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An Investigation of the Batch Adsorption Capacity for the Removal of Phosphate from Wastewater Using Both Unmodified and Functional Nanoparticle-Modified Biochars

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Abstract: One of the most widely employed methods for adsorption is the utilization of biochar produced during pyrolysis. Biochar has attracted considerable attention due to its oxygen-containing functional groups and relatively high specific surface area. In alignment with the principles of cleaner production, the sludge generated from sewage treatment plants is typically classified as waste. However, it can be effectively repurposed as an adsorbent following pyrolysis and subsequent nanoparticle modification. This environmentally friendly approach presents an ecological alternative to conventional water treatment methods. The objective of this study is to evaluate the efficiency of batch adsorption for the removal of phosphate from wastewater using both unmodified and modified sewage sludge biochars (SSBs) that were produced at various temperatures (300 °C, 400 °C, 500 °C, and 600 °C) and modified with zero-valent iron nanoparticles (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600). The findings indicate that biochar modified with functional nanoparticles is a highly effective adsorbent for the removal of phosphate from wastewater. As demonstrated by the research results, the adsorption capacity of modified biochar is approximately 3 to 3.5 times greater than that of the unmodified variants. The phosphate removal efficiency with modified biochars was optimal with nZVI-SSB600. In experiments with a phosphate concentration (25 mg/L), the modified sorbent biochar exhibited an equilibrium adsorption capacity of 23.74 mg/g, translating to a phosphate removal efficiency of 60%. Under similar test conditions, at an initial phosphate concentration of 50 mg/L, the adsorption capacity improved to 25.67 mg/g (75% efficiency); at 75 mg/L, it reached 27.97 mg/g (80%); at 100 mg/L, it was 28.44 mg/g (85%); and at 125 mg/L, it achieved 29.48 mg/g (89%). The models confirmed the observed adsorption behavior, yielding a maximum phosphate adsorption capacity (q_e) of 19.00 mg/g for the 600 °C pyrolysis of modified biochar at the primary phosphate concentration (25 mg/L). Furthermore, this study indicates that the influence of solution pH on phosphate adsorption remains stable and maximal (nZVI-SSB600, ranging from 16.87 to 20.46 mg/g) within the pH range of 3 to 8. On average, the modified biochar (nZVI-SSB) demonstrated 20 to 30% superior adsorption performance compared to the unmodified biochar (SSB). Additionally, significant differences were noted between various ambient temperatures, ranging from 5 °C to 25 °C. As the ambient temperature increased, the sorption capacity of the adsorbent exhibited a considerable improvement. With a primary concentration of phosphate (100 mg/g) at 5 °C, the adsorption capacity of nZVI-SSB600 was measured at 7.99 mg/g; this increased to 14.33 mg/g at 10 °C, 21.79 mg/g at 20 °C, and 28.44 mg/g at 25 °C. This research highlights the potential application of biochar in wastewater treatment for phosphate removal, simultaneously enabling the effective utilization of generated sewage sludge waste through pyrolysis and coating with zero-iron nanoparticles, resulting in a sustainable solution.

Keywords: wastewater; removal of phosphate; modified biochar of sewage sludge; functional nanoparticle-coated biochar; zero-valent iron nanoparticles; batch adsorption; adsorption capability



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1. Introduction

Improper human activities have resulted in elevated levels of phosphorus in both surface and groundwater, which subsequently contributes to the eutrophication of aquatic ecosystems. This situation presents a significant threat to the health of ecosystems and human well-being. Researchers are actively developing and implementing various purification methods to mitigate these environmental challenges. These include techniques such as filtration, reverse osmosis, biological and chemical purification methods, ion exchange, membrane filtration, aerobic and oxic processing utilizing phosphorus-accumulating organisms, and the deposition of phosphorus through metals or metal oxides [1].

Several previously discussed methods of water treatment exhibit both advantages and disadvantages. Implementing biological processes for water treatment poses certain risks, as these methods can be challenging to manage and control, often leading to substantial fluctuations in phosphorus concentrations within the wastewater. While chemical water treatment is highly effective in phosphate removal, it may introduce additional anions into the cleaning solution due to various chemical reactions, potentially resulting in unforeseen chemical processes. Among the diverse array of phosphate removal technologies, adsorption is frequently viewed as a viable and significant approach due to its simplicity, durability, and cost-effectiveness [2–11].

In the last decade, the utilization of biochar obtained through pyrolysis has emerged as a prominent method for adsorption. Biochar has garnered significant attention due to its oxygen-containing functional groups and remarkably high specific surface area. Numerous studies have demonstrated that biochar is an effective adsorbent for removing contaminants from wastewater. The isoelectric point of biochar lies between 2 and 3.19, which affects its interaction with phosphates that possess a negative charge at various pH levels. Consequently, the capacity of biochar to adsorb phosphates is limited by its weak electrostatic forces. Therefore, modifying biochar is essential to alter its surface charge characteristics, enhancing its phosphate adsorption capacity. This fundamental principle improves biochar's adsorption properties through nanoparticle treatment, increasing adsorption efficiency. Different nano-metal oxide/hydroxide–biochar composites, such as MgO, MgCl₂, ZnCl₂, CaCl₂, and KMnO₄, have been employed to remove phosphates from wastewater effectively. A notable advancement in phosphate water purification is the application of nano-scale zero-valent iron (nZVI). These nanoparticles are recognized for their substantial active surface area, high diffusion activation energy, and significant quantum effects [12]. Their effective application, achieving removal rates of up to 99%, has been reported in the cleaning processes of contaminated water (with antibiotics, organochlorine substances, and heavy metals) [13]. This indicates that the processes of pollutant adsorption are significantly enhanced in the presence of zero-valent iron nanoparticles [14]. Furthermore, modifying biochar with iron nanoparticles may inhibit particle aggregation and enhance reactivity. This method can potentially increase the number of reaction sites, subsequently improving the capacity for pollutant adsorption over time [15]. However, it is important to acknowledge that further research is needed to verify these potential benefits thoroughly.

In alignment with cleaner production principles, the sludge generated from sewage treatment plants is typically regarded as waste. However, this material can be utilized more effectively as an adsorbent through pyrolysis followed by nanoparticle modification. This environmentally sustainable approach presents a viable ecological alternative to traditional water treatment methods. The general aim was to analyze the batch adsorption for the removal of phosphate from wastewater using unmodified SSB and modified zero-valent iron nanoparticle sewage sludge bio-solids (nZVI-SSB) produced at various temperatures of 300 °C, 400 °C, 500 °C, and 600 °C. The current study examined the relationship between adsorption capacity and several variables, including contact time of the wastewater solution (120 min, 240 min, 360 min, and 480 min), varying pH levels (2, 4, 6, 8, and 10), ambient temperature conditions (5 °C, 10 °C, 20 °C, and 25 °C), and different initial concentrations of phosphate (25 mg/g, 50 mg/g, 75 mg/g, 100 mg/g, and 125 mg/g). The adsorption kinetics,

isotherm parameters, and phosphate adsorption capacity (q_e , mg/g) were determined based on the experimental findings.

Biochar (such as those made from biomass, municipal waste, field residues, and animal waste) has recently attracted much scientific interest in environmental protection for treating phosphorus in wastewater. This wide acceptance of biochar in environmental applications is due to its relatively high surface area, good texture, and high porosity as a sorbent. Despite these properties, biochar has disadvantages, such as limited anion sorption capacity and poor mechanical properties [11–15]. On this basis, to avoid the drawbacks mentioned above of biochar, this paper focuses on the complex aspects of biochar research as a sorbent: that is, how the efficiency of phosphate removal depends on unmodified and modified biochar, the removal efficiency of phosphate under the different effects of the contact time, the effect of pH on the adsorption of phosphate by modified biochar, and the impact of various ambient temperature values of the solution on the sorption of phosphate. The results and discussion section provide further details of the mentioned research aspects.

