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Original Article

Assessing the Efficiency of Chemically Modified Biochars in Removing Nickel From Aqueous Solutions

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Abstract

Background: Modification methods can significantly alter the adsorption properties of biochar by changing its structure. This study aimed to optimize the removal of $Ni^{2+}$from aqueous solutions using unmodified pristine biochar (PB) and acid-modified biochar (ACB) and alkali-modified biochar (ALB) treatments.

Methods: After producing unmodified and modified biochars, their efficacy (PB, ACB, ALB) in optimizing nickel (Ni) removal from aqueous solutions, affected by various factors including initial Ni concentration, solution pH, adsorbent dose and contact time was evaluated using the response surface methodology (RSM: Box-Behnken design).

Results: Comparative analysis employing Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) confirmed that ACB and ALB biochars exhibited an improved aromatic structure and smoother surfaces compared to PB. However, the modification process resulted in a decline in specific surface area (SSA) for ACB and ALB, consequently reducing their Ni adsorption capacity compared to PB. It was observed that acidic and alkaline treatments caused dissolution and rearrangement of biochar components, leading to a decrease in porosity and SSA. Consequently, the modified biochars demonstrated diminished effectiveness in removing Ni from solutions. Furthermore, the study revealed that pH, contact time, and adsorbent dose directly affected the Ni removal, while the initial Ni concentration exhibited an inverse effect.

Conclusions: The current study revealed that the modification of biochar does not invariably enhance its pollutant adsorption properties. Further research is needed to explore the influence of feedstock types and the specific method of biochar modification on its pollutant adsorption efficiency.

Keywords: Aqueous solutions, Modified biochars, Heavy metals, Response surface methodology, Sorption

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Introduction

Nowadays, the excessive release of particular elements identified as heavy metals (HMs) into the environment has become a growing concern. This undesirable situation can be linked to industrial operations and technological progress, leading to the pollution of both water and soil resources. Unlike organic pollutants, HMs do not naturally degrade, and they tend to accumulate within the bodies of living organisms.[1] Among these troublesome HMs, nickel (Ni) is of particular concern. $Ni^{2+}$is the dominant form of Ni found in water, and its presence poses a significant risk to living organisms due to its highly toxic and cancer-causing properties.[2] This problematic element is abundant in various industrial waste streams, including metal plating, battery manufacturing, mineral processing, steam power plants, paint formulations, and porcelain glazes.[3] To ensure the safety of drinking water, the Environmental Protection Agency (EPA) and World Health Organization (WHO) have established strict limits for Ni content. The EPA sets the maximum allowable limit at 0.1 mg/L, while the WHO sets a lower limit of 0.02 mg/L. These regulations aim to protect public health by maintaining the quality of drinking water.

Over the years, various techniques have been utilized to address the presence of Ni and other HMs in water solutions. These techniques include membrane filtration, chemical precipitation, ion exchange, electrochemical purification, solvent extraction, and co-precipitation.[4] However, these approaches often face challenges when treating low metal concentrations, and are burdened with various drawbacks. These drawbacks include high costs for equipment and operations, the generation of sludge or toxic waste, significant energy consumption, and space requirements.

Considering these challenges, the process of adsorption has emerged as a widely recognized and effective method for removing HM ions. This method is preferred for its simplicity, cost-effectiveness, selective removal of contaminants, lack of hazardous residues, and suitability for treating wastewater with low concentrations of contaminants.[5] In the past few years, there has been significant research into different types of adsorbents for the removal of HMs. Notably, activated carbon (AC), zeolite, polymers, and clay minerals have emerged as prominent options in this field.[6]

While AC has been widely recognized for its effectiveness in removing HM ions at low concentrations, its high cost remains a limiting factor. Consequently, there has been considerable focus on researching low-cost materials as potential alternatives for adsorbents in HM removal. According to the study by Alalwan et al,[7] agricultural waste products are a promising class of inexpensive adsorbents that provide the double advantages of waste management and environmental pollution reduction. These agricultural leftovers have special qualities, such as a porous surface structure, numerous surface functional groups (O-H and COOH) for metal adsorption, and remarkable mechanical strength. As such, these natural characteristics can be used to transform them into efficient organic sorbents.

