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Research of batch and fixed-bed column adsorption for phosphorus removal from wastewater using sewage sludge biochar

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Abstract: Wastewater treatment and the efficient use of sewage sludge biochar are critical in addressing the needs of ever-increasing population in the world. Recently, phosphorus (P) removal from wastewater has become highly relevant and important, primarily to reduce eutrophication in surface waters. Using sewage sludge biochar as an adsorbent for phosphate removal from wastewater offers an opportunity to reuse sewage sludge (SS) and return phosphorus to the biogeochemical cycle. In this study, the efficiency of two phosphate removal methods - batch adsorption and fixed-bed column process – was investigated using pyrolyzed sewage sludge biochar (PSSB) produced at different temperatures (300 °C, 400 °C, 500 °C, 600 °C). In the batch adsorption experiment, direct mixing of 600 °C pyrolyzed sewage sludge biochar with wastewater resulted in a relatively low phosphate removal efficiency (only about 18 %) at an initial phosphate concentration of 100 mg/l. In contrast, the fixed-bed column process, using PSSB as a filter for phosphate adsorption, showed significantly better results. The highest phosphate removal efficiency (up to 90%) was achieved after 30 min of filtration, using an initial phosphate concentration of 30 mg/l initial and biochar pyrolyzed at 600 °C.

Introduction

Nowadays, one of the most commonly known environmental concerns is wastewater treatment. There is a strong need to reduce, among other things, the number of organic contaminants and total suspended solids, as they, along with high phosphorus and nitrogen levels, play a major role in water eutrophication (Jóźwiakowska and Marzec, 2020).

Due to rapid urbanization and industrialization in recent decades, large amounts of urban sewage sludge have been generated in sewage treatment plants. However, sewage sludge typically contains high concentrations of phosphorus, nitrogen, heavy metals, organic trace pollutants, and pathogens, that of which pose significant environmental hazards after disposal. The treatment of sewage sludge (SS) is a major concern, as improper handling can lead to cross-contamination and seriously impact human health.

Phosphorus is one of the essential elements in food production, as it is naturally present in all organisms and resistant to modification by other substances. However, phosphate rocks, a key source of phosphorus, are scarce. Their formation takes about 10–15 million years, making the supply limited (Havukainen et al. 2016). Phosphorus shares similarities with nitrogen, as both are non-volatile, do not form stable gaseous compounds, and cannot circulate in the air. For these reasons, improving phosphorus recovery strategies is crucial.

Some researchers argue that sewage sludge is one of the most promising resources for phosphorus recovery. However, sewage sludge often contains organic contaminants and heavy metals, including personal care and pharmaceutical products, which prevent its direct use in products. The organic matter in sewage sludge can be removed through incineration, resulting in sewage sludge ash (SSA). SSA is enriched with minerals and serves as a secondary phosphorus source (Herzel et al. 2016).

One way to use sewage sludge is by converting it into biochar. Biochar is a carbon-rich material produced during the pyrolysis, a process that typically involves heating biomass with little or no oxygen (Jamaludin et al. 2019). The collection and treatment of wastewater, along with the efficient use of sewage sludge biochar, are critical for managing a growing population, rapidly developing industries, and pollution abatement efforts aimed at controlling harmful by-products. As sewage sludge waste streams increase, this issue becomes even more urgent. It is a global concern that the European Union is addressing through domestic legal requirements, unified guidelines, and indicators.

In a water purification device developed at Vilnius Gediminas Technical University, Department of Environmental and Water Engineering, biochar made from sewage sludge is used as a filter. With the depletion of non-renewable energy resources, rising fuel prices on the global market, and increasing waste production, it is crucial to explore new opportunities to harness potential. Biochar produced from sewage sludge offers a greener, cheaper, and more sustainable alternative to current water treatment methods.

The study aims to determine the efficiency of two selected methods − batch adsorption and fixed-bed column process − for removing phosphorus from wastewater using sewage sludge biochar produced at different temperatures. In the batch adsorption experiment, pyrolyzed sewage sludge biochar (PSSB) samples were used at temperatures of 300°C, 400°C, 500°C, and 600°C. For the fixed-bed column experiment, PSSB samples were used at 400°C, 500°C, and 600°C.

Material and methods

The experiment lasted approximately one year, during which nearly 500 samples were taken for this analysis.

Preparation of sewage sludge biochar

The chosen adsorbent was pyrolyzed sewage sludge. Municipal sewage sludge (SS) was obtained from a municipal WWTP in Vilnius, Lithuania. The wastewater treatment plant produces 9 tons of sewage sludge pellets annually and uses both biological and mechanical treatment processes.

SS from primary and secondary stages is mixed in septic tanks, compressed, heated, hydrolyzed, and then anaerobically digested under moderate temperature conditions. After digestion, the sludge is dried to a moisture content of 70%, and then further dried to a moisture content of 5% using special equipment, resulting in odorless, darkened pellets.

Samples of sewage sludge pallets were dried at a temperature of 100 °C until a constant mass was achieved, indicating that the moisture content of the raw material was 4.2 ± 0.1% based on weight loss. Biochar was produced from SS plates by pyrolysis in a tubular furnace, with a nitrogen flow rate set at 2 l/min during the pyrolysis process (Januševičius et al. 2022).

We placed 30 g of sewage sludge pellets in a pot without an aluminum foil cover. Pyrolysis was performed at four different temperatures (300 ± 1, 400 ± 1, 500 ± 1, and ± 600 ± 1 °C) for 2 hours. A large amount of sludge pallet biochar (approximately 100 g) was obtained by repeating the pyrolysis process. The heating rate was calculated to be around 12–13 °C/min (Januševičius et al. 2022).

Before using sewage sludge biochar, the sludge was ground. For the first method of phosphate adsorption, the biochar samples from the sewage sludge were ground and sieved to pass a 100-µm mesh-size sieve. In the second method, the sewage sludge biochar samples were sifted and sorted to achieve a particle size of 1 – 1.6 mm diameter. Different particle sizes were selected to increase the surface area of the adsorbent.