2. Materials and Methods

2.1. The Preparation of Sewage Sludge (SS)

Sewage sludge, prepared for subsequent analyses, was collected on 20 September 2023, from the Vilnius Sewage Treatment Plant, situated in Vilnius, the capital of the Republic of Lithuania. This largest wastewater treatment plant generates about 20–25% of the country's sewage sludge, about 30,000 tonnes of dried sludge, and about 9000 tonnes of solids when the waste is finally dried using special equipment. Sewage sludge (SS) was formed due to the deposition of solids from wastewater during treatment. In the sewage treatment plant, SS is usually broken down and dried (to 75% moisture content) until gray granules are formed. The sewage sludge pellets were subsequently dried to a constant mass at 100 °C, and the moisture content of the resulting raw material was determined through weight loss, yielding a value of $4.2 \pm 0.1\%$. Biochar was produced via pyrolysis in a controlled furnace setting. During the pyrolysis processes, a nitrogen flow rate of 2 L/min was maintained. A sample of 30 g of pelleted sewage sludge was placed in a test container without an aluminum foil lid. The pyrolysis was conducted at four distinct temperatures: 300 °C, 400 °C, 500 °C, and 600 °C. The temperature range was selected based on the assumption that higher temperatures can enhance the phosphate removal efficiency. However, as the energy consumption will also increase, this study was performed up to 600 °C only.

Repeating the procedure, a substantial quantity of pyrolyzed sewage sludge biochar (SSB), approximately 100 g, was obtained. The heating rate was estimated to be between 12 and 13 °C per minute. Before the utilization of the SSB, the sludge underwent grinding. For the initial method of phosphate adsorption, biochar samples derived from the sewage sludge were ground and subsequently sieved through a 100 µm mesh size. Following this process, samples of SSB were further sifted to achieve a diameter of 1–1.6 mm.

2.2. The Process of Preparing Sewage Sludge Modified with Zero-Valent Iron Nanoparticles (nZVI-SSB)

The nZVI-SSB materials were synthesized at temperatures of 300 °C, 400 °C, 500 °C, and 600 °C using a liquid-phase method. A total of 12.44 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 250 mL of deionized water. Subsequently, the SSB was dispersed in this solution and stirred for one hour. Following this, 250 mL of a NaBH_4 solution (0.55 mol/L) was added to the mixture. All procedures were conducted in an inert nitrogen atmosphere. The prepared suspension was then filtered using a vacuum pump, and the solid was washed three times with 300 mL of ethanol before being dried under vacuum. The final material was stored in a sealed glass bottle and protected with nitrogen to prevent oxidation (Figure 1).

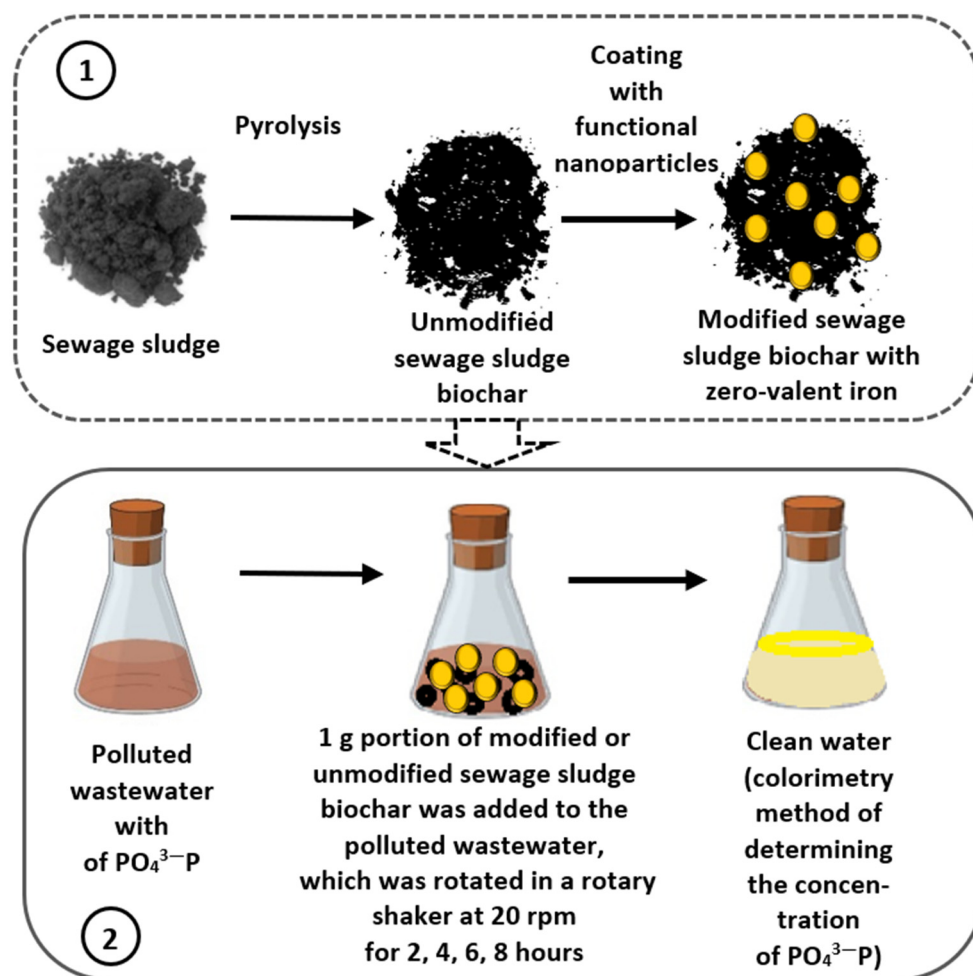


Figure 1. Scheme for removing phosphate from wastewater using both unmodified and modified biochars integrated with functional nanoparticles: 1—preparation of modified sewage sludge containing zero-valent iron nanoparticles; 2—execution of the batch adsorption experiment.

The elemental and compositional formulas of modified and unmodified biochar were determined using several methods. These included a scanning electron microscope (SEM), X-ray diffraction (XRD) with an FEI Helios Nanolab 650 (650, FEI, Hillsboro, OR, USA) dual-beam system, infrared spectroscopy (FTIR) using FTS 3000MX FT-IR spectrometer (Varian Instruments, Randolph, MA, USA), for specific surface area and pore distribution using a Quanta chrome Autosorb-iQ-KR/MP analyzer (Autosorb-iQ, Quantachrome Instruments Japan GK, Kanagawa, Japan), and the pore size distribution using the QSDFT technique.

2.3. The Assessment of pH in Phosphate Solutions

To assess the pH levels of the samples, 1 g of SSB and nZVI-SSB was collected at various temperatures (300 °C, 400 °C, 500 °C, and 600 °C) and subsequently combined with 20 mL of deionized water. Initial phosphate concentrations of 25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, and 125 mg/L were incorporated into the prepared solutions, which were adjusted to different pH levels (2, 4, 6, 8, 10). The mixtures were incubated for 24 h in a shaker (Barnstead Thermolyne Big Bill Digital Orbital Shake Model 73625 (American Laboratory Trading, East Lyme, CT, USA)) at approximately 50 rpm. Afterward, samples, along with CaCl_2 and deionized water, were filtered using a filter with a porosity of $<0.45\ \mu\text{m}$ and the pH of each sample was subsequently measured using a pH meter (Hanna pHep[®] Pocket pH tester (Hanna HI 98108, Merck Life Science Sp.z.o.o., an affiliate of Merck KGaA, Darmstadt, Germany)). Phosphate concentration was measured employing

the colorimetric method, utilizing the KFK-2 photoelectric colorimeter (Zagorsk Optical-Mechanical Plant, Sergiyev Posad, Russia) for accurate quantification.

2.4. The Study of Batch Adsorption Processes Concerning Phosphate

This experimental study was conducted using artificially polluted deionized water with varying concentrations of phosphates. The levels of pollutants measured exceeded all permissible limits set for wastewater (refer to Figure 1). In this investigation, a mixing method was employed to assess the potential adsorption of phosphates onto biochar. This experiment was conducted utilizing a specified amount (g) of SSB and nZVI-SSB at varying temperatures of 300 °C, 400 °C, 500 °C, and 600 °C, along with different phosphate concentrations of 25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, and 125 mg/L. The range of initial phosphate concentrations selected for this study was determined based on realistic environmental conditions. However, we anticipate future investigations involving increased initial phosphate concentrations. Potassium dihydrogen orthophosphate (KH_2PO_4) was dissolved in deionized water to prepare the required phosphate solution. All the experiment's chemicals, reagents, and mixtures adhered to high analytical quality standards. The mixing process was conducted using a Gerhardt Laboshake rotary shaker, capable of accommodating up to 12 analytical bottles concurrently.