However, it is important to note that utilizing these agricultural residues in their raw form without undergoing activation processes yields limited efficiency in pollutant adsorption.[8] Hence, the transformation of organic biomass into active adsorbents, such as biochar, has become imperative. The biochar, generated through the process of pyrolysis (specifically, dry-pyrolysis), has garnered significant attention from researchers as a promising material for removing various contaminants from aqueous solutions via the adsorption process.[9,10]

The effectiveness of biochar in removing substances is greatly influenced by the origin of the materials (known as feedstock) used in their creation.[8] For instance, the biochar crafted from wood-based materials, such as various types of wood and nuts, possessing well-defined structures, primarily engages in physical adsorption on surfaces. This leads to the adsorption of metals through relatively weak reactions. In contrast, biochar derived from less structurally complex source materials, such as rice husk and wheat straw, primarily relies on a combination of metal chelation involving functional groups and cation exchange, both on the surfaces and within the porous structure of the biochar matrix. This intricate interplay leads to elevated biochar adsorption efficiency, often accompanied by robust metal interactions, as documented by Trakal et al.[11] Consequently, it becomes essential to subject these feedstocks to post-pyrolysis or in-situ modifications to enhance the adsorption capacities of biochar, particularly when sourced from lignocellulosic materials. This imperative to enhance adsorption efficiency is highlighted in the findings of Trakal.[12] The production of modified biochars can be achieved through a selection of three distinct methodologies: chemical techniques, encompassing H_2O_2 treatment and acid or alkali modification; physical techniques such as ball milling and microwave-assisted modification; and biological techniques like anaerobic digestion or bacterial conversion.[13] It is noteworthy that the choice of the modification method exerts a direct influence on the resulting alterations in the characteristics of the biochars themselves, as exemplified by Ahmed et al.[14] In a study conducted by Vithanage et al, it was found that treating biochar derived from bur cucumber plants with a 30% sulfuric acid solution resulted in a significant 250-fold increase in its SSA compared to untreated biochar.[15]

Cypress cones represent a plentiful resource within the urban green landscapes of Iran. Their resilient wooden composition and resistance to natural degradation pose significant challenges when it comes to their removal from the environment. Nonetheless, a promising solution lies in repurposing this abundant material as a valuable foundation for removing elements from aqueous solutions. This innovative approach not only contributes to the effective management of urban waste but also harnesses the potential of cypress cones to serve as practical HMs removal.

Gaining insights into the fundamental factors that impact the elimination of HMs from aqueous solutions holds paramount importance for researchers striving to attain their desired objectives.[8] Achieving these optimal outcomes necessitates extensive experimentation and significant financial investments. To address this challenge, an alternative method, known as response surface methodology (RSM), was introduced with the goal of minimizing testing while still yielding valuable insights.[16] RSM aims to establish accurate relationships between multiple independent variables and one or more dependent variables using mathematical models.

Until now, there have been relatively few investigations into adapting biochar for the specific purpose of removing Ni in aquatic settings. Notable research in this area includes studies by Mahdi et al,[17] Georgieva et al,[18] and Saffari and Moazallahi.[8] The primary goal of our study was to assess and contrast the efficiency of cypress cone-derived biochar, modified by both acids and alkalis, in eliminating Ni from water-based solutions. This comprehensive evaluation considered various variables, such as Ni concentration, solution pH, contact time, and the quantity of adsorbents employed. To meet these research objectives, we employed a Box–Behnken design (BBD) as part of the RSM framework. Furthermore, a detailed analysis of the chemical and structural properties of the adsorbents was conducted, utilizing techniques such as Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), and Brunauer-Emmett-

Teller (BET) assessments to facilitate comparison.

Materials and Methods

In this research, cypress cones were selected as the primary source material of biochar production, specifically designated as 'R'. These cypress cones were gathered from urban green spaces. The production of pristine biochar (PB) followed a sequential process.

Initially, the cypress cone samples underwent a thorough washing procedure, with each sample being washed three times using distilled water. Subsequently, the samples were dried in an oven at 65 °C for 48 hours. Once dried, the samples were finely crushed into particles smaller than 0.5 cm. These crushed particles were then introduced into a biochar reactor with dimensions of 40 cm in length and 20 cm in internal diameter.

The production of PB was conducted under controlled conditions, maintaining a temperature of 500 °C and a residence time of 4 hours. Nitrogen gas (N_2) was introduced into the system at a flow rate of 5 liters per minute for 5 minutes. The resulting product, referred to as PB, was finely pulverized into particles ranging from 10 to 20 μm and stored in a desiccator for the subsequent production of modified biochar materials.