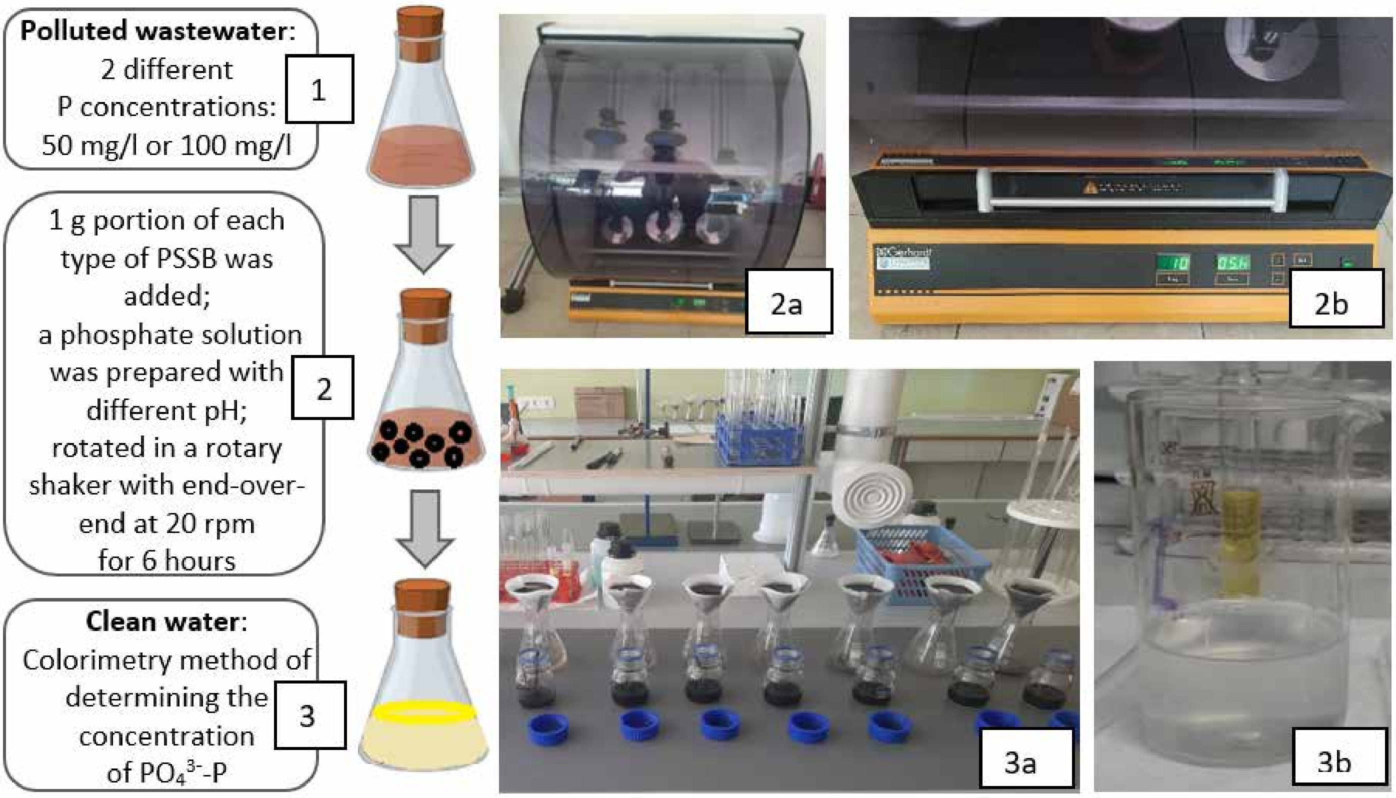

Figure 1. Scheme of phosphate batch adsorption experiment: 1 – polluted wastewater; 2 – polluted wastewater with PSSB (2a – the rotary shaker, 2b – the solution was then rotated in a rotary shaker with end-over-end at 20 rpm for six hours); 3 – clean water (3a – after mixing, the samples were filtered using gravity filtration and a < 0,45 µm filter; 3b – the pH of the filtered samples was measured using a pH meter)

Determination of sewage sludge biochar pH

To determine the natural pH of the samples, 1 g of pyrolyzed sewage sludge biochar produced at different temperatures (300 °C, 400 °C, 500 °C, and 600 °C) was mixed with 20 ml of deionized water. The mixtures were left to shake for 24 hours on a shaker (Barnstead Thermolyne Big Bill Digital Orbital Shake Model 73625) at ~ 50 rpm. Afterward, all samples, including those with $CaCl_2$ and deionized water, were filtered using a filter with a pore size < 0.45 µm. The pH of each sample was then analyzed using a pH-meter (Hanna pHep® Pocket pH tester).

Phosphate batch adsorption experiment

In this experimental study, artificially contaminated deionized water was used to create different concentrations of phosphate that exceeded the permitted amounts of pollutants in wastewater (Figure 1).

The study aimed to investigate phosphate adsorption on biochar using a mixing method. The experiment was conducted using a fixed mass of pyrolyzed sewage sludge biochar and two varying phosphate concentrations, specifically 50 mg/l and 100 mg/l. To achieve these concentrations, potassium dihydrogen orthophosphate (KH_2PO_4) was dissolved in deionized water to prepare a phosphate stock solution. The chosen phosphate concentrations were based on previous research studies conducted by Li et al. 2019, Wang et al. 2021, and Yin et al. 2019. It is important to note that all chemicals, reagents, and mixtures used in the experiment were of high analytical quality. The mixing process was carried out using a Gerhardt Laboshake rotary shaker, which can hold up to 12 bottles simultaneously.

Two separate experiments were conducted, varying the solution's pH and mixing time:

In the first experiment, 1 g of each type of PSSB was added to the prepared phosphate solutions of 50 mg/l and 100 mg/l. The solutions were then rotated end-over-end in a rotary shaker at 11 rpm for 2 hours.

In the second experiment, 1 g portion of each type of PSSB was added to the 50 mg/l and 100 mg/l phosphate solutions with different pH values (2, 4, 6, 10, 12). The solutions were rotated end-over-end in a rotary shaker at 20 rpm for 6 hours.

The condition was changed to determine the effects on phosphate adsorption and increase efficiency.

After mixing, the samples were filtered through gravity filtration using a < 0,45 µm filter. The pH of the filtered samples was then measured with a pH meter. Following the adsorption process, the phosphate concentration was determined using the colorimetry method. The blank samples were also included in the initial phosphate solution as controls.

Colorimetry method for determining the concentration of PO_4^{3-}-P:

1. 5 ml of water sample mixed with 0.2 ml of analytical solution.
2. The sample was placed into a spectrophotometer at a wavelength of 410 nm.
3. The absorbance results were converted to PO_4^{3-}-P concentration by multiplying the absorbance by 18.

