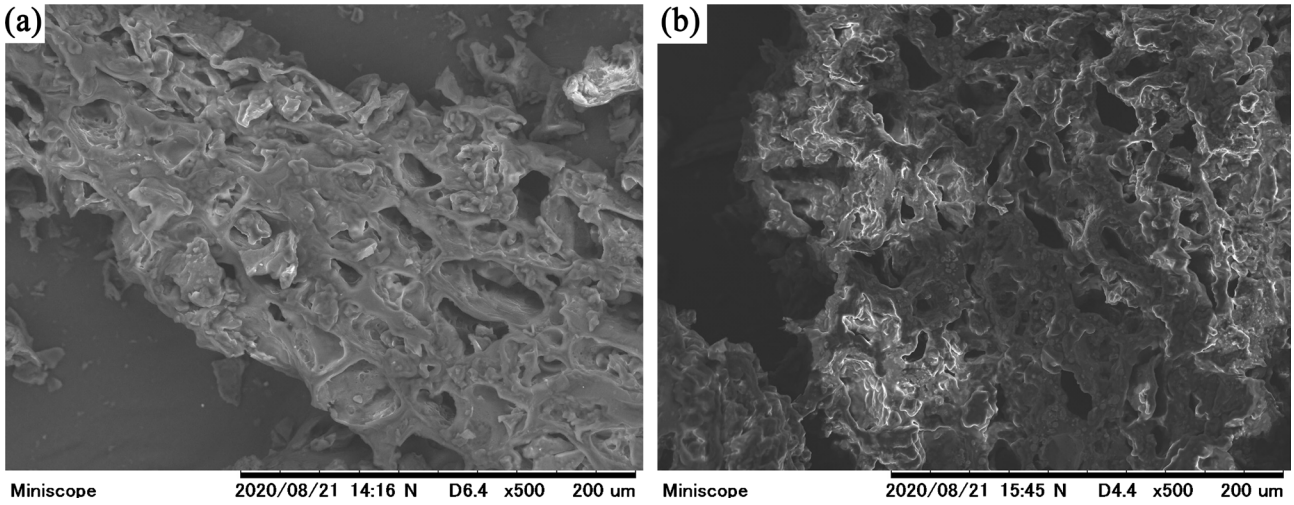

Figure 1. Scanning Electron Microscopy (SEM) images of (a) original and (b) modified Spent Coffee Ground.