The modification of the biochar involved a series of distinct steps, resulting in the creation of acid-modified biochar ('ACB') and alkali-modified biochar ('ALB'). Detailed information regarding these steps can be found in Figure 1.

To determine a variety of physical, chemical, and morphological characteristics of the biochars, different analytical methods were employed. These methods include FE-SEM (TESCAN FE-SEM MIRA3), FTIR (TENSOR II from Bruker), and BET (BELSORP Mini II).

In order to examine how various independent variables affect the removal of Ni from aqueous solutions, a series of batch experiments were conducted. These experiments involved creating 25-mL solutions with different Ni concentrations (30, 60, and 90 mg/L) derived from $Ni(NO_3)_2{\cdot}6H_2O$, and adjusting the pH to 3, 5, and 7 using 0.1 M NaOH and 0.1 M HCl solutions. Each solution was then transferred to sterile centrifuge tubes, and different amounts (2.5, 5, and 7.5 g/L) of the prepared adsorbents (R, PB, ACB, ALB) were added to the tubes individually. The tubes were vigorously agitated for 20, 40, and 60 minutes at a temperature of 25 °C ± 2, followed by centrifugation at 3500 rpm. After centrifugation, the supernatant was filtered and the concentration of Ni in the clear extract solution was determined using an atomic absorption spectrophotometer (Varian SpectrAA-10).

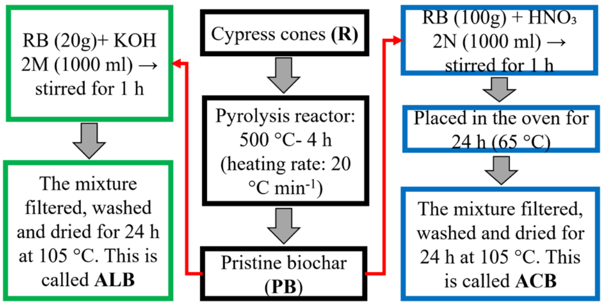

Figure 1. The production chart of PB and modified-biochars

The percentage of Ni removal (denoted as "q") was calculated using equation 1:

$$q = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i and C_f represent initial and final Ni concentrations (mg/L), respectively.

The impact of Ni removal, as well as the optimization and prediction of the removal rate, was investigated using the Box Benken Methodology (BBM) within the framework of RSM. The performance of Ni removal was assessed in terms of its influence on independent variables. These variables, including initial Ni^{+2} concentration (A), pH (B), adsorbent dose (C), and contact time (D), were set at three different levels namely low, medium, and high. The number of experiments required for the BBM was determined using the formula N = 2K(K-1) + C, where N represents the number of test samples, K denotes the number of variables (in this case, n = 4), and C represents the number of central points (n = 5). Consequently, a total of 29 tests were conducted for each adsorbent as part of the BBM.

For the purpose of RSM, individual models were developed for each dependent variable, specifically the efficiency of Ni removal. These models were designed to capture both the primary and interaction effects of the factors on each independent variable. To predict the optimal point, an RSM model was formulated according to Equation 2:

$$Y = \beta_0 + \sum_{i=1}^{m} \beta_i X_i + \sum_{i=1}^{m} \beta_{ii} X_i^2 + \sum_{j=i+1}^{m} \beta_{ij} X_i X_j + \varepsilon \qquad (2)$$

In this equation, *Y* represents the predicted value of the response variables. The intercept coefficient is denoted by β_0, the linear coefficient is represented by β_i, the quadratic coefficient is indicated by βii, the interaction coefficient is denoted by β_{ij}, and ε represents the residual term. To determine the optimal conditions for Ni removal, Design-Expert 7.00 software was utilized to generate regression equations and response surface plots within the RSM framework.

Results and Discussion

Chemical and Morphological Characteristics of the Studied Absorbents

Figure 2 illustrates the spectral bands of the biochars analyzed in this study. Upon analyzing the ALB (alkali-treated) sample, the peak at 1060 1/cm, representing C-O stretching, disappeared. In contrast, the peaks at 1577 1/cm, indicating aromatic compounds (aromatic C=C vibration), and 1378 1/cm, representing C=H vibration in alkanes and alkyl groups, increased in intensity compared to the PB sample. Similarly, the ACB (acid-