A quantity of 1 g of various types of biochars (SSB300, SSB400, SSB500, SSB600, nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, nZVI-SSB600) was introduced to a series of phosphate solutions prepared at concentrations of 25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, and 125 mg/L. The phosphate adsorption experiment was selected based on various mixing times of the solutions (120, 240, 360, and 480 min) and was conducted at different temperatures (5 ± 0.5 °C, 10 ± 0.5 °C, 20 ± 0.5 °C, and 25 ± 0.5 °C). This temperature range was chosen to reflect realistic conditions for wastewater treatment. However, plans for future research at elevated temperatures are also anticipated. Subsequently, the prepared solution was agitated in a rotary shaker at a speed of 20 rpm. Following this step, samples were filtered using gravity filtration followed by a <0.45 μm filter. The concentration of phosphate was then assessed utilizing colorimetric analysis. The colorimetry method was employed for the determination of concentration levels of $\text{PO}_4^{3-}\text{-P}$:

1. Combine 5 mL of the water sample with 0.2 mL of the analytical solution.
2. The sample is positioned in a spectrophotometer for analysis with a 700–725 nm wavelength (this interval is due to other interference pollutants present in the SSB) [16,17].
3. The results for absorption are derived by multiplying the $\text{PO}_4^{3-}\text{-P}$ concentration by 18.

The average experimental results were derived from three replicates of each treatment condition and are presented as the mean $\pm$ standard deviation. Data analysis was conducted using variance analysis, with a significance threshold set at a p -value of less than 0.05. The analysis aimed to identify any significant differences in the adsorption capacity of pyrolyzed sewage sludge biochar with varying phosphate concentrations and pH values.

2.5. Computations and Modeling

To evaluate the adsorption efficiency of pyrolyzed and modified sewage sludge biochar (SSB, nZVI-SSB) concerning phosphates ($\text{PO}_4^{3-}\text{-P}$), two key indicators were selected: the equilibrium adsorption capacity (q_e , mg/g) and the removal efficiency (E , %). The quantity of phosphate adsorbed by biochar at equilibrium was determined using the following equation:

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

In the equation, q_e (mg/g) denotes the equilibrium adsorption capacity, defined as the amount of adsorbate adsorbed per gram of biochar. The variable V represents the volume of the solution in liters, while C_0 and C_e indicate the initial and final concentrations of the adsorbate in milligrams per liter, respectively. Additionally, m refers to the weight of the biochar adsorbent (SSB, nZVI-SSB) in grams [18].

By utilizing the initial and final phosphate concentrations in the solutions, the removal efficiency (E , %) was calculated using the specified Equation (2):

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) denote the initial and final concentrations of the adsorbate in milligrams per liter, respectively, and m signifies the mass of the biochar adsorbent (SSB, nZVI-SSB) in grams [19].

The relationship between sewage sludge biochars (SSBs, nZVI-SSBs) and phosphate removal efficiency was analyzed using experimental measurements and models. The Freundlich isotherm and the Langmuir model were employed to analyze the interaction between biochar (solid matter) and phosphate molecules [20]. This analysis can be correlated with the adsorption capacities of various types of biochars that were pyrolyzed at the following temperatures: 300 °C, 400 °C, 500 °C, and 600 °C, including SSB and nZVI-SSB.

The kinetic parameters for the adsorption of phosphate onto SSB and nZVI-SSB are provided for the pseudo-first-order (Equation (3)) and pseudo-second-order models (Equation (4)):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

In this context, q_t and q_e (mg/g) represent the amounts of phosphate adsorbed at time t (h) and at equilibrium, respectively. The constants k_1 (1/h), k_2 (g/mg h), and k_d (g/mg 0.5 h) correspond to the pseudo-first-order, pseudo-second-order, and intra-particle diffusion rate constants, respectively.

The experimental results of these isotherms are presented for the Langmuir (Equation (5)) and Freundlich models (Equation (6)):

$$q_e = q_m K_L C_e / (1 + K_L b C_e) \quad (5)$$

$$q_e = K_F C_e^{1/n}, \quad (6)$$

In this context, q_m (mg/g) denotes the maximum adsorption capacity at a given time; C_e (mg/L) indicates the concentration of phosphorus in the solution at equilibrium; K_L and K_F are the constants associated with the Langmuir and Freundlich adsorption isotherms, respectively; and n represents the linearity constant within the Freundlich model [18,21].

The average results of the experiments were calculated from three replicates for each experimental treatment and are presented as the mean $\pm$ standard deviation. Data analysis was conducted using variance analysis, with a significance threshold set at a p -value of less than 0.05. The study aimed to assess whether there are significant differences in the adsorption capacity of pyrolyzed sewage sludge biochar (SSB and nZVI-SSB) with varying phosphate concentrations and pH values.

3. Results and Discussion

3.1. The Characterization of SSB and nZVI-SSB

Based on the X-ray diffraction (XRD) analysis of the nZVI-SSB, the peak at 30° is more intense, and there is a higher production of zero-valent iron ions. As shown in Figure 2, the more the biochar has been pyrolyzed at a higher temperature, the higher its intensity is. In this case, this is reflected by the biochar modified with iron nanoparticles at 600 °C and zero valence. The intensity peak of this biochar is fixed at 45°.

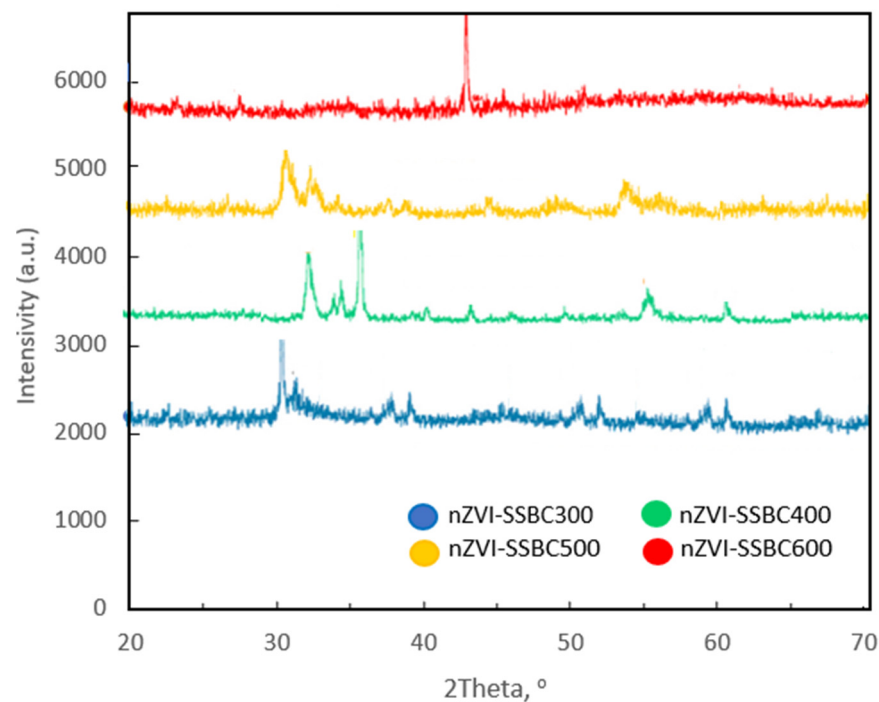


Figure 2. XRD (X-ray diffraction) patterns of pyrolyzed (at 300 °C, 400 °C, 500 °C and 600 °C) and with zero-valent iron nanoparticle-modified (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) biochars.

Fourier transform infrared (FTIR) spectra analysis of pyrolyzed (at 300 °C, 400 °C, 500 °C, and 600 °C) and zero-valent iron nanoparticle-modified (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) biochars was performed. FTIR analysis was performed. As shown by the results of these studies (Figure 3), the functional groups' wavelength range of synthesized materials from 500 to 4000 cm^{-1} was established. The most intense stretching and bending vibration curves were recorded from 500 to within 1500 cm^{-1} ; after that, it practically did not change. The stretching and bending vibration curves shown in the figure represent the electrons of the atoms formed during the chemical reactions, which have formed the existing chemical bonds, such as carbon bonding with oxygen, hydrogen, or an aromatic ring.