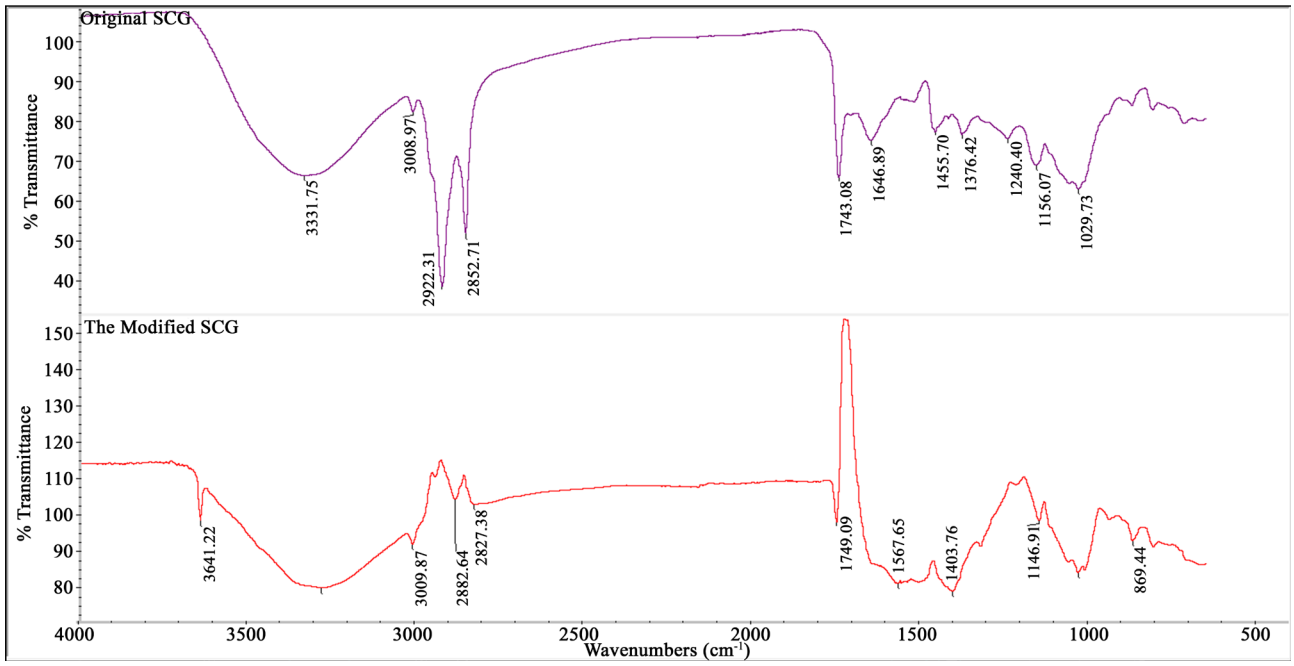

Figure 2. FTIR analysis of original and modified SCG.

electrostatic adsorption of anions, such as nitrate [10]. The two sharp bands at 2923 and 2852 cm^{-1} are attributed to C-H stretching vibration. The original SCG has peak between 1700 and 1600 cm^{-1} is highly associated with chlorogenic acids and caffeine [11]. However, in modified SCG the peak has shifted become 1567 cm^{-1} due to carboxylate groups [12].

3.2. Adsorption Phosphate ad Nitrate

Based on **Figure 3** and **Figure 4**, the figures show that the adsorption capacity of the modified SCG increases than original SCG. The adsorption capacity for PO_4^{3-} is 36.74 mg/g and for NO_3^- is 20.21 mg/g, respectively. The pH of the solution is an important variable in the adsorption process because it affects the surface charge of the adsorbent and also the chemical speciation of the adsorbate [13]. The effect of pH is showed in **Figure 5**, in the case of PO_4^{3-} the optimum adsorption occurs at pH 3 and pH 1 - 3 for NO_3^-. The modified SCG surface would be positively charged when the solution pH was lower, which enhanced

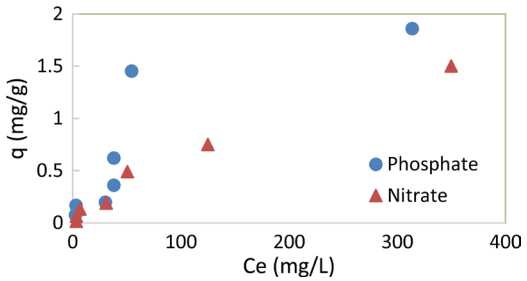

Figure 3. Adsorption of PO_4^{3-} and NO_3^- by the original SCG (C_o 10 - 500 mg/L, initial pH solution 3 - 4, ratio liquid/solid 0.1 L/10g, 30˚C).

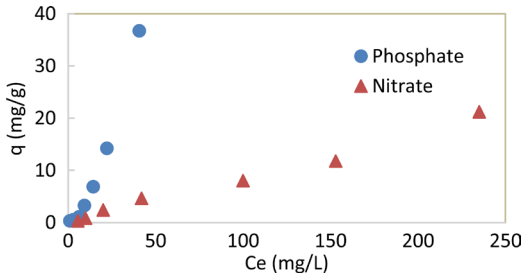

Figure 4. Adsorption of PO_4^{3-} and NO_3^- by (a) the modified SCG (C_o 10 - 500 mg/L, initial pH solution 3 - 4, ratio liquid/solid 0.016 L/0.2g, 30˚C).