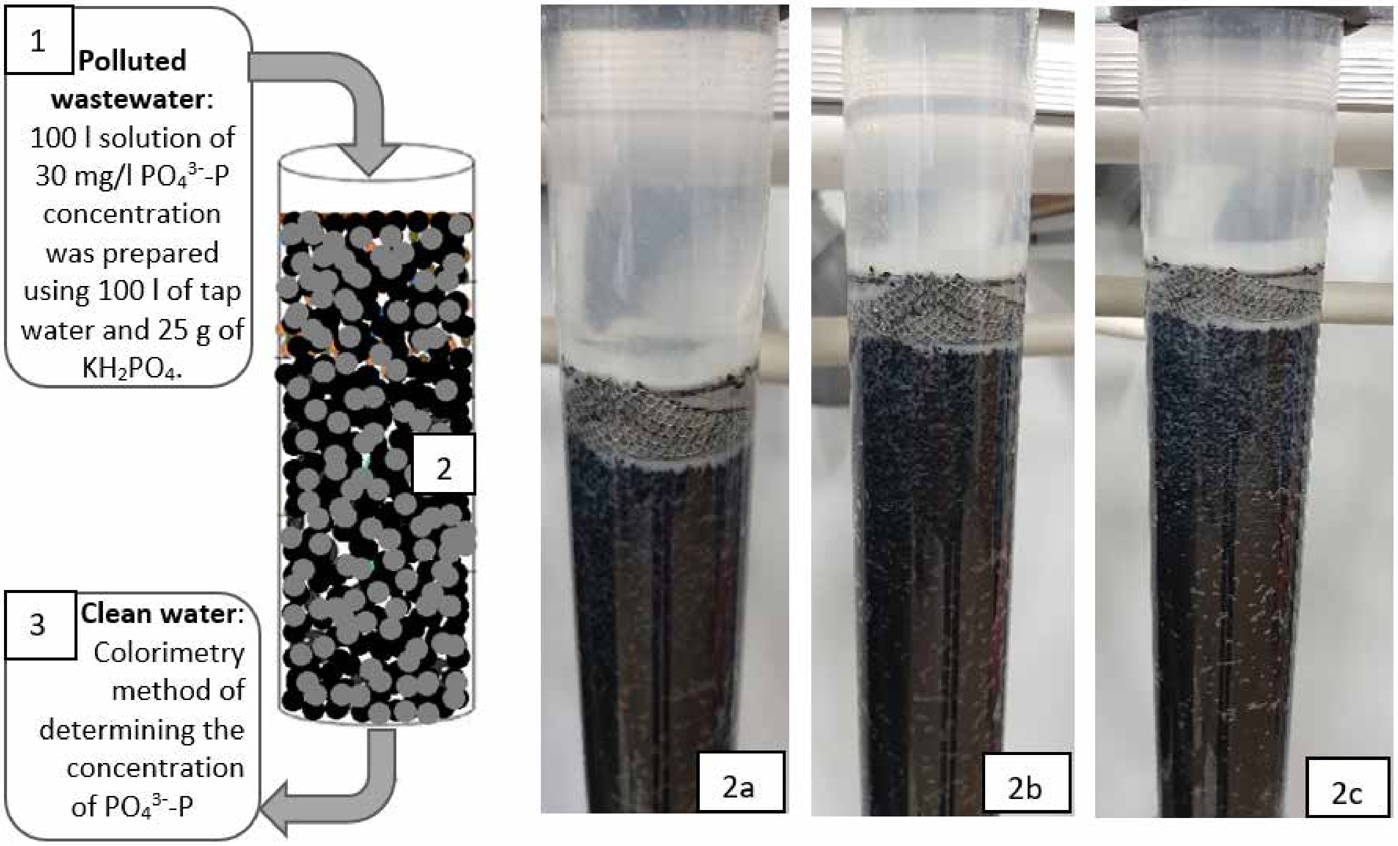

Figure 2. Scheme of phosphate adsorption during fixed-bed column process: 1 – polluted wastewater; 2 – the filter charge preparation involved taking 400 ml of pyrolyzed biochar at a specific temperature (2a – 400 °C PSSB; 2b – 500 °C PSSB; 2c – 600 °C PSSB); 3 – clean water (concentration of PO_4^{3-}-P was determined using the colorimetry method)

Phosphate adsorption during fixed-bed column process

Pyrolyzed sewage sludge biochar (PSSB), produced at 400 °C, 500 °C, and 600 °C, was used as a filtration medium to evaluate its ability to adsorb phosphates during a continuous waste flow (Figure 2).

The columns used had a diameter of 4.5 cm, with a supporting layer of approximately 100 ml of small stones placed at the base. Three different sewage sludge biochars, produced at 400 °C, 500 °C, and 600 °C, were added to three separate columns. The filter media preparation involved taking 400 ml of biochar, pyrolyzed at the specific temperature, and sieving it to achieve a particle size of 1–1.6 mm. The height of the biochar in the columns was measured both before and after compaction.

A 100 l solution with a 30 mg/l PO_4^{3-}-P concentration was prepared using 100 l of water from the city water supply and 25 g of KH_2PO_4. The solution was passed simultaneously through the three columns at a flow rate of approximately 16–20 ml/min. The water flow speed was calculated to be around 1.08 ± 0,005 l/h.

Samples from the three different columns were collected every 1 or 2 hours, and the concentration of PO_4^{3-}-P was determined using colorimetry method.

Calculations and modeling

Two indicators - equilibrium adsorption capacity (q_e, mg/g) and removal efficiency (R, %) - were selected to evaluate the efficiency of pyrolyzed sewage sludge biochar (PSSB) in adsorbing phosphates (PO_4^{3-}-P).

The amount of adsorbate adsorbed by the biochar at equilibrium was calculated according to equation (1):

$$q_e = V \times \frac{C_0 - C_e}{m} \qquad (1)$$

Where q_e (mg/g) represents the equilibrium adsorption capacity, which is the amount of adsorbate adsorbed per gram of biochar. V is the volume of the solution in liters, C_0 and C_e represent the initial and final concentrations of the adsorbate in milligrams per liter, respectively, and m is the weight of the biochar adsorbent in grams (Mo et al. 2024).

The removal efficiency (R, %) was calculated using initial and final phosphate concentrations in the solutions according to equation (2):

$$R\ (\%) = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (2)$$

Where C_0 and Ce represent the initial and final concentrations of the adsorbate in milligrams per liter, respectively, and m is the weight of the biochar adsorbent in grams (He et al. 2022).

In the current experiment, the relationships between sewage sludge biochar and phosphate removal efficiencies were modeled based on experimental measurements using the Freundlich isotherm and Langmuir models. These models were used to determine the reaction behavior between the sewage sludge biochar (solid material) and phosphate molecules, as well as to correlate to the adsorption capacities of different types of sewage sludge biochar (Zhou et al. 2017).

The results of these isotherms are presented for the Langmuir (equation (3) and Freundlich models (equation (4):

$$q_e = q_m K_L C_e / (1 + K_L b C_e) \qquad (3)$$

$$q_e = K_F C_e 1/n, \qquad (4)$$

Where q_m (mg/g) represents the maximum adsorption capacity at any given time; C_e (mg/l) represents the concentration of P in the solution at equilibrium; K_L and K_F are the Langmuir and Freundlich constants, respectively; and n is the linearity constant in the Freundlich model (Mo et al. 2024).