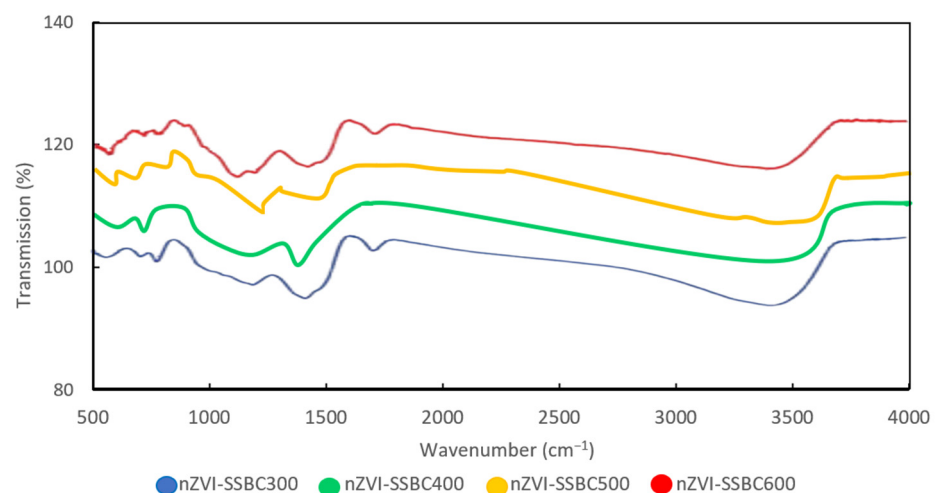


Figure 3. FTIR (Fourier transform infrared) spectra of pyrolyzed (at 300 °C, 400 °C, 500 °C and 600 °C) and zero-valent iron nanoparticles-modified (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) biochars.

The surface morphology and microstructure of the unmodified SSB and the modified with zero-valent iron nanoparticles nZVI-SSB were analyzed using SEM (Figure 4). Both modified and unmodified biochars have irregular shapes, porous structures, and uneven surfaces. After the adsorption, the modified biochar had more micropores and a more porous surface. This is reflected in the elemental and compositional formula of the modified (nZVI-SSB) and unmodified biochar (SSB) presented in Table 1, where the properties of modified char (total pore volume (cm^3/g), average pore size (nm), specific surface area (cm^2/g)) in sorption processes are significantly better than those of unmodified char.

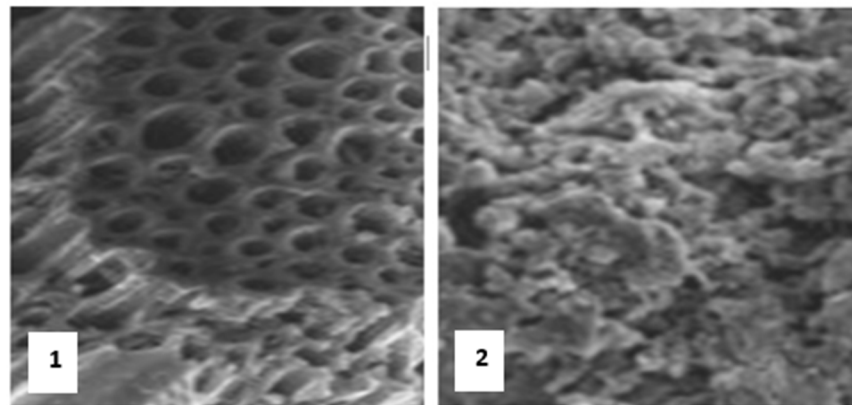


Figure 4. SEM images of sewage sludge biochar samples (pyrolyzed at 600 °C): 1—the unmodified SSB600 at 100× magnification; 2—the modified with zero-valent iron nanoparticles nZVI-SSB600 after the adsorption at 100× magnification.

Table 1. The elemental and compositional formula of the modified (nZVI-SSBs) and unmodified biochars (SSBs).

Adsorbents	C (%)	H (%)	N (%)	Fe (%)	Total Pore Volume (cm^3/g)	Average Pore Size (nm)	Specific Surface Area (cm^2/g)
nZVI-SSB	48.67	3.05	0.55	10.89	0.095	11.5	35.55
SSB	67.45	3.67	0.54	0.02	0.002	5.89	1.34

By applying higher temperature pyrolysis, the amount of biochar formed decreased, its pH changed from acidic to alkaline, the specific surface area of biochar improved, the amount of oxygen functional groups decreased, the fixation of metals improved, and a stable polycyclic aromatic carbon fraction was formed from total organic carbon (TOC). In this case, it can be said that the negative impact of pyrolyzed biochar on the environment has been reduced.

The complex studies discussed in this chapter show that the sorbent materials' physical and chemical stability (significantly modified biochar) has been determined to be sufficiently high. Future research will devote more attention to the influence of different pyrolysis temperatures, selectivity experiments with other competing anions and selectivity toward phosphates, and the modifying effect of nanoparticles regarding biochar stability (the ratio O:C depends on pyrolysis temperatures). Continuing this theme, the goal must be to use sludge as waste in sorption processes to clean wastewater of phosphates, to regenerate sorbents sustainably, and to use phosphates in agriculture as fertilizers. To that end, a cost-benefit assessment of biochar will be carried out in the future using a life cycle assessment.

3.2. The Efficiency of Phosphate Removal Under Varying Contact Times with Both Unmodified and Modified Biochar Was Evaluated

This experiment was conducted to analyze the adsorption capacity concerning the contact time (ranging from 120 to 480 min) between the sewage sludge biochar and the wastewater solution. The selected range for contact time was based on realistic biochar applications. Future studies are also anticipated to explore increased contact times. The results regarding phosphate equilibrium adsorption capacity (q_e , mg/g) using various sewage sludge biochars pyrolyzed at temperatures of 300 °C, 400 °C, 500 °C, and 600 °C are presented in Figure 5. It is important to highlight that the results indicated higher equilibrium adsorption capacities associated with higher pyrolysis temperatures (300 °C to 600 °C) and for biochar modified with zero-valent iron nanoparticles. Following an experiment lasting 480 min with unmodified biochar (SSB600), the equilibrium of adsorption capacity (q_e , mg/g) was determined to be 12.63 mg/g. In contrast, under identical experimental conditions, the equilibrium adsorption capacity of biochar modified with zero-valent iron nanoparticles (nZVI-SSB600) reached as high as 20.31 mg/g. This study demonstrated that the functional nanoparticle-coated biochar was, on average, 30–38% more efficient than the unmodified biochar. Other experimental investigations corroborated that adsorption capacity increased with different sewage sludge biochar and varied with the contact duration between the biochar and sewage solution. Testing the pyrolyzed biochar at 600 °C and the modified biochar (nZVI-SSB600) revealed an 18% increase in absorption capacity over six hours (from 120 to 480 min). No significant differences ($p > 0.05$) were observed in the equilibrium adsorption capacity of phosphates (q_e , mg/g) across various pyrolyzed sewage sludge biochars at differing contact times. Additionally, other researchers have documented a similar trend in their studies [22–27]. When tested, the best equilibrium adsorption capacity results for pyrolyzed (at 300 °C, 500 °C, 700 °C, and 800 °C) and modified paper sludge biochar were obtained at five hours, showing minimal changes post that duration. Notably, the highest equilibrium adsorption capacity recorded was as much as 25 mg/g, achieved with biochar that had been previously pyrolyzed at 800 °C and modified with zero-valent iron nanoparticles [28].

