Adsorption of Phosphate from Aqueous Solution by Calcination of Silicified Coal: Kinetic and Isotherm Studies

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Abstract – Silicified coal (SC) consisting of SiO₂ is a promising raw material for adsorbent. The present study aimed to utilize silicified coal bottom ash (SCBA) adsorbent by calcination of the SC at temperatures of 600, 800, and 1000 °C for 1 hour. The FTIR result showed that the SCBA_600, SCBA_800, and SCBA_1000 had chemical functional groups such as the asymmetric Si-O-Si, the symmetric Si-O-Si and Si-O-Si bond rocking for adsorption of phosphate (PO₄³⁻) with the lowest percentage of transmittance of SCBA_1000. The adsorption test showed that rapid adsorption occurred in the first 10 minutes of contact time, and it did not change significantly for the rest of contact time until reaching an equilibrium time of 30 min. The PO₄³⁻ adsorption efficiency and capacity fluctuated over the initial PO₄³⁻ in solution in the 60.02–480.29 mg/L range. The highest PO₄³⁻ adsorption efficiency and capacity were at 480.29 mg/L, 95.49 %, and 45.86 mg/g, respectively, using the SCBA-1000. The adsorption kinetic fitted better to the pseudo-second-order kinetics model (average R² = 0.999) with the adsorption capacity of 45.454, 45.662, and 45.872 for the SCBA_600, SCBA_800, and SCBA_1000, respectively, and the PO₄³⁻ adsorption rate was 0.0007, 0.0008 and 0.001 g/mg.min, respectively. The adsorption isotherm followed Langmuir model (average R² = 0.873), with the adsorption capacity being 2.357, 1.198, and 8.196 mg/g, respectively, and the pore volume being 0.0316, 0.0364 and 0.2103 L/mg, respectively.

Keywords: Silicified coal, phosphate, calcination, adsorption, kinetic, isotherm

Introduction
Phosphate is essential for plants and animals to grow, which plays a vital role in food production (Krouk & Kiba, 2020). It is also an indicator for evaluating water quality because it is a limiting nutrient for aquatic plants in natural water. Likes other nutrients, it might be an essential food source for other organisms such as phytoplankton (Yuan et al., 2015). Therefore, the biological condition and water quality were impacted significantly by small phosphate concentration changes.

The coastal zone can be accumulated by organic and inorganic compounds, including phosphorus compounds, due to many anthropogenic pollutants from domestic waste, agricultural activities, fish farming, and mining operations (Strokal & Kroeze, 2013). Phosphate is released to water bodies from many sources, such as human activities in industrial and agricultural applications (Mangwandi et al., 2014; Mor et al., 2016). The extensive release of this phosphorus compound into the environment can cause water quality damage and decrease in aquatic species (Kuwayama et al., 2020). It also needs much cost to treat phosphate pollutants (Jesse et al., 2021). It also needs much cost to treat phosphate pollutants (Karaca et al., 2016). According to the World Health Organization (WHO) standard, the maximum phosphate limit in surface water is 5 mg/L (WHO, 2004). Therefore, reducing phosphate in water by low-cost process is a challenge and a significant environmental duty.

Several treatment methods have been proposed for the removal of phosphate from wastewater. The often used technique include physical and biological processes (Wang et al., 2009, Acevedo et al., 2012), chemical precipitation (Greenlee et al., 2010), ion exchange (Martin et al., 2009), and adsorption (Liu & Hesterberg, 2011). Physical techniques such as reverse electrodialysis and osmosis are too expensive and inefficient (Huang et al.,...
The environmental factors, including water quality in biological treatment, impact the removal ratio of phosphate, which causes it to be unsteady (Bunce et al., 2018). Meanwhile, chemical treatment needs more cost for effluent neutralization, sludge handling, and solid waste disposal (Özacar, 2003; Liu et al., 2013). Among the processes and treatments, adsorption is a promising process to reduce phosphate in wastewater (Yadav et al., 2017; Xiong et al., 2017).