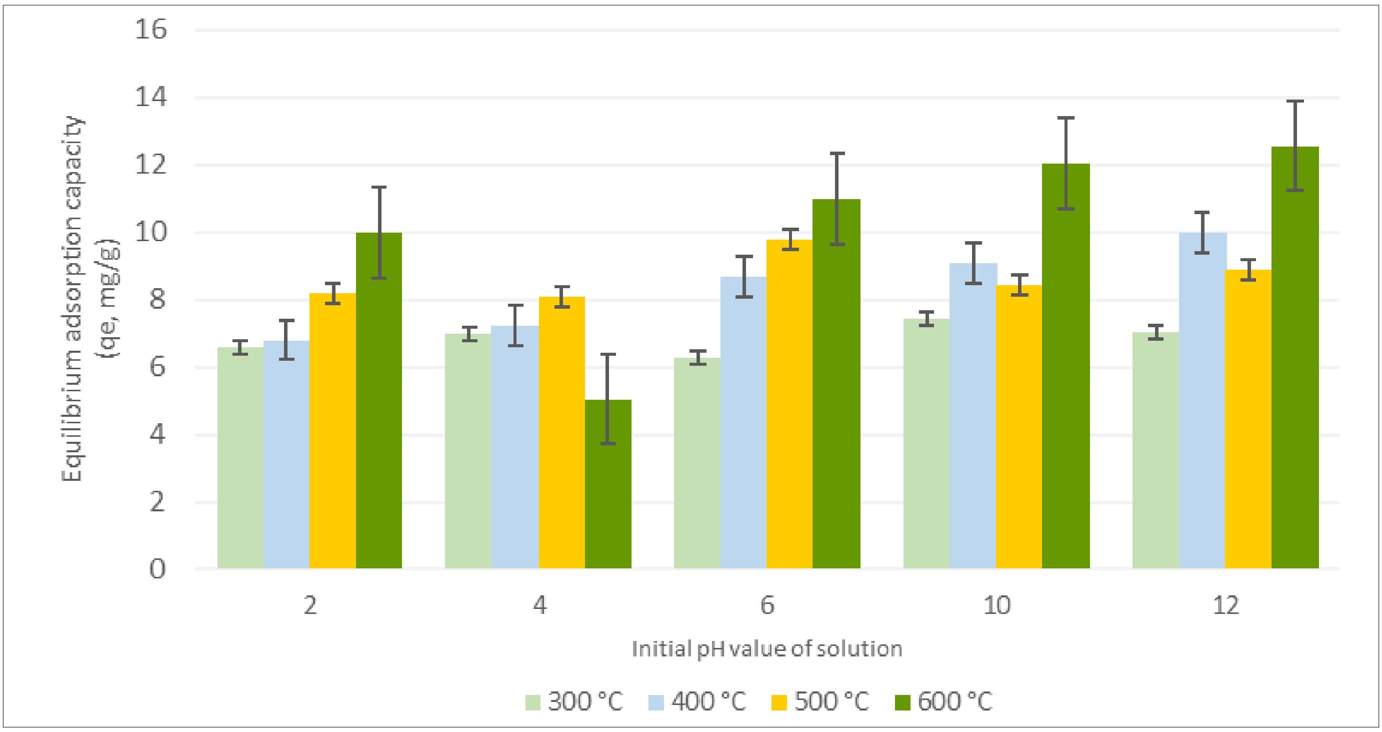

Figure 3. Different types of sewage sludge biochar equilibrium adsorption capacity (q_e, mg/g) of PO_4^{3-}-P at different pH values of the solution (the lines above each column represent significant differences at $p < 0.05$)

The average experimental results were calculated from three replicates of each experimental treatment and reported as the mean ± standard deviation. The data were analyzed using variance analysis, with only values having a p-value less than 0.05 considered significant. This analysis was performed to determine if there were significant differences in the adsorption capacity of pyrolyzed sewage sludge biochar across different phosphate concentrations and pH values.

Results And Discussion

The research used the batch adsorption method to evaluate the potential of PSSB as an adsorbent for removing phosphates from wastewater. The influent pH and initial phosphorus concentration can impact the adsorption performance of the adsorbent during the batch adsorption experiment (Jung et al. 2017; Nguyen et al. 2015).

Effect of pH

It is well-known that the adsorption capacity depends on various pH values. An experiment was conducted to determine the optimal initial pH values for phosphate adsorption for each biochar sample, and the results are presented in Figure 3.

The study investigated the impact of solution pH on phosphate adsorption onto biochar derived from sewage sludge across a pH range of 2 to 12. During the batch adsorption experiment, various initial pH values were evaluated for their effect on phosphorus adsorption capacity (Figure 1). The highest equilibrium adsorption capacities were observed with 600 °C sewage sludge biochar at pH 10 (12.04 mg/g) and pH 12 (12.56 mg/g), while the lowest capacity was recorded at pH 4 (5.05 mg/g). Among all samples, the highest equilibrium adsorption capacity was again associated with 600 °C sewage sludge biochar, whereas the lowest results across all pH values were observed for the 300 °C sewage sludge biochar. Notably, the weakest phosphorus adsorption capacity was seen at a pH value of 4. This may suggest that an acidic pH value of 4 is unsuitable for this type of biochar, potentially leading to phosphate leaching rather than enhancing the adsorption process. On the other hand, acidic conditions can sometimes be favorable for phosphate adsorption by biochar (Li et al. 2019). However, the results of this experiment show that under alkaline conditions (pH of 10 and 12), two out of four types of biochar (400 °C and 600 °C) exhibited the highest adsorption capacities.

The natural pH values of the biochar may explain the differences in equilibrium adsorption capacities among the various biochar samples. To investigate this, the natural pH values of the initial sewage sludge biomass were determined for biochar produced at 300 °C, 400 °C, 500 °C and 600 °C. The pH values of the solution ranged from 7.91 to 9.96 mg/g. Notably, the pH value of the 600 °C PSSB (9.91) is closer to the optimal pH value of 10, suggesting that using the natural pH of biochar could enhance its capacity to remove pollutants.

Effect of contact time

The experiment was conducted to determine whether the adsorption capacity depends on the contact time between sewage sludge biochar and the solution.

Results of the equilibrium adsorption capacity of phosphates (q_e, mg/g) using 300 °C, 400 °C, 500 °C and 600 °C sewage sludge biochar are shown in Figure 4.