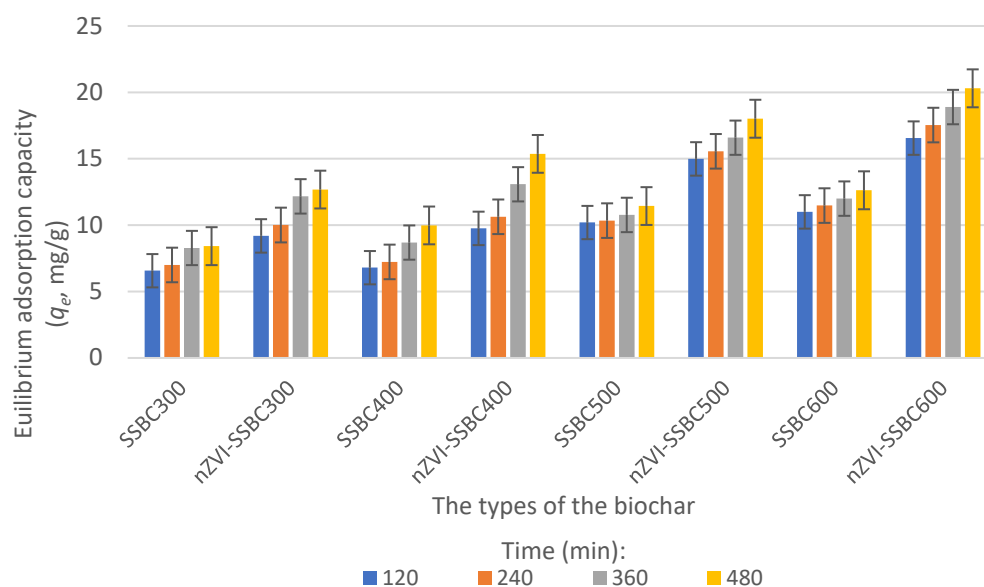


Figure 5. The equilibrium adsorption capacity of phosphates (q_e , mg/g) was evaluated utilizing various pyrolyzed sewage sludge biochars at temperatures of 300 °C, 400 °C, 500 °C, and 600 °C. The biochars were assessed in both their unmodified forms (SSB300, SSB400, SSB500, and SSB600) and in forms modified with zero-valent iron nanoparticles (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600). Different contact times were examined, with vertical bars above each column indicating significant differences at $p < 0.05$.

Based on the experimental results, functional nanoparticle-coated biochar adsorption isotherms were constructed using the Langmuir and Freundlich models (Figure 6). The observed isotherms were non-linear, indicating that the adsorption process occurred on the surface of the adsorbent, in this case, biochar. The findings demonstrated that the most effective absorption results were obtained with nZVI-SSB600, which was pyrolyzed at 600 °C and modified with zero-valent iron nanoparticles. Upon evaluating the Langmuir model results, it was determined that the adsorption capacities of nZVI-SSB300 and nZVI-SSB400 were comparable, ranging from 9.19 to 14.37 mg/g. The adsorption rate declined as phosphate ions occupied available sites on the adsorbent's surface. Furthermore, the adsorption capacity of nZVI-SSB500 recorded an increase of 3.5%, while nZVI-SSB600 exhibited a 4% higher capacity compared to the previously mentioned nZVI-SSB300 and nZVI-SSB400 biochars [29,30]. According to the scientific literature, it is observed that many biochars are not effective in removing phosphates from water due to their typically negatively charged surfaces [31–33].

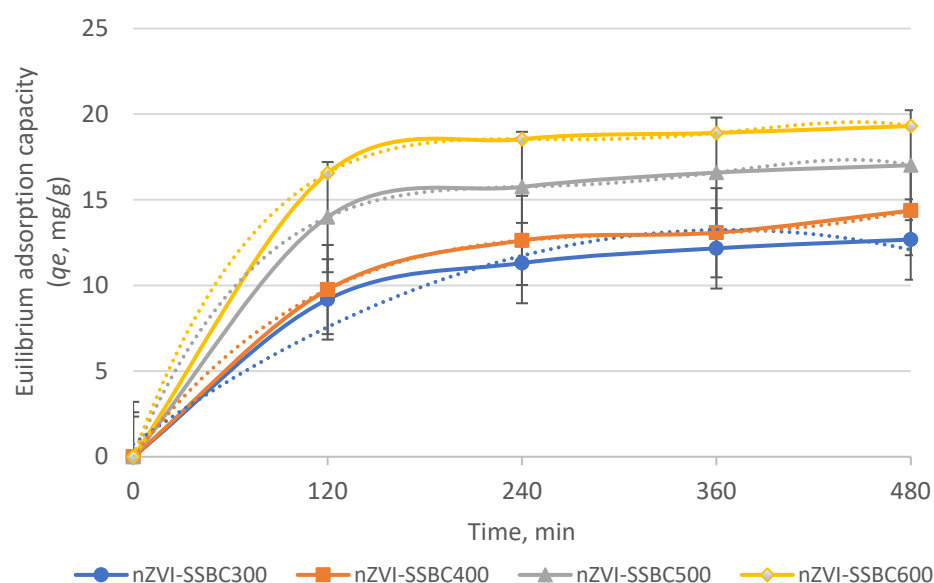


Figure 6. The isotherms of phosphates (q_e , mg/g) using various pyrolyzed biochars (300 °C, 400 °C, 500 °C, and 600 °C) and zero-valent iron nanoparticle-modified biochars (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) were assessed at different contact times. The solid lines represent the curves of the Langmuir adsorption model, while the dotted lines illustrate the Freundlich adsorption model curves. The error bars indicate $\pm$ standard errors at $p < 0.05$.

Other researchers have reported that this usually causes electrostatic repulsion between biochar and phosphate anions, which inhibits phosphate adsorption. Numerous scientists have found that biochar may contain phosphates, which can subsequently enter the treated wastewater and hinder adsorption [34–36].

As part of ongoing research, future studies will determine how long the modified biochar with zero-valent iron nanoparticles is effective. According to studies by other researchers [35], this sorbent effectively removes phosphate for up to seven adsorption and desorption cycles.

3.3. An Analysis of Phosphate Removal Efficiency by Unmodified and Modified Biochars

Phosphate removal efficiency studies in wastewater were conducted to assess the relationship between the effective use of various initial phosphate concentrations (25 mg/g, 50 mg/g, 75 mg/g, 100 mg/g, and 125 mg/g) and different pyrolyzed–modified biochars (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600). The experimental studies utilized a batch experiment method, as illustrated in Figure 7. The results demonstrated that the optimal absorption outcomes were achieved with nZVI-SSB600, which was py-

rolyzed at 600 °C and modified with zero-iron nanoparticles. With nZVI-SSB600, the equilibrium adsorption capacity for phosphates was recorded at 23.74 mg/g (corresponding to a phosphate removal efficiency of 60%) at an initial concentration of 25 mg/L; 25.67 mg/g (75%) for 50 mg/L; 27.97 mg/g (80%) for 75 mg/L; 28.44 mg/g (85%) for 100 mg/L; and 29.48 mg/g (89%) for 125 mg/L. No significant differences ($p > 0.05$) were noted in the equilibrium adsorption capacity of phosphates (q_e , mg/g) when utilizing different pyrolyzed sewage sludge biochars at varying initial phosphate concentrations (mg/L). This may be attributed to the activation of oxygen-containing functional groups present in the pyrolyzed and modified biochar, which substantially enhanced the number of active adsorbent sites and facilitated the formation of iron oxide on the surface of the studied biochar. Consequently, complexes with phosphates were generated, increasing the energy of the adsorbent (in this case, the modified and pyrolyzed biochar). No significant differences ($p > 0.05$) were observed in the equilibrium adsorption capacity of phosphates (q_e , mg/g) across the various pyrolyzed sewage sludge biochars.

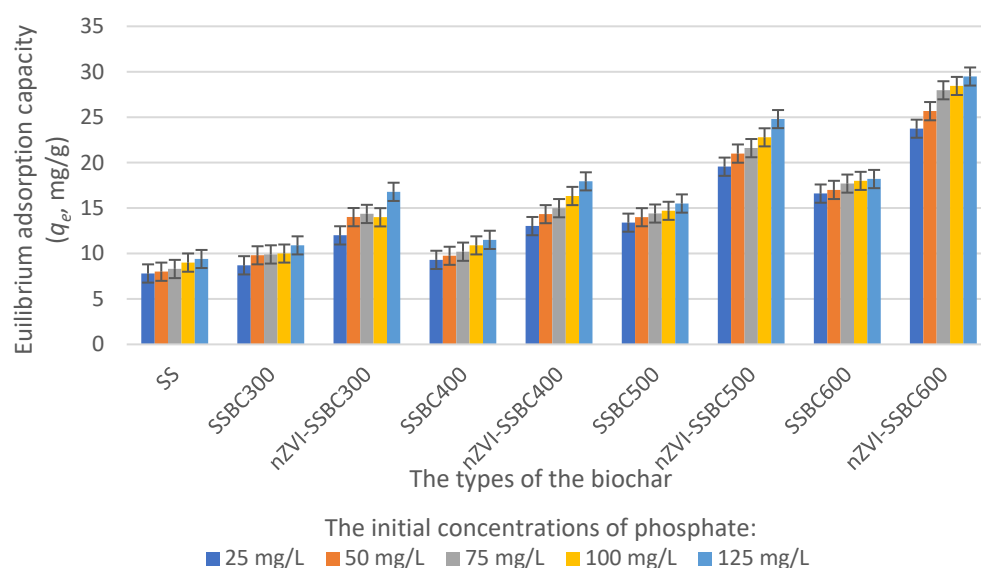


Figure 7. The equilibrium adsorption capacity of phosphates (q_e , mg/g) using different pyrolyzed 300 °C, 400 °C, 500 °C, and 600 °C sewage sludge biochars: unmodified (SSB300, SSB400, SSB500, and SSB600) and modified with zero-valent iron nanoparticles (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) at various initial concentrations of phosphate (mg/L) (the vertical bars above each column represent significant differences at $p < 0.05$).