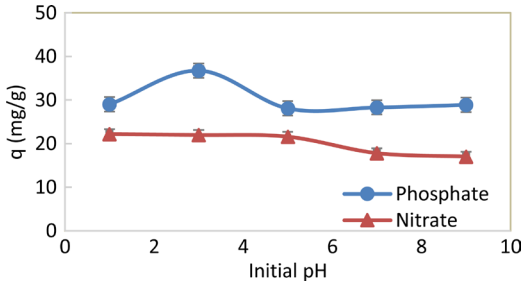

Figure 5. The effect of initial pH for adsorption PO_4^{3-} and (b) NO_3^-.

the adsorption possibility for the negatively charged PO_4^{3-} and NO_3^-.

Figure 6 shows that the increasing mass of adsorbent doesn't increase the adsorption capacity of PO_4^{3-} and NO_3^-. Furthermore, the addition of calcium hydroxide has an important role in the adsorption process of PO_4^{3-} and NO_3^- The less amount of adsorbent, the more active sites are formed.

3.3. Adsorption Isotherm Model

Adsorption isotherm model provide information about the capacity of the adsorbent and the solute-sorbent interaction. In the present work, the Langmuir and Freundlich isotherms were used to analyze the experimental equilibrium data. Table 1 shows the data of (a) Langmuir and (b) Freundlich isotherm models. Figure 7 shows the best fit of adsorption PO_4^{3-} and NO_3^-.

The Langmuir model is indicating that there is monolayer coverage of adsorbate on a homogeneous adsorbent surface. The Langmuir isotherm equation is [14]:

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (4)$$

where q_m (mg/g) is the maximum of the adsorption capacity in monolayer condition, q_e (mg/g) is equilibrium capacity, K_L (L/mg) and C_e (mg/L) is equilibrium concentration. The applicable of isotherm equation is compared on the basis of

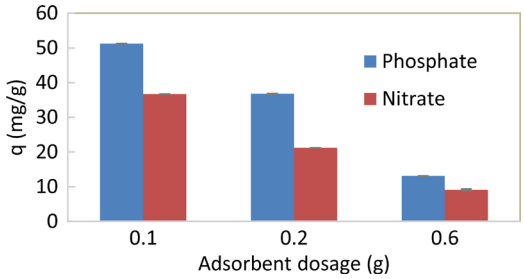

Figure 6. The effect of adsorbent dosage with adsorption capacity.

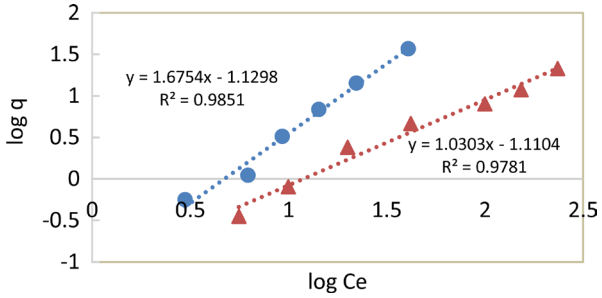

Figure 7. Freundlich isotherm model of PO_4^{3-} and NO_3^-.

Table 1. Isotherm models of PO_4^{3-} and NO_3^- adsorption.

Phosphate						Nitrate					
Freundlich			Langmuir			Freundlich			Langmuir		
K_f	n	R^2	K_L	q_m	R^2	K_f	n	R^2	K_L	q_m	R^2
0.07	0.59	0.98	0.023	8.82	0.64	0.07	1	0.97	0.0001	909	0.0014

correlation coefficients (R^2). However, R^2 of Langmuir isotherm model was lower than that of the Freundlich isotherm.

The Freundlich isotherm model is based in assumption that the heterogeneity of the adsorbent material and multi-layer coverage of the adsorbate. The Freundlich isotherm equation is:

$$\log q = \log K_L + 1/n \log C_e \tag{5}$$

where K_f (L/mg) is the Freundlich isotherm, n is the adsorption intensity, C_e (mg/L) is equilibrium concentration, and q_e (mg/g) is the equilibrium capacity.

The best fit of adsorption PO_4^{3-} and NO_3^- were obtained by the Freundlich with R^2 values was 0.98 for PO_4^{3-} and 0.97 for NO_3^-. The data was indicating that adsorption of PO_4^{3-} and NO_3^- onto the adsorption are not monolayer adsorption. The addition of calcium hydroxide played important role in adsorption PO_4^{3-} and NO_3^-, which is indicating not only physical adsorption but also chemical adsorption.