The equilibrium adsorption capacity of phosphates among the same type of biochar showed no significant differences,

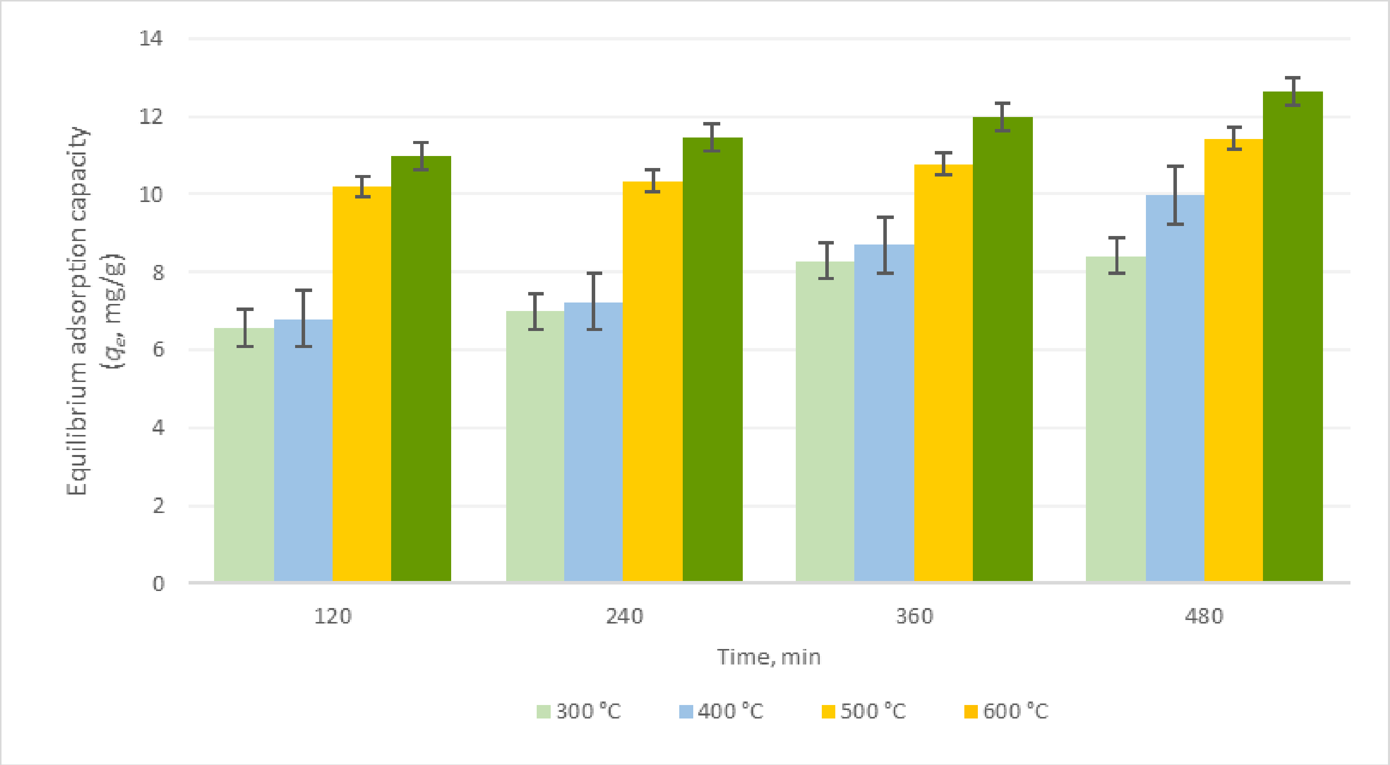

Figure 4. Equilibrium adsorption capacity of phosphates (q_e, mg/g) using 300 °C, 400 °C, 500 °C and 600 °C sewage sludge biochar (the lines above each column represent significant differences at $p < 0.05$)

Table 1. Phosphate adsorption capacity (mg/g) and parameters of isotherms using pyrolyzed biochar at 600°C

Samples of biochar	Adsorbate	Langmuir			Freundlich		
		q_e (mg/g)	K_L	R^2	$1/n$	K_F	R^2
PSSB (300 °C)	PO$_4^{3-}$-P	8.42	0.15	0.96	1.72	1.51	0.99
PSSB (400 °C)	PO$_4^{3-}$-P	9.98	0.16	0.96	1.55	1.40	0.99
PSSB (500 °C)	PO$_4^{3-}$-P	11.44	0.11	0.97	1.47	1.34	0.98
PSSB (600 °C)	PO$_4^{3-}$-P	12.63	0.13	0.99	1.63	1.48	0.99

except for PSSB produced at 400 °C. PSSB 400 °C exhibited an average equilibrium adsorption capacity of 7.23 mg/g after 240 min (or 4 hours) of contact time. Increasing the duration of shaking enhanced the adsorption capacity, with the highest value of 9.98 mg/g observed after 480 min (or 8 hours).

This type of biochar was the only one that showed a decrease in adsorption capacity with prolonged contact time. Zhang et al. (2021) observed a tendency for adsorption capacity to increase with longer contact times. The lack of a similar trend in this research may indicate that unmodified sewage sludge biochar does not significantly impact adsorption capacity over time when using the batch adsorption method, as it likely reaches its total capacity early in the process. In conclusion, the contact time in the batch adsorption method does not appear to yield significant differences, suggesting that further research is needed to explore this phenomenon.

The equilibrium adsorption capacity of PO$_4^{3-}$-P during the batch adsorption method did not meet the expected levels. Compared to other studies involving different types of biochar, the concentrations and amounts of adsorbed phosphates in this research are low (Jung et al. 2017, Li et al. 2019, Wang et al. 2021). Additionally, when comparing this study to previous research on modified sewage sludge biochar, the results are also unsatisfactory (Li et al. 2019, Ma et al. 2020, Yang et al. 2018). Several studies have analyzed the factors influencing phosphate adsorption capacity using sewage sludge, the kinetics of adsorption, and potential biochar modifications to enhance adsorption capacity (Almanassra et al. 2021, Nobaharan et al. 2021, Rangabhashiyam et al. 2022).

Like findings by other researchers (Li et al. 2019, Liu et al. 2020, D. Zhang et al. 2021), this study observed that phosphate adsorption capacity is proportional to the temperature of pyrolyzed biochar. Previous studies have demonstrated that the sorption capacity of biochar increases with higher pyrolysis temperatures, with biochar produced at 600°C exhibiting the highest sorption capacity compared to those made at 300°C, 400°C and 500°C. Consequently, phosphorus sorption was greater with biochar that had undergone using higher pyrolysis temperatures.

The resulting correlation coefficient aligns well with the particle diffusion model, which describes the movement of phosphate molecules from areas of higher concentration to areas of lower concentration, following a concentration gradient until uniform distribution is achieved. This model suggests that the adsorption mechanism operates through diffusion; wherein the pollutant molecules enter the interior of the adsorbent from the solution. The adsorption process involves four stages: the movement of pollutant molecules towards the surface of the biochar, diffusion in the boundary layer and across the surface, and diffusion of phosphate into the interior of the adsorbent. These findings were further confirmed by Langmuir and Freundlich simulations, which indicated a maximum phosphorus adsorption capacity (q_e) of 12.63 mg/g when utilizing biochar pyrolyzed at 600°C was used (1 Table). The coefficients calculated from these models serve as important indicators of adsorption efficiency, particularly at an initial phosphorus concentration of 30 mg/l.