Low-cost raw materials for the adsorption of phosphate have been proposed, such as aluminum hydroxide (Tanada et al., 2003), dolomite (Karaka et al., 2004), fly ash (Li et al., 2006), alunite (Özacar, 2003), blast furnace slag (Kostura et al., 2005), iron oxide tailings (Zeng et al., 2004), and zirconium oxide (Su et al., 2013). SiO$_2$-based adsorbents of zeolite and bentonite containing 41.4 and 58.1 % of SiO$_2$, respectively, have been studied for phosphate removal from the aqueous solutions with more than 90% removal efficiency. However, the phosphate adsorption capacity of the adsorbents was not calculated (Aljbour et al., 2016; Yan et al., 2010). A novel adsorbent from silicified coal consisting of 67.11–78.80 wt.% of SiO$_2$ was studied for Cu (II) adsorption, and the Cu (II) adsorption capacity of 14.358 mg/g was obtained using NaOH-activated silicified coal. The chemical activation still needs more cost for NaOH reagent and distilled water for decanting and washing it after it was activated, as presented in the previous study (Muslim et al., 2022).

Silicified coal (SC) consisting of SiO$_2$ is a promising raw material for adsorbent. The SC has not been studied for the adsorption of phosphate. Therefore, the present study aimed to utilize the adsorbent of SC bottom ash (SCBA). The SCBA was produced by calcination of the SC at the temperature of 600, 800, and 1000 °C for 1 hour. The SCBA adsorption capacity was evaluated over calcination temperature, adsorption contact time, and initial phosphate ions concentration. The adsorption kinetics and isotherms were studied to determine each parameter’s value.

Materials and Methods

Material

The SC was obtained from a coal mining area at West Aceh. It belongs to PT Mifa Bersaudara, operated in the district of Peunaga Cut Ujong. The phosphate stock solution was prepared using KH$_2$PO$_4$ (99% pure from Aldrich), and the phosphate concentration was determined using a UV-Vis Spectrophotometer (UVS, UH5300 Hitachi, Japan).

Adsorbent Preparation

The SC lumps of 1 kg were rinsed using Reserve Osmosis water and then dried at 110 °C (± 1 °C) in a Memmert oven (Type NN-ST342, Western Germany) for 1 hour. It was crushed, milled, and sieved to get the SC powder with 100-120 mesh size. The SC powder of 100 g was calcinated at 600 °C for 1 hour in a furnace (Neycraft, Model JFF-2000) (Liaquat and Ahmed, 2022). The SCBA was collected from the furnace 30 min after turning off it. The SCBA was placed in a sealed sample bottle and labeled the SCBA_600. The procedure of utilizing the SCBA was repeated to produce the SCBA_800 and the SCBA_1000, which was for 6800 °C and 1000 °C of calcination temperature, respectively.

Analyses Method

All the SCBA functional groups were analyzed using Fourier Transform Infrared Spectroscopy (FTIR, Prestige 21 Shimadzu Japan). The phosphate concentration was determined using a UV-Vis Spectrophotometer (UVS, UH5300 Hitachi, Japan).

Adsorption Experimental Method

All the adsorption tests using the SCBA_600, SCBA_800, and SCBA_1000 were conducted separately in a batch mode at room temperature (27 ± 1 °C) and pH of 5 based on the previous study (Muslim et al., 2022). The SCBA phosphate system consists of 1 g of each SCBA and 100 mL of aqueous phosphate solution in a beaker glass of 200 mL. The adsorption capacity of each SCBA over independent variables was determined. The independent variables were the contact time, CT (0–30 min), initial concentration of phosphate, $C_0$ (60.02–480.29 mg/L), and temperature of the furnace for utilizing the SCBA. The phosphate ($PO_4^{3-}$) solution of 1 mL was sampled at 0, 5, 10, 15, 20, 25, and 30 min, and each sample was prepared for the UVS based on the previous study was taken into account (Muslim et al., 2017a).
Quantification of the Adsorption Capacity

The SCBA adsorption capacity was quantified using Equation (1):

\[ q_t = \frac{(C_0 - C_t)V_t}{m_{AC}} \]  

Where \( C_t \) and \( C_0 \) (mg/L) are the concentration of PO₄³⁻ at the time of \( t \) and 0 (min), respectively; \( q_t \) is the SCBA adsorption capacity at \( t \); \( V_t \) (L) is as the volume of solution (L) at \( t \); and \( m_{AC} \) (g) is the SCBA mass.