Phosphate adsorption kinetics in modified (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) and unmodified (SSB300, SSB400, SSB500, and SSB600) biochars were validated through the models presented in Table 2. The calculated coefficients from these models serve as critical indicators of adsorption efficiency at an initial phosphate concentration of 25 mg/L. Analysis of the regression coefficients (R^2) indicates that the pseudo-second-order model is more suitable than the pseudo-first-order model. This conclusion suggests that the adsorption equilibrium capacity derived from the pseudo-second-order kinetic model closely aligns with the experimental adsorption values. Furthermore, the intra-particle diffusion model posits that the phosphate adsorption rate is a primary factor influencing phosphate adsorption on both modified and unmodified biochars. As detailed in Table 1, the phosphate adsorption process exhibited greater intensity, as evidenced by the k_1 values being higher than k_2 values. Consistent with findings from researchers such as Ahmed et al., Hou et al., and Feng et al. [35–38], this observation indicates that phosphates are initially adsorbed onto the biochar surface before being sorbed within the adsorbent. In the intra-particle diffusion model, phosphate molecules from contaminated wastewater migrate from higher to lower concentration areas, adhering to a concentration gradient

until uniform distribution is achieved. This demonstrates that the adsorption process is influenced by both the adsorption rate and the complex chemical interactions occurring externally and internally within the adsorbent. According to other researchers, such as Xu et al. and Ahmed et al. [38,39], zero-valent iron nanoparticles enhance phosphate removal through adsorption and overall precipitation, forming Fe-O-P ternary complexes. Additionally, the iron oxides generated facilitate the magnetic separation of biochar from treated wastewater.

Table 2. The parameters for the adsorption kinetics of phosphate onto modified biochars (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) and unmodified biochars (SSB300, SSB400, SSB500, and SSB600) are presented.

Adsorbents	Pseudo-First-Order			Pseudo-Second-Order		
	q_e (mg/g)	k_1 (1/h)	R^2	q_e (mg/g)	k_1 (1/mg h)	R^2
SSB300	0.98	1.12	0.96	1.42	1.18	0.93
nZVI-SSB300	6.22	4.21	0.98	6.98	1.29	0.95
SSB400	1.08	1.15	0.97	1.60	1.32	0.96
nZVI-SSB400	7.12	5.20	0.78	7.24	1.59	0.95
SSB500	1.46	2.13	0.88	1.68	1.87	0.94
nZVI-SSB500	8.19	6.18	0.89	8.35	2.05	0.96
SSB600	2.67	2.14	0.95	1.85	1.43	0.99
nZVI-SSB600	9.00	7.17	0.97	8.59	2.33	0.99
Intra-particle diffusion	k_{d1}	C_1	R^2	k_{d2}	C_2	R^2
SSB300	0.43	0.28	0.92	0.031	0.54	0.96
nZVI-SSB300	1.17	3.32	0.94	0.035	6.45	0.98
SSB400	0.66	0.45	0.96	0.039	0.87	0.95
nZVI-SSB400	2.16	4.33	0.97	0.044	7.23	0.88
SSB500	0.87	0.55	0.94	0.050	1.34	0.88
nZVI-SSB500	3.07	5.54	0.98	0.054	8.45	0.90
SSB600	0.98	0.67	0.99	0.056	1.64	0.95
nZVI-SSB600	4.56	6.78	0.99	0.064	9.47	0.96

The intra-particle diffusion model was validated through the Langmuir and Freundlich models, with the maximum phosphate adsorption capacity (q_e) calculated to be 19.00 mg/g when utilizing the pyrolyzed biochar modified with zero-valent iron nanoparticles (nZVI-SSB600) at a temperature of 600 °C (see Table 3). As previously mentioned, the coefficient values determined through these models serve as key indicators of adsorption efficiency, particularly when the initial phosphate concentration was set at 125 mg/L. The Langmuir coefficient (K_L) values emerged as critical indicators for assessing the adsorption process, suggesting a uniform progression. Specifically, the K_L values ranged from 0.13 to 0.21, indicating that the adsorption phenomenon was monolayer. Furthermore, the Freundlich constant derived from the $1/n$ equation provided insight into the adsorption capacity and intensity. Values for the $1/n$ constant falling within the 1–3 range indicate a moderate and more effective phosphate adsorption capacity when employing pyrolyzed carbons processed at elevated temperatures and modified with zero-valent iron nanoparticles. The K_F coefficient values, ranging from 1.37 to 2.05, further substantiate these findings. As illustrated in Tables 2 and 3, the statistically determined results are credible, with values ranging from 0.92 to 0.99. Consequently, it can be inferred that the adsorption process is heterogeneous and multilayered [39–41].

Table 3. The phosphate adsorption capacity (q_e , mg/g) and the isotherm parameters were evaluated using both modified (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) and unmodified (SSB300, SSB400, SSB500, and SSB600) biochars.

Adsorbents	Adsorbate	Langmuir			Freundlich		
		q_e (mg/g)	K_L	R^2	$1/n$	K_F	R^2
SSB300	PO_4^{3-} -P	8.63	0.16	0.96	1.52	1.38	0.99
nZVI-SSB300	PO_4^{3-} -P	11.22	0.21	0.98	1.98	1.79	0.99
SSB400	PO_4^{3-} -P	10.08	0.15	0.97	1.60	1.42	0.99
nZVI-SSB400	PO_4^{3-} -P	15.12	0.20	0.98	2.24	1.99	0.99
SSB500	PO_4^{3-} -P	11.46	0.13	0.98	1.68	1.37	0.99
nZVI-SSB500	PO_4^{3-} -P	17.19	0.18	0.99	2.35	2.05	0.99
SSB600	PO_4^{3-} -P	12.67	0.14	0.99	1.85	1.53	0.99
nZVI-SSB600	PO_4^{3-} -P	19.00	0.17	0.99	2.59	2.13	0.99

In alignment with the findings presented in the previous subsection, Langmuir and Freundlich adsorption isotherms were developed based on experimental results (Figure 8). Utilizing nZVI-SSB600, the equilibrium adsorption capacity for phosphates was observed to be 20.74 mg/g at an initial phosphate concentration of 25 mg/L in the solution. This capacity was noted to increase correspondingly at higher concentrations, with values of 25.67 mg/g at 50 mg/L, 27.97 mg/g at 75 mg/L, 28.44 mg/g at 100 mg/L, and 29.48 mg/g at 125 mg/L.

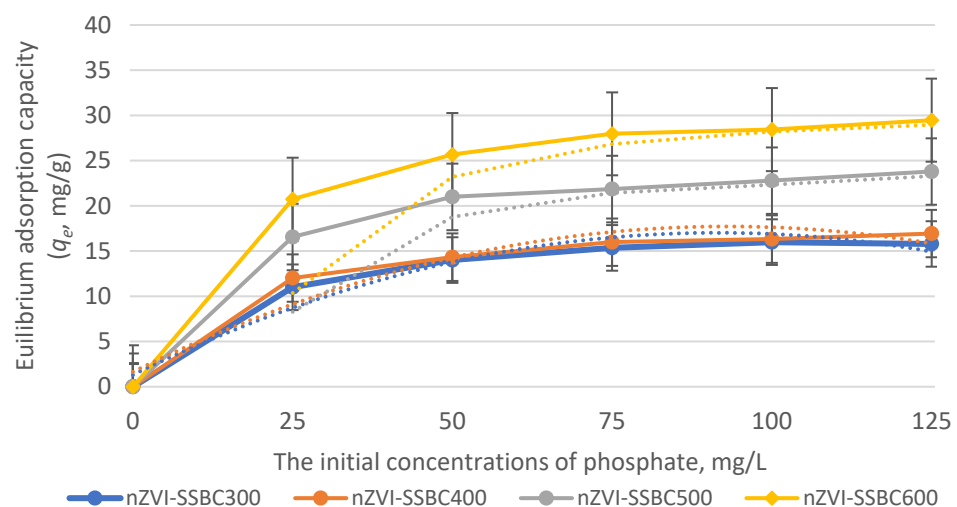


Figure 8. The isotherms for phosphate adsorption (q_e , mg/g) utilizing biochars that have been pyrolyzed at temperatures of 300 °C, 400 °C, 500 °C, and 600 °C, as well as zero-valent iron nanoparticle-modified biochars (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600), were evaluated at various initial phosphate concentrations (mg/L). The solid lines represent the curves of the Langmuir adsorption model, while the dotted lines illustrate the Freundlich adsorption model. Error bars denote $\pm$ standard errors with a significance level of $p < 0.05$.