The Langmuir coefficients (K_L) is a critical indicator for evaluating the adsorption process, as it reflects the uniformity of adsorption across the surface area. In this study, the K_L values ranged from 0.13 to 0.15. Additionally, the Freundlich constant (1/n) also indicates the adsorption capacity and intensity. When the values of the *1/n* constant fall between 1 and 2, it suggests that the phosphorus adsorption capacity is moderate and more efficient with biochar produced at higher pyrolysis temperatures. The Freundlich constant (K_F) values were found to range from 1.48 to 1.51 (Almanassra et al. 2021, Jung et al. 2017, Li et al. 2019, Liu et al. 2020, Ma et al. 2020, D. Zhang et al. 2021).

Removal efficiency

A comparison of two initial phosphate concentrations and biochar samples pyrolyzed at four different temperatures was conducted to evaluate the relationship between the efficient use of biochar and the reduction of phosphate concentration in wastewater. Original sewage sludge biomass was selected as the control for producing biochar samples. The efficiency of PO$_4^{3-}$-P removal varied with different pyrolysis temperatures. The results of the batch experiment, shown in Figure 5, indicated a phosphorus removal efficiency of 9.8% at an initial concentration of 50 mg/l. Among all four biochar samples, the lowest removal efficiencies were observed for the biochar produced at 300 °C PSSB (9.8% phosphorus removal efficiency at an initial phosphorus concentration of 50 mg/l in the solution) and at 400 °C (9.75% phosphorus removal efficiency at 50 mg/l).

Additionally, when the concentration in the solution was 100 mg/l, the removal efficiencies were also low. The efficiency of this wastewater treatment may have been influenced by the incomplete conversion of organic compounds to carbon during the pyrolysis process at 300 °C and 400 °C. Moreover, many researchers note that PSSB produced at low temperatures tends to retain higher levels of total organic carbon (as demonstrated in this study) and nitrogen content. However, it may contain lower levels of Na, K, and P elements (Khanmohammadi et al., 2015), which could have influenced the lower pollutant adsorption process.

During a batch adsorption experiment, direct mixing occurred between the pyrolyzed sewage sludge biochar (PSSB) at 600 °C and the wastewater. This resulted in a relatively low phosphate removal efficiency of only about 18% when the initial phosphorus concentration was 100 mg/l. Similarly, at an initial phosphorus concentration of 50 mg/l, the phosphorus removal efficiency using PSSB at 600 °C reached 17%. However, these results are not high compared to other research experiments, where phosphate adsorption using various types of biochar typically reaches up to 30% (Li et al. 2019). Additionally, modified biochar has demonstrated a significant enhancement in pollutant sorption capacity compared to non-modified biochar, as reported by Jung et al. 2017, Li et al. 2019, Liu et al. 2020, Ma et al. 2020, Yang et al. 2018, Zhang et al. 2021.

It should be noted that there is a significant difference in the equilibrium adsorption capacity of phosphorus (q_e, mg/g) and phosphate removal efficiency (%) between the 600 °C sewage sludge biochar and the other three PSSBs (300 °C, 400 °C, 500 °C). Only the 600 °C sewage sludge biochar shows potential for wastewater treatment using the batch adsorption method.

Research conducted by other scientists confirms that using biochar pyrolyzed at higher temperatures increases the efficiency of phosphorus removal from wastewater (Jung et al. 2017, Li et al. 2019, Wang et al. 2021, Yin et al. 2019, Zhang et al. 2021). This trend provides a promising foundation for further research aimed at achieving higher removal efficiency. However, Li et al. (2019) used biochar produced at pyrolysis temperatures of 400 °C, 600 °C and 800 °C, and their findings indicated that 600 °C was the optimal temperature for phosphate adsorption and minimizing heavy metal leaching. This suggests that further increasing the pyrolysis temperature does not always lead to a steady increase in adsorption capacity.

Phosphate removal using biochar is affected by various factors, including surface area, zeta potential value, and mineral composition (Almanassra et al. 2021). As a result, the conclusions of the batch experiment require further experimental studies to validate the results. Most researchers believe that phosphate adsorption in biochar is primarily due to the presence of elements such as Mg, Ca, Fe, or Al on the biochar surface (Almanassra et al. 2021).

Phosphate adsorption during the fixed-bed column process results

Three different sewage sludge biochar samples (400 °C, 500 °C, and 600 °C) were used in this experimental study to remove phosphates from phosphate solution using a fixed-bed column process. Initial phosphate concentrations in the water were 30 mg/l of PO_4^{3-}-P.

Figures 6 and 7 show that sewage sludge biochar as a filler effectively adsorbed PO_4^{3-}-P from the prepared solution. Filtration through the biochar filler had a positive impact on pollutant removal, with particularly good results observed in the first two hours. After filtering 15 l of solution, the adsorption efficiency of the sewage sludge biochar began to decrease, showing signs of saturation within a few hours. As noted by Mekonnen et al. (2021), that the adsorption capacity of biochar gradually becomes "full", leading to a decline in efficiency over time. The highest phosphate removal efficiency was achieved