The values of adsorption kinetic parameters were quantified using the linearized Lagergren model (Equations (2)) of the pseudo-first-order (PFO) kinetic model and Ho model (Equations (3)) of the pseudo-second-order (PSO) kinetic model (Lagergren, 1989, Ho et al., 1996):

\[ \log(q_e - q_t) = \log q_e - \left( \frac{k_1 t}{2.303} \right) \]  

\[ \frac{t}{q_t} = \frac{1}{k_H q_e^2} + \frac{t}{q_e} \]

where \( q_e \) (mg/g) is the adsorption capacity at equilibrium, and \( k_1 \) (/min) and \( k_H \) (g/mg.min) are the PFO and PSO constants of the adsorption rate, respectively. The slope and intercept of related graphs were used to work out the values (Muslim et al., 2017b).

The values of adsorption isotherm parameters were quantified using the linearized Langmuir model (Equations (4)) and Freundlich model (Equations (5)) (Langmuir, 1918, Freundlich, 1906):

\[ \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} \frac{C_e}{K_F} \]  

\[ \log q_e = \frac{1}{n} \log C_e + \log K_F \]

Where \( q_m \) (mg/g) is adsorption capacity based on Langmuir; \( K_L \) (L/mg) and \( K_F \) (mg/g) is pore volume based on Langmuir and Freundlich, respectively; and \( 1/n \) is the intensity of adsorption. The slope and intercept of related graphs were used to determine the constants' value (Muslim et al., 2017b).

Results

Functional groups of the SCBA_600, SCBA_800, and SCBA_1000

Figure 1 shows the SCBA_600, SCBA_800, and SCBA_1000 transmission spectrum at 400-4000 cm⁻¹. A weak band was at 3692–3712 cm⁻¹ of wavenumber, with the peak at 3701.40 cm⁻¹. This weak band was attributed to the O-H stretch (Lee et al., 2015). A wide band at 1223-915 cm⁻¹ with the 2 peaks at 1161.15 and 1055.06 cm⁻¹ was associated with the asymmetric Si-O-Si (Ade et al., 2021). A strong band at 761-829 cm⁻¹ with a peak at 796.60 cm⁻¹ represented the symmetric Si-O-Si. A weak band at 449-472 cm⁻¹ with a peak at 462.92 cm⁻¹ was attributed to Si-O-Si bond rocking (Muslim et al., 2022; Visa and Popa, 2015; Bange et al., 2008).

Effect of contact time on efficiency and capacity of adsorption

The efficiency and capacity of PO₄³⁻ adsorption by the SCBA_600, SCBA_800, and SCBA_1000 for \( C_0 = 480.29 \) mg/L were shown in Figures 2(a) and 2(b). As shown in Figure 2(a), the adsorption efficiency for the SCBA_600, SCBA_800, and SCBA_1000 increased sharply at the first 10 min of adsorption time, which was approximately 93.42, 95.01 and 95.42 %, respectively. Then, it did not change considerably until reaching an equilibrium time of 30 min with the adsorption efficiency for the SCBA_600, SCBA_800, and SCBA_1000 was 94.55, 94.89 and 95.49 %, respectively. Meanwhile, the trend of adsorption capacity was also the same as the adsorption efficiency. It also increased sharply at the first 10 min of adsorption time, which was 44.87, 45.63, and 45.83 mg/g for the SCBA_600, SCBA_800, and SCBA_1000, respectively. It also did not change...
considerably until reaching an equilibrium time of 30 min, and it was approximately 45.41, 45.58, and 45.86 mg/g, respectively.

**Figure 1.** The FTIR spectra of the SCBA_600, SCBA_800 and SCBA_1000

**Figure 2.** Effect of contact time on (a) adsorption efficiency and (b) adsorption capacity for \( C_0 = 480.29 \) mg/L

**Effect of initial PO\(_4^{3-}\) concentration on the efficiency of adsorption**

Figures 3(a), 3(b) and 3(c) demonstrated the efficiency of PO\(_4^{3-}\) adsorption at the various \( C_0 \) (60.02–480.29 mg/L). As can be seen in Figure 3(a), the PO\(_4^{3-}\) adsorption capacity of the SCBA_600 at equilibrium was approximately 47.58, 38.25, 33.49, 14.70 and 94.55 % at the \( C_0 \) being 60.02, 119.70, 128.35, 192.15 and 480.29 mg/L, respectively. It was approximately 34.57, 11.51, 45.58, 25.46, and 94.89 % for the SCBA_800, as revealed in Figure 3(b). Meanwhile, it was approximately 38.60, 57.18, 64.86, 49.85, and 95.49 % for the SCBA_1000 can be seen in Figure 3(c). It fluctuated in the \( C_0 \) range of 60.02–480.29 mg/L, but the highest PO\(_4^{3-}\) absorption efficiency was consistent at the \( C_0 \) of 480.29 mg/L.