The prepared isotherms exhibited non-linearity, indicating that the adsorption occurred at the initial phosphate concentrations. An analysis of research conducted by various scientists revealed that the adsorption capacity of biochar increased with elevated pyrolysis temperatures, ranging from 300 °C to 600 °C.

This increase is typically associated with a corresponding rise in biochar surface area, which expanded from 1.2 m²/g to 34 m²/g. These findings are further supported

by the results of other researchers, including Ahmed et al., Hou et al., Feng et al., and Jiang et al. [39–42]. Consequently, the research results indicate that the adsorption capacity of 29.48 mg/g is greater when utilizing biochar that has been pyrolyzed at higher temperatures.

The adsorbents utilized in the research demonstrate significant effectiveness; however, their application in practical settings may encounter certain challenges. A primary concern is the efficient regeneration of phosphates from the adsorbents, as used sorbents may be classified as hazardous waste. Additionally, it is important to note that phosphate adsorption is an endothermic process, necessitating possible heating of the system for optimal phosphate removal, which could incur extra energy and financial costs. Furthermore, maintaining the appropriate pH level—generally above 4—is critical for the phosphate removal process to occur effectively.

3.4. The Influence of pH on the Adsorption of Phosphate by Modified Biochar

Numerous scientific publications have demonstrated that varying pH values influence adsorption capacity. This study examined the impact of solution pH on the adsorption of phosphate onto biochar derived from pyrolyzed sewage sludge, which was treated at different temperatures (300 °C, 400 °C, 500 °C, 600 °C). The pH value of the treated wastewater solution is a critical environmental factor affecting phosphate adsorption. This phenomenon influences the adsorbent by altering the configuration of surface functional groups and their interaction with phosphate ions in aqueous solutions. The relationship between solution pH values and phosphate adsorption is illustrated in Figure 9. It is noteworthy that no significant differences ($p > 0.05$) were detected in the equilibrium adsorption capacity of phosphates (q_e , mg/g) across different pyrolyzed sewage sludge biochars at varying pH levels of the solution.

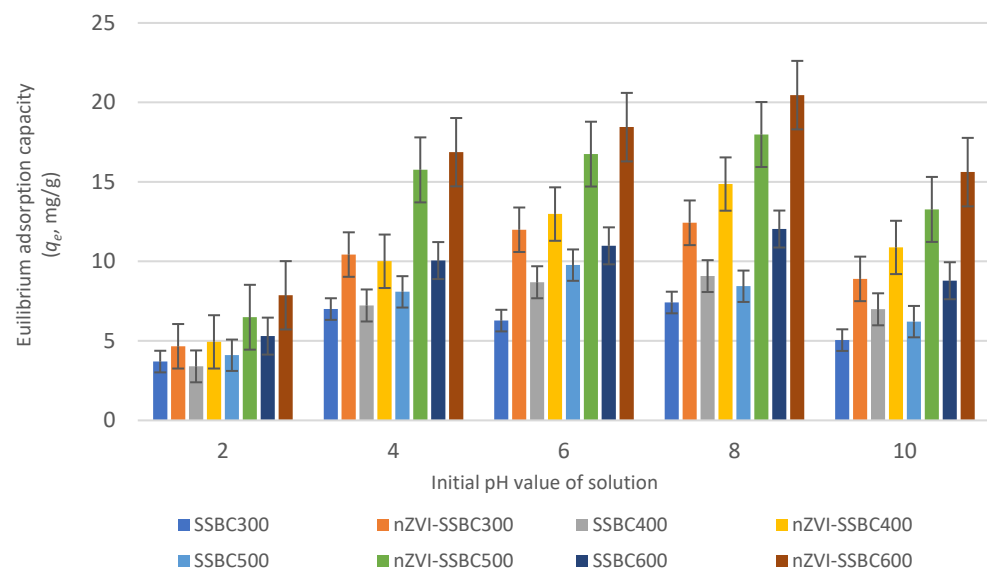


Figure 9. The equilibrium adsorption capacity of phosphates (q_e , mg/g) was evaluated using various pyrolyzed sewage sludge biochars at temperatures of 300 °C, 400 °C, 500 °C, and 600 °C. The biochars were assessed in both their unmodified forms (SSB300, SSB400, SSB500, and SSB600) and modified with zero-valent iron nanoparticles (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) across different pH levels of the solution. The vertical bars above each column indicate statistically significant differences at $p < 0.05$.

The adsorption capacity of the biochar was maintained at a stable and optimal range (nZVI-SSB600, from 16.87 to 20.46 mg/g) when the solution pH values were between 3 and 8. This observation applied to both pyrolyzed biochar and zero-valent iron nanoparticle-modified biochar. Notably, on average, the modified biochar exhibited 20–30% enhanced

adsorption performance compared to its unmodified counterpart. Conversely, at a solution pH of 2, phosphate adsorption experienced a significant reduction, dropping to 7.87 mg/g for nZVI-SSB600. At elevated solution pH values of 10 and above, the phosphate adsorption capacity further declined (nZVI-SSB600, 15.62 mg/g), representing a decrease of approximately one-third compared to the adsorption results observed between pH values of 3 and 8.

Previous studies conducted by Qian et al., Conz et al., Arbelaez Breton et al., and Tag et al. [42–45] identified that the variability in phosphate adsorption capacity can be attributed to the uneven charge distribution on the biochar's surface. Phosphates exist in polyacidic forms, and solution pH levels influence their various species. When the solution pH is below seven, the modified biochar surface carries a positive charge, facilitating electrostatic attraction between the adsorbate and adsorbent. However, when the pH exceeds 7, the biochar surface becomes negatively charged, which impedes electrostatic attraction with the adsorbate. This shift may also reduce adsorption capacity due to competitive adsorption from other compounds, such as hydroxyl (OH) groups. Enhanced electrostatic repulsion and competitive adsorption from OH groups may contribute to decreased phosphate adsorption capacity.

These findings emphasize that the electrostatic interactions of phosphates with modified biochar are mediated by the surface charge, whether negative or positive, and the nature of the anionic phosphates involved. The pH of the solution significantly influences the interaction forces and their efficacy between the sorbent and phosphates. Based on the empirical data, the adsorption isotherms for functional nanoparticle-coated biochar were formulated according to Langmuir and Freundlich models (Figure 10). All isotherms exhibited non-linearity, which indicates that the adsorption process occurs on the biochar's surface, aligning the model outcomes with the experimental findings.