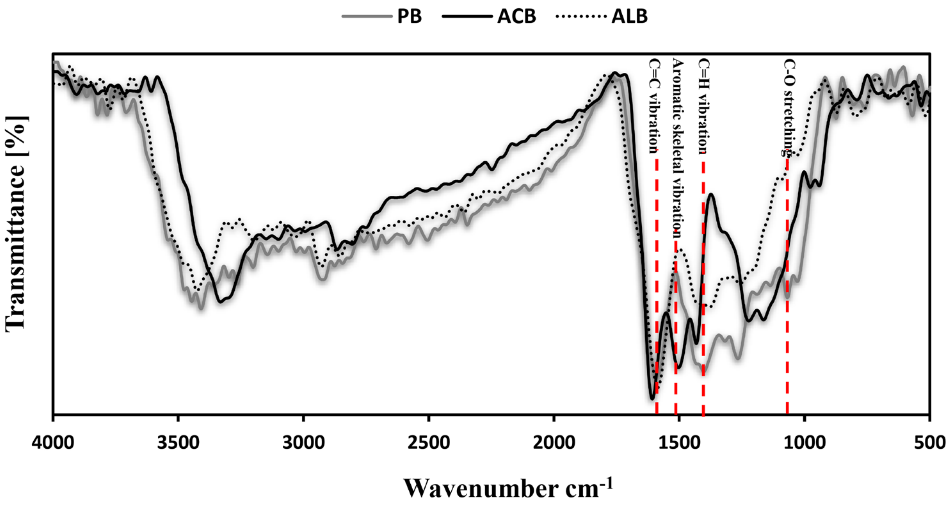

Figure 2. The FTIR Spectra of the Studied Adsorbents

treated) sample exhibited higher intensity at 1510 1/cm representing aromatic skeletal vibration, compared to the PB sample. These findings suggest that both acid and alkali treatments enhanced the aromatic structure of the biochar produced compared to the PB sample. In a related study by Xu et al, acid-modified biochars derived from corn straw were investigated, and it was found that acid treatment increased the presence of oxygen-containing functional groups on the biochar's surface.[19] Additionally, Hu et al examined acid- and alkali-modified biochars for their effectiveness in nitrate removal and observed that acid treatment increased the presence of C-OH and C-H functional groups.[20]

The SEM images of the biochars analyzed in this study are shown in Figure 3. The images clearly demonstrate significant changes on the surface of the studied samples compared to PB. The application of acid and alkali treatments resulted in the disruption of the non-planar structure of biochar, leading to relatively smoother surfaces in the two modified biochar samples.

These changes are evident when examining the SSA values, as detailed in Table 1, where ACB and ALB exhibited a reduction of specific surface values by 1.2 and 1.4 times compared to PB, respectively. The decrease in SSA in the ALB and ACB samples can be attributed to the removal of surface functional groups, disruption of the pore structure, and chemical reactions induced by acid and alkali treatments. Acid treatment removes oxygen-containing functional groups that contribute to surface reactivity and increase SSA. Additionally, acid and alkali treatments disrupt the non-planar structure, resulting in smoother surfaces with reduced surface roughness and decreased available SSA for adsorption. Furthermore, chemical reactions such as carbonization and activation further alter the surface morphology and pore structure, leading to a decrease in SSA.

Ni Removal Efficiency and Experimental Design

The investigation into the effects of PB, ACB, and ALB adsorbents on Ni removal from aqueous solutions, under varying factors and conditions, revealed that PB exhibited higher efficiency in Ni adsorption compared to ACB and ALB (Table 2). The Ni removal values for PB, ACB, and ALB were found to be 14.17%-51% (average 30.23%), 7.8%-45.7% (average 24.23%), and 4.5%-38.8% (average 19.72%), respectively (Table 2). The main hypothesis of the study was to enhance Ni adsorption by modifying biochars through acidic and alkaline treatments. However, the findings did not support this hypothesis. Despite an increase in aromatic functional groups in the modified biochar, the SSA actually decreased. This decrease in SSA, attributed to structural changes during modification, resulted in a reduced Ni adsorption capacity. The acidic and alkaline treatments caused dissolution and rearrangement of biochar components, leading to a reduction in porosity and SSA. Consequently, the modified biochars were less effective in removing Ni from solutions. These findings highlight the importance of considering SSA when evaluating modification methods for biochar adsorption.