**Effect of calcination temperature on efficiency and capacity of adsorption**

Figures 4(a) and 3(b) showed the effect of calcination temperature on the efficiency and capacity of PO\(_4^{3-}\) adsorption at the \( C_0 \) of 480.29 mg/L. The efficiency of PO\(_4^{3-}\) adsorption at 600, 800, and 1000 °C of calcination temperature was 94.55, 94.89 and 95.49 %, respectively. Meanwhile, the capacity of PO\(_4^{3-}\) adsorption was 45.41, 45.58 and 45.86 mg/g, respectively. Overall, increasing calcination temperature in the 600-1000 °C range increased the efficiency and capacity of PO\(_4^{3-}\) adsorption.
Figure 3. Effect of $C_0$ on adsorption efficiency for (a) the SCBA_600, (b) SCBA_800, and (c) SCBA_1000

Figure 4. Effect of calcination temperature on (a) adsorption efficiency and (b) adsorption capacity

**Adsorption kinetic and isotherm**

The PFO and PSO adsorption kinetic linear plots are shown in Figures 6(a) and 6(b), respectively. From the values of the correlation coefficient, it is clear that the PSO model gave the best fitting of the experimental data, with the $R^2$ value being 0.999, 0.999, and 1 for the $PO_4^{3-}$ adsorption using the SCBA_600, SCBA_800, and SCBA_1000, respectively.
Figure 5. The linear plots of (a) the PFO adsorption kinetic model and (b) the PSO adsorption kinetic model

Figures 6(a) and 6(b) showed the linear plots of Langmuir and Freundlich isotherm models, respectively. As shown by the values of the correlation coefficient, the PO₄³⁻ adsorption on the SCBA_600, SCBA_800, and SCBA_1000 followed the Langmuir isotherm model, and the R² value is 0.986, 0.7787, and 0.853 (average R² of 0.873), respectively.

Figure 6. Linear plots of (a) Langmuir isotherm model and (b) Freundlich isotherm model

Discussions

Functional groups of the SCBA_600, SCBA_800, and SCBA_1000

As can be seen in Figure 1, the Si-based functional groups showed in the FTIR result. These active sites should be for the adsorption of PO₄³⁻, especially to the asymmetric Si-O-Si (siloxane groups), which are active sites for the adsorption of metal ions, anions, or cations (Ade et al., 2021). The effect of calcination temperature change was shown in Figure 1, whereas the SCBA_1000 curve was under the other two curves of SCBA_600 and SCBA_800. This result showed that the absorbency of the SCBA_1000 was more than the absorbency of SCBA_600 and SCBA_800. For example, the asymmetric Si-O-Si peak had a transmittance of 82.57 %, more than the SCBA_600 and SCBA_800 (82.12 and 82.26 %, respectively). It means that the SCBA_1000 should adsorb more PO₄³⁻ than the SCBA_600 and SCBA_800. The same result was also found in the previous (Muslim et al., 2022).

Effect of contact time on efficiency and capacity of adsorption

As shown in Figures 2(a) and 2(b), the initial stage of PO₄³⁻ adsorption onto the SCBA_600, SCBA_800, and SCBA_1000 was in the first 10-min contact time wherein the diffusion of PO₄³⁻ in the liquid phase to the solid phase on the SCBAs. This view was supported by the previous study (Medhi et al., 2020). Therefore, the PO₄³⁻ adsorption efficiency and capacity on the SCBAs increased sharply during this stage. For the rest of time, there was less diffusion of PO₄³⁻ in the aqueous phase to the solid phase, leading to a very small change (increase and decrease) of PO₄³⁻ on the SCBAs due to the weak of the Van der Waals interaction, functional group bonds, or electrostatic attraction until reaching equilibrium state (Marlina et al., 2020).
Effect of initial PO$_4^{3-}$ concentration on the efficiency of adsorption