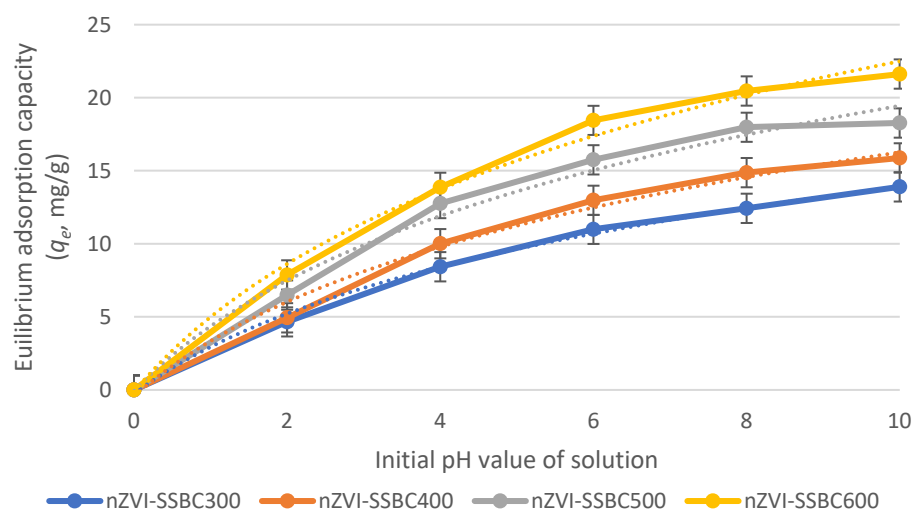


Figure 10. The isotherms for phosphate adsorption (q_e , mg/g) utilizing various pyrolyzed biochars (at temperatures of 300 °C, 400 °C, 500 °C, and 600 °C) and zero-valent iron nanoparticle-modified biochars (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) were assessed across a range of solution pH values. The solid lines represent the curves derived from the Langmuir adsorption model, while the dotted lines reflect the curves from the Freundlich adsorption model. The error bars denote $\pm$ standard errors at a significance level of $p < 0.05$.

3.5. The Impact of Different Ambient Temperature Values of the Solution on the Adsorption of Phosphate by Modified Biochar

To investigate the effect of ambient temperature on phosphate adsorption, we selected a representative modified adsorbent, nZVI-SSB600, which has demonstrated excellent adsorption properties in prior experiments. The adsorption capacity (mg/g) and isotherms for phosphates (q_e , mg/g) at varying temperatures are presented in Figure 11. The experi-

mental results indicate that the adsorption isotherms for the functional nanoparticle-coated biochar are consistent with the Freundlich model, illustrating a strong alignment between the model and the empirical data. No significant differences ($p > 0.05$) were observed in the equilibrium adsorption capacity of phosphates (q_e , mg/g) when utilizing different pyrolyzed sewage sludge biochars across a range of ambient temperatures. Furthermore, the studies highlighted noteworthy differences in adsorption efficacy at ambient temperatures ranging from 5 °C to 25 °C.

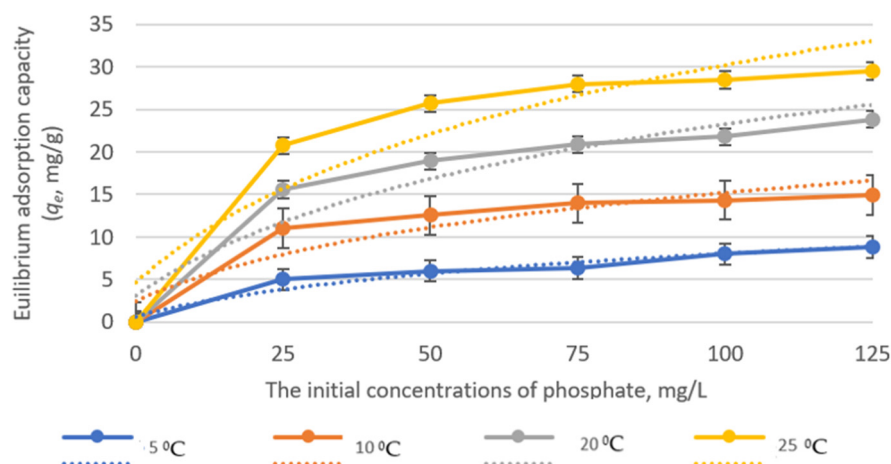


Figure 11. The equilibrium adsorption capacity (illustrated by continuous lines) of phosphates (q_e , mg/g) and the corresponding isotherms (represented by dotted lines) for phosphates (q_e , mg/g) utilizing pyrolyzed sewage sludge biochar modified with zero-valent iron nanoparticles (nZVI-SSB600) at various ambient temperature values of the solution are presented. The dotted lines depict the Freundlich adsorption model curves, with error bars indicating $\pm$ standard errors at $p < 0.05$.

Specifically, the adsorbent's sorption capacity was significantly enhanced as the ambient temperature increased. For instance, at a phosphate concentration of 100 mg/g, the adsorption capacity of nZVI-SSB600 was recorded at 7.99 mg/g at 5 °C, 14.33 mg/g at 10 °C, 21.79 mg/g at 20 °C, and 28.44 mg/g at 25 °C. These findings suggest that the initial concentration of phosphates in the cleaning solution and elevated ambient temperatures substantially influence the adsorption equilibrium capacity.

The experimental results indicate that endothermic adsorption occurs, suggesting increased ambient temperatures facilitate phosphate adsorption. Similar trends have been noted by other researchers, including Conz et al., Arbelaez Breton et al., Tag et al., Tang et al., and Saadat et al. [43–47], in their studies on phosphate adsorption in corn biochar, peanut shell biochar, and other materials. The rising temperature of the solution enhances the random thermal movement of ions, thereby increasing the probability of phosphate ions making contact with the biochar surface.

4. Conclusions

By utilizing higher-temperature pyrolysis, biochar formation was reduced, resulting in a shift in its pH from acidic to alkaline. Additionally, the specific surface area of the biochar was enhanced while the quantity of oxygen functional groups diminished. Consequently, the adverse environmental impacts associated with pyrolyzed biochar have been mitigated.

This study concludes that biochar modified with functional nanoparticles (nZVI-SSB300, nZVI-SSB400, nZVI-SSB500, and nZVI-SSB600) serves as a highly effective adsorbent for cleaning phosphate from wastewater. The research findings indicate that the adsorption capacity of modified biochar is 3 to 3.5 times better than unmodified (SSB300, SSB400, SSB500, SSB600).

The phosphate removal efficiency, assessed under varying contact times (ranging from 120 to 480 min) for both unmodified and modified biochar, leads to the conclusion that

functional nanoparticle-coated biochar outperformed unmodified biochar by an average of 30 to 38%. After experimenting for 480 min with unmodified biochar (SSB600), the equilibrium adsorption capacity (q_e , mg/g) was determined to be 12.63 mg/g. In contrast, under identical experimental conditions, the equilibrium adsorption capacity (q_e , mg/g) of biochar modified with zero-valent iron nanoparticles (nZVI-SSB600) reached an impressive 20.31 mg/g.

The removal efficiency of phosphate by modified biochars demonstrated that optimal absorption results were achieved with nZVI-SSB600. Using this biochar, phosphate's equilibrium adsorption capacity was measured at 23.74 mg/g (corresponding to a phosphate removal efficiency of 60%) at the solution's primary concentration of phosphate (25 mg/L). The results were as follows: 25.67 mg/g (75%) at 50 mg/L, 27.97 mg/g (80%) at 75 mg/L, 28.44 mg/g (85%) at 100 mg/L, and 29.48 mg/g (89%) at 125 mg/L.

Both models corroborated the intra-particle diffusion model applied in this study. These calculations indicated a maximum phosphate adsorption capacity (q_e) of 19.00 mg/g for pyrolysis at 600 °C when using modified biochar (nZVI-SSB600) at an initial phosphate concentration of 25 mg/L in solution.

The findings of this research reveal that the influence of solution pH on phosphate adsorption remains stable and maximal (nZVI-SSB600, ranging from 16.87 to 20.46 mg/g) for pH values between 3 and 8. On average, the modified biochar (nZVI-SSB) exhibited 20–30% enhanced adsorption performance compared to the unmodified biochar (SSB).

Moreover, significant differences in phosphate adsorption capacities correspond to varying ambient temperatures ranging from 5 °C to 25 °C. An increase in ambient temperature resulted in a substantial enhancement in the adsorbent's sorption capacity. Specifically, at an initial phosphate concentration of 100 mg/g, the phosphate adsorption capacity of nZVI-SSB600 was recorded as 7.99 mg/g at 5 °C, 14.33 mg/g at 10 °C, 21.79 mg/g at 20 °C, and 28.44 mg/g at 25 °C.

In conclusion, this study, alongside research by others such as Dutta et al. [48–50], illustrates the significant potential of biochar and other nanomaterials in wastewater treatment applications. This approach allows for the effective utilization of generated sewage sludge waste, which is pyrolyzed and coated with zero-iron nanoparticles, resulting in a superior product that is both successful and sustainable.

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Conflicts of Interest: The authors declare no conflicts of interest.

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