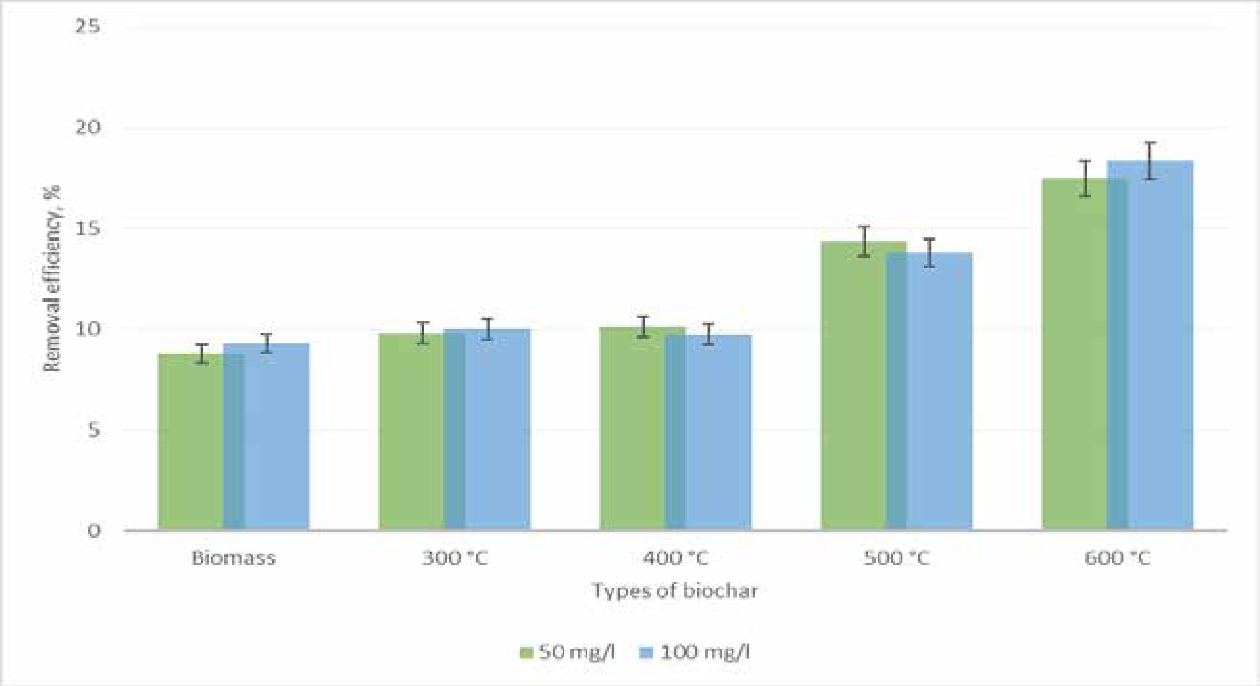

Figure 5. Phosphate removal efficiency (%) on the different PSSBs when the initial concentration of phosphate was 50 mg/l and 100 mg/l (the lines above each column represent significant differences at $p < 0.05$)

after 30 minutes of filtration (400 °C – 44%, 500 °C – 71%, 600 °C – 90%). Minimal efficiency value was observed after 10 hours, likely due to the biochar reaching its adsorption limit earlier. In addition, Figure 6 shows the change in phosphate adsorption as a function of contact time. The experiment continued for up to 34 hours, with a slight increase in removal efficiency (%) after 11 hours and a reduction in phosphate concentration (mg/l) after filtering 13 l of water Figs 6 and 7).

In a study aimed at improving phosphorus removal in a stationary column process, we observed pollutant removal in all three filters, where different sewage sludge biochars were used. Our findings showed that phosphorus removal efficiency declined after 10 hours in all three columns. This suggests that after 12 hours, the biochar of differently pyrolyzed sludge does not affect the phosphorus removal efficiency and sorption balance in these studies. Other researchers have noted that fixed-bed systems never reach proper sorption equilibrium. As the solution passes through the loading layer, it continually encounters fresh adsorbent, attempting to establish new adsorption equilibrium. However, due to limited contact time in the fixed-bed column, proper equilibrium is never fully achieved (Deng et al. 2014).

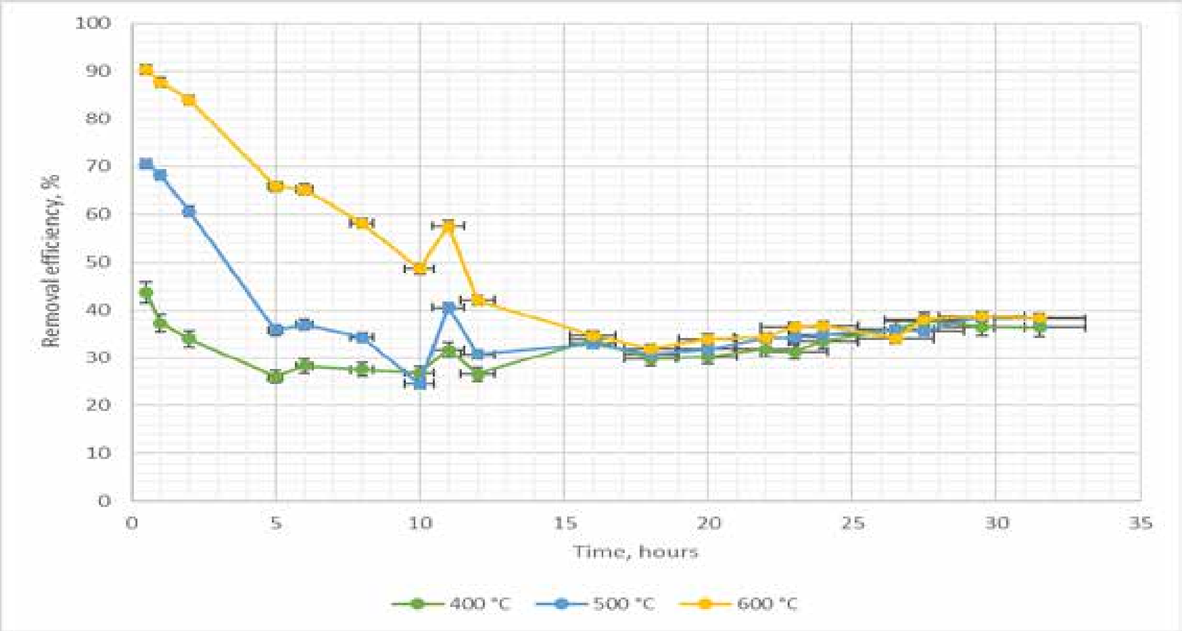

Figure 6. Removal efficiency (%) of phosphate (PO_4^{3-}-P) from solution using the fixed-bed method and different sewage sludge biochar samples (the lines above each point represent significant differences at $p < 0.05$)