3.4. Adsorption Kinetic Model

Figure 8 shows the equilibrium time for PO_4^{3-} adsorption is 240 minutes and the optimum time for NO_3^- is 90 minutes. The kinetic model is used to determine the speed of the adsorption process and the stages that control the adsorption process. The kinetic data obtained is in the form of adsorption capacity, which can be obtained through modeling using pseudo-first order and pseudo-second order models. To find out the appropriate kinetic model for the adsorption system of PO_4^{3-} and NO_3^-, it is necessary to describe the relationship between the concentration of PO_4^{3-} and NO_3^- adsorbed and equilibrium with time. The kinetics of PO_4^{3-} and NO_3^- adsorption by modified SCG was investigated by pseudo-first order and pseudo-second order models [15], were determined using the following equations:

$$\ln\left(q_e - q_t\right) = \ln q_t - k_1 t \tag{6}$$

$$t/q_t = \left(1/k_2 q_e^2\right) + t/q_e \tag{7}$$

where k_1 is the pseudo-first order adsorption rate constant, k_2 is the pseudo-second order rate constant, q_e (mg/g) is the adsorption capacity at equilibrium, and q_t (mg/g) is the adsorption capacity at t (minute). Figure 9 shows that both adsorption data is more linear using the pseudo-second order adsorption

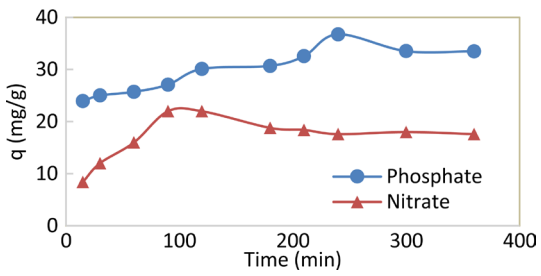

Figure 8. Equilibrium time of PO_4^{3-} and NO_3^- adsorption.

kinetic model, evidenced by the R^2 value of 0.9791 for PO_4^{3-} and 0.9347 for NO_3^-.

3.4. Desorption Studies

Adsorption by chemical bonding or ion exchange or combination of both, then desorption can be effected by stronger desorbent like acid or alkali solution. If the adsorption is by physical bonding then the loosely bound metal ion can be easily desorbed with distilled water in most of the cases. The result of PO_4^{3-} desorption rate using sodium hydroxide solution showed results reaching 24.35%, while the optimum value for desorption of NO_3^- reached 39.39%. These results indicate that the adsorption on the adsorbent modified SCG is not completely reversible and bonding between it and adsorbed PO_4^{3-} and NO_3^- is likely to be be strong. Thus, it is relatively difficult to desorb PO_4^{3-} and NO_3^- from the modified SCG [16].

3.5. Application for Plant Growth

The application of modified SCG after enrichment with PO_4^{3-} and NO_3^- for plant growth (*Raphanus sativus*) can be seen in **Figure 10** and **Figure 11**. The dose of 0.3% was a significant growth in the plant height and leaf width. However, seeds can grow on the third day. It is estimated because of the chemical bonds between PO_4^{3-} and NO_3^- in the active site of modified SCG are quite strong. Therefore, nutrients need time to release into the soil. It is linear with a desorption

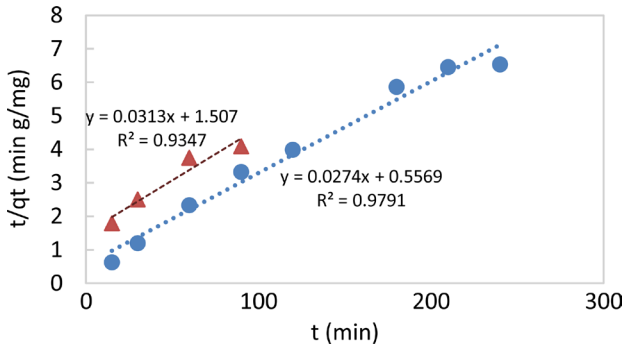

Figure 9. Pseudo-second order of (a) PO_4^{3-} and (b) NO_3^-.