In general, more adsorbate in the liquid phase results in more adsorbate being adsorbed on the adsorbent surface (Muslim et al., 2017a; Marlina et al., 2020). However, PO$_4^{3-}$ in the liquid phase over the C$_0$ change (60.02–480.29 mg/L) fluctuated based on the UVS result. Therefore, the efficiency of PO$_4^{3-}$ adsorption also fluctuated over the C$_0$. This fluctuating amount of PO$_4^{3-}$ being adsorbed on the SCBAs showed that the adsorption of PO$_4^{3-}$ on the SCBAs was not fully controlled by the driving force of the different PO$_4^{3-}$ concentrations between the liquid phase and solid phase, but it would also be by the chemical bonding between the PO$_4^{3-}$ and active sites of the chemical functional group. The chemical bonding could be due to reversible reactions between PO$_4^{3-}$ and the chemical functional group, which caused the adsorbate to be partially desorbed into the liquid phase (Chai et al., 2021). This view also showed the previous study wherein the adsorption of adsorbate fluctuated over the initial adsorbate concentration in solution (Muslim, 2017).

Effect of calcination temperature on efficiency and capacity of adsorption

As shown in Figures 4(a) and 3(b), increasing calcination temperature in the 600-1000 °C range increased the efficiency and capacity of PO$_4^{3-}$ adsorption. This result was in line with the FTIR analysis. In contrast, the transmittance of the asymmetric Si-O-Si, the symmetric Si-O-Si, and Si–O–Si bond rocking (Ade et al., 2021), as shown in the FTIR result. The slope of PSO linear plots for the SCBA_600, SCBA_800, and SCBA_1000 was approximately 0.022, 0.0219 and 0.0218, respectively. The equilibrium PO$_4^{3-}$ adsorption capacity ($q$) obtained from these values was approximately 45.454, 45.662, and 45.872 mg/g for the SCBA_600, SCBA_800 and SCBA_1000, respectively. Although the increase in adsorption capacity was insignificant, it showed that increasing calcination temperature from 600 to 800 and 1000 oC increased the PO$_4^{3-}$ adsorption capacity from 45.454 to 45.662 and 45.872 mg. This result was supported by the FTIR result, where the transmittance decreased, leading to an increased absorbance degree (Visa and Popa, 2015; Bange et al., 2008) due to the calcination temperature increase. Meanwhile, the PO$_4^{3-}$ adsorption rate ($k_{i1}$) was 0.0007, 0.0008, and 0.001 g/mg. min, respectively. Overall, the SCBA_1000 had the maximum adsorption capacity and the faster adsorption rate.

From the slope of Figures 6(a) and 6(b), the $q_m$ value based on Langmuir was approximately 2.357, 1.198, and 8.196 mg/g for the SCBA_600, SCBA_800 and SCBA_1000. The SCBA_1000 had the maximum adsorption capacity, suitable for the adsorption kinetic and the prediction-based FTIR result. Meanwhile, the pore volume based on Langmuir was 0.0316, 0.0364, and 0.2103 L/mg, respectively, corresponding to the maximum adsorption capacity of SCBA_1000.

Conclusion

The silicified coal bottom ash (SCBA) adsorbent was prepared by calcination of the SC at 600, 800, and 1000 °C for 1 hour. Chemical functional groups of the asymmetric Si-O-Si, the symmetric Si-O-Si, and Si-O-Si bond rocking were found by the FTIR analysis. The SCBA could be used for the adsorption of PO$_4^{3-}$, and the PO$_4^{3-}$ adsorption efficiency and capacity fluctuated over initial PO$_4^{3-}$ concentration in solution in the range of 60.02–480.29 mg/L, but overall, it tended to increase within initial PO$_4^{3-}$ concentration. The highest PO$_4^{3-}$ adsorption efficiency and capacity were at 480.29 mg/L, 95.49 %, and 45.86 mg/g, respectively, using the SCBA-1000. The pseudo-second-order kinetics model was suitable for the adsorption kinetic with average fitting R$^2$ being 0.999 and the maximum adsorption capacity of 45.872 using the SCBA_1000 with the PO$_4^{3-}$ adsorption rate was 0.001 g/mg—minute, respectively. Langmuir model was satisfactory for the PO$_4^{3-}$ adsorption with average fitting R$^2$ being 0.873. The adsorption capacity based on Langmuir model was 8.196 mg/g using the SCBA_1000, with the pore volume being 0.2103 L/mg.
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References