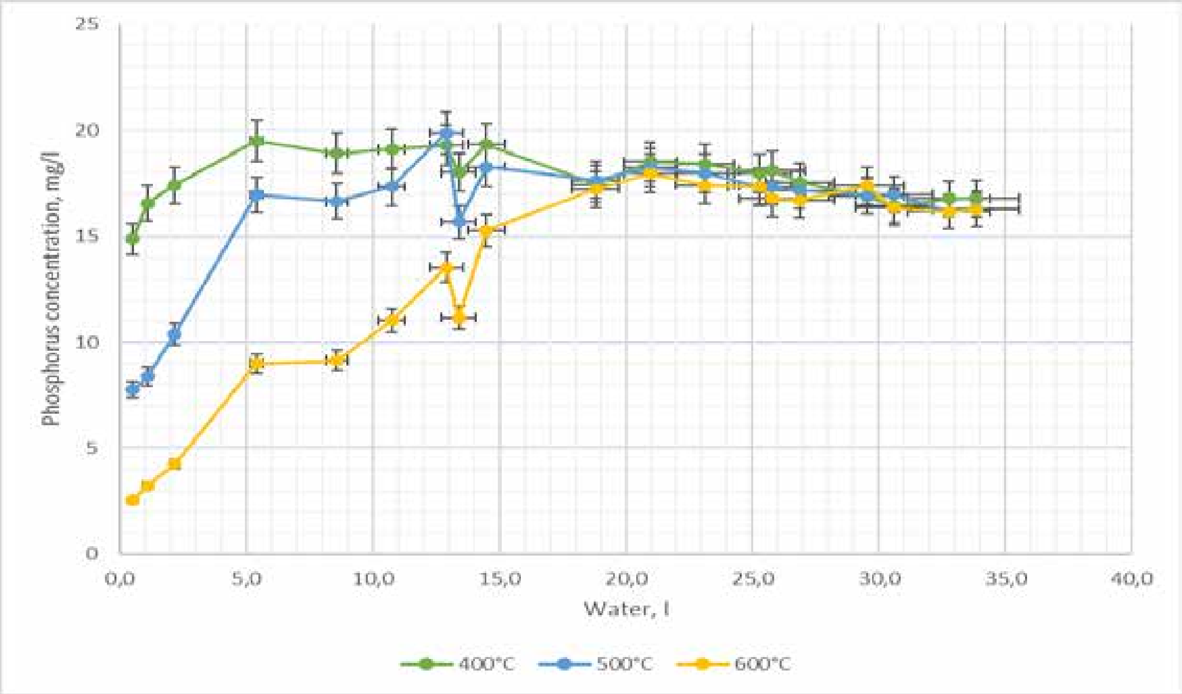

Figure 7. The concentration of phosphate (PO_4^{3-}-P) during the fixed-bed process using different sewage sludge biochar samples (the lines above each point represent significant differences at $p < 0.05$)

It was observed that the adsorption rate gradually decreased and eventually stabilized, though equilibrium was not achieved within the experimental timeframe. This may be a limitation of the study, possibly due to an insufficient volume of solutions or an excessively fast wastewater flow rate.

Using three different pyrolyzed sewage sludge biochars as a filler, the initial removal efficiency of phosphate phosphorus varied significantly across the different biochar temperatures (Figure 7). The difference was evident only at the beginning of the process. However, after filtering about 16 l of contaminated wastewater, the phosphorus concentration and removal efficiency converged to approximately 16 mg/l, and this trend continued until the end of the experiment. Even the biochar pyrolyzed at 600°C, with its higher adsorption capacity, eventually achieved the same phosphorus removal efficiency as the other biochars. Only the 600 °C biochar maintained more than 50% removal efficiency during the first ten hours, whereas the 400 °C biochar never reached 50% efficiency at any point during this study.

Other research has also concluded that higher pyrolysis temperatures result in greater removal efficiencies when using biochar as a filler in the filtration process (Deng et al. 2014; Jourak et al. 2011; Jung et al. 2017; Mekonnen et al. 2021; Nguyen et al. 2015). These findings align with trends observed in other experiments, providing a positive outlook for further research. For example, recent studies on sewage sludge biochar have primarily focused on two aspects: first, improving the adsorption performance of sludge biochar through structural enhancements and other methods; second, enhancing the catalytic ability of sludge biochar in advanced oxidation processes via modification techniques such as heteroatom doping (Lv et al. 2023).

Given the potential of sewage sludge biochar, its high removal efficiency offers promise for its application in wastewater treatment plants through the implementation of a filtration process (Jourak et al. 2011). However, the high removal efficiency of sewage sludge biochar is sustained for only a short period (approximately 5 hours). This presents a significant limitation, as the frequent need to replace the biochar every 5 hours would not be efficient or practical in a wastewater treatment plant.

According to the results, the phosphate removal efficiency was excellent, as anticipated. The type of biochar used plays a crucial role in this process, with sewage sludge biochar pyrolyzed at 600 °C demonstrating the best phosphate removal performance, likely due to the advantages of high pyrolysis temperatures. This type of biochar has a great capacity for phosphate adsorption. Research has shown that using modified biochar in fixed-bed processes can lead to even better results. Most researchers have observed that modified biochar demonstrates a higher PO_4^{3-}-P adsorption capacity than unmodified biochar (Almanassra et al. 2021, Deng et al. 2014, Jung et al. 2017, Li et al. 2019, Liu et al. 2020, Ma et al. 2020, Yang et al. 2018, D. Zhang et al. 2021, Y. Zhou et al. 2017). Modifications to biochar can involve the addition of metals (Huang et al. 2022, Ma et al. 2020, Yang et al. 2018) or other substances and salts (Jung et al. 2017, Li et al. 2019, Liu et al. 2020, D. Zhang et al. 2021). This trend provides a promising foundation for further research aimed at achieving higher removal efficiencies by changing the physicochemical properties of biochar, including its structure.

Conclusions

In a batch adsorption experiment, the highest removal efficiency was achieved with 600 °C sewage sludge biochar, showing a phosphate removal efficiency of 17% at an initial P concentration of 50 mg/l and 18% at 100 mg/l.

Among all four biochar samples tested in the batch adsorption experiment, the lowest phosphate removal efficiency was observed with sewage sludge biochar pyrolyzed at 300 °C, achieving a removal efficiency of 9,8% at an initial P concentration of 50 mg/l and 9.75 % at 400 °C with an initial P concentration of 100 mg/l.

Sewage sludge biochar pyrolyzed at 400 °C exhibited an average equilibrium adsorption capacity of 7.23 mg/g after 240 min (4 hours) of contact time. However, extending the shaking duration to 480 min (8 hours) increased the adsorption capacity to its maximum value of 9.98 mg/g.

During the fixed bed column process, the highest phosphate removal efficiency was observed after 30 min of filtration: 44% for PSSB at 400 °C, 71% for PSSB at 500 °C, and 90% for PSSB at 600 °C. This indicates that the most effective removal efficiency was achieved using sewage sludge biochar pyrolyzed at 600 °C.

This research showed that phosphorus removal efficiency decreased after 12 hours in all three columns. This indicates that, beyond 12 hours, the differently pyrolyzed biochars do not significantly affect the phosphorus removal efficiency or sorption balance.

Both the batch adsorption experiment and the fixed-bed column process revealed a trend of increasing removal efficiency with higher pyrolysis temperatures. This finding provides a solid foundation for further research aimed at achieving better removal efficiency results.

Our fixed-bed column research showed that phosphorus removal efficiency decreased after 10 hours in all three columns. This suggests that, beyond 10 hours, the differently pyrolyzed biochars do not affect phosphorus removal efficiency or sorption balance. This may represent a limitation of this study, as the selected solution volume may have been insufficient, or the wastewater flow rate may have been too fast.

In both the batch adsorption experiment and the fixed-bed column process, it was observed that using pyrolyzed biochar at higher temperatures increased phosphate removal efficiency from wastewater. This trend provides a solid foundation for further research aimed at enhancing removal efficiencies by modifying the physicochemical properties of biochar, such as its structure.

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