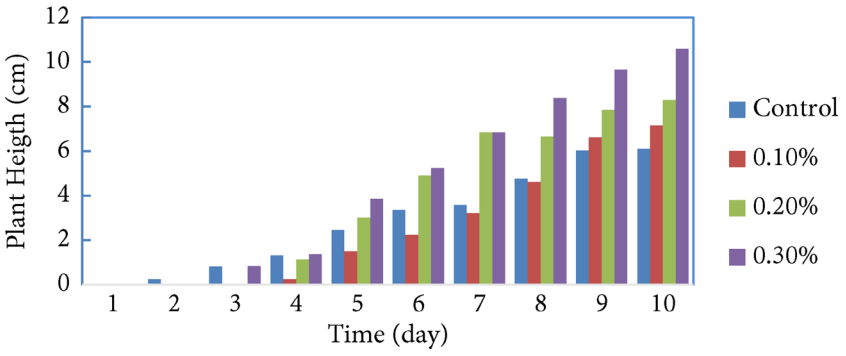

Figure 10. The effect of modified SCG enrichment on stem height of *Raphanus sativus*.

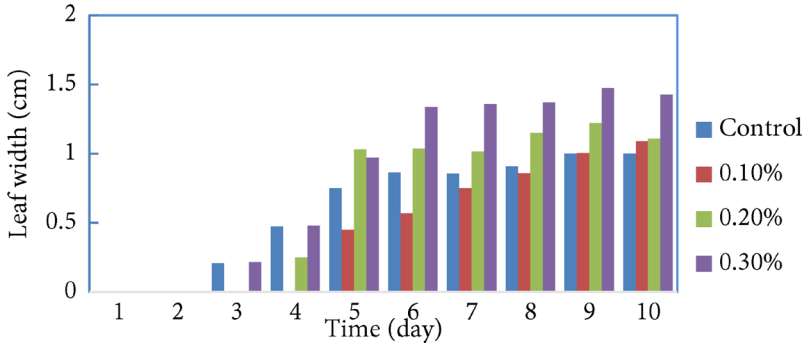

Figure 11. The effect of modified SCG enrichment on leaf width of *Raphanus sativus*.

Table 2. Germination Index (GI) of *Raphanus sativus*.

Concentration	Germination Index (%)	Root Length (cm)
0.10%	177	3.4
0.20%	200	3.8
0.30%	203	3.9

rate of only 26% - 30%.

The original SCG is characterized by a strong phytotoxic impact, such as caffeine content [17]. Caffeine (1.8 mg/g) present in SCG may serve as a chemical defense mechanism in some plants [5]. FTIR data on the original SCG indicated that there was a peak associated with caffeine content. However, the addition of sodium hydroxide has the effect of lowering caffeine levels in SCG. The effect of toxicity can also be seen from the germination rate test. The result of germination rates in **Table 2** shows that even though the small dose of fertilizer can contribution to plant growth significantly.

4. Conclusion

The optimum adsorption capacity at equilibrium (q) of PO_4^{3-} was 36.74 mg/g when pH and contact time of PO_4^{3-} solution were 3 and 240 minutes. The optimum adsorption capacity at equilibrium adsorption capacity at equilibrium of NO_3^- was 20.21 mg/g when pH and contact time were 1 - 3 and 90 minutes, respectively. The best fit of the experimental data PO_4^{3-} and NO_3^- were obtained by the Freundlich isotherm and pseudo-second order. The desorption rate of the modified SCG ranged from 24% - 39%. It can be concluded that the modified SCG can be used as an adsorbent to remove PO_4^{3-} and NO_3^- in wastewater. The fertilizer from modified SCG after enrichment with PO_4^{3-} and NO_3^- can contribute to plant growth even though in small dose, so it can use as an alternative source of nutrients that contribute to plant growth.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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