Table 1. Porosity characteristics of the studied adsorbents

Adsorbent	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
PB	2.1328	0.006346	10.977
ACB	1.7616	0.0061006	13.852
ALB	1.5379	0.0045737	11.896

In a study conducted by Mahdi et al,[17] the researchers explored the utilization of modified biochar derived from date seed biomass for the adsorption of HMs from aqueous solutions. Various modification techniques, such as pre-treatment and post-treatment with NaOH and HCl, were employed. The acid treatment played a crucial role in enhancing the porous structure of the biochar and enriching functional groups on the surface, thereby facilitating the adsorption of metal ions. On the other hand, alkali treatment had a comparatively lesser impact on the functional groups. The modification process significantly improved the adsorption capacity for all metals, with the pre-treated biochar demonstrating the highest adsorption capacities for Pb^{2+}, Cu^{2+}, and Ni^{2+} ions. Notably, the study

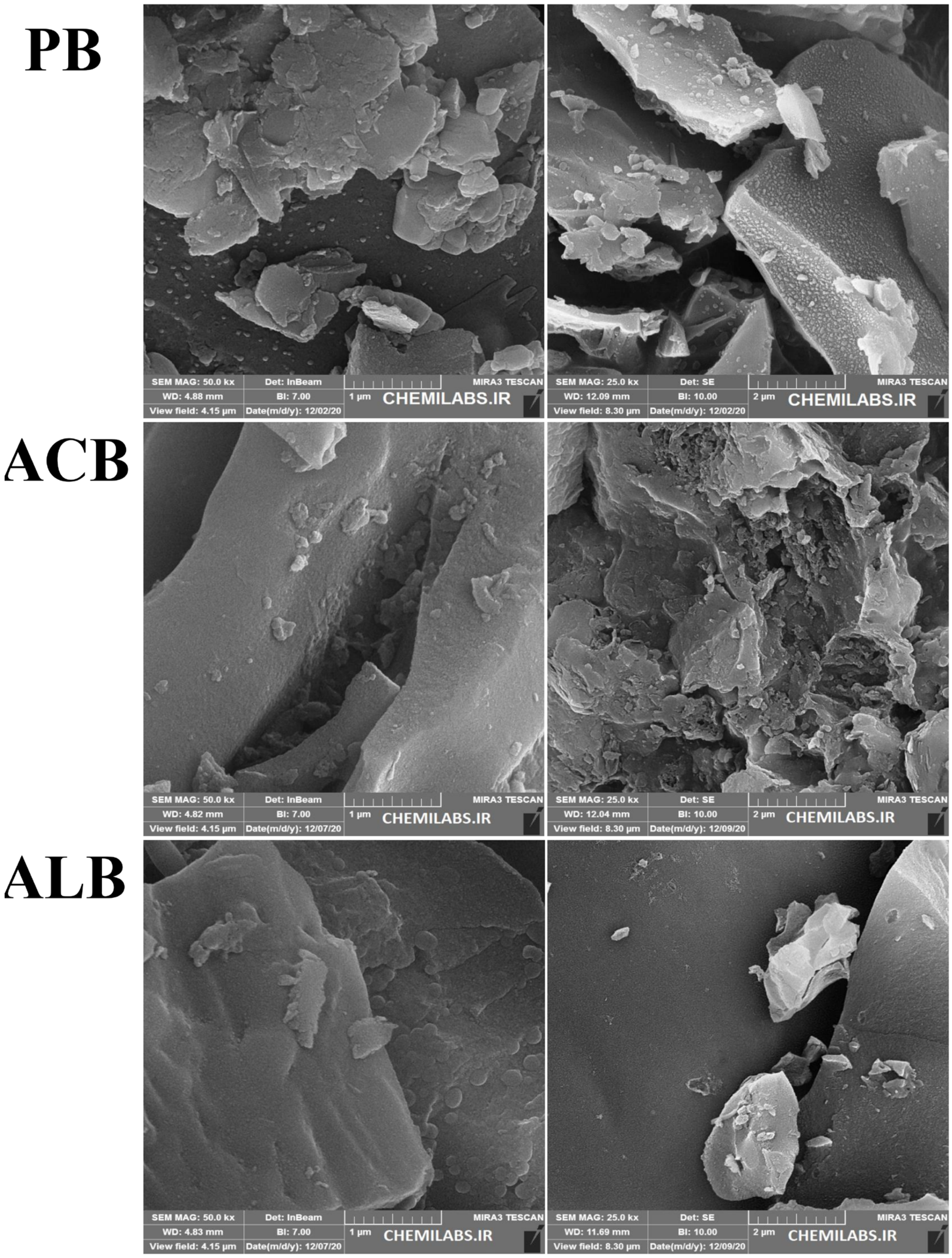

Figure 3. FE-SEM Images of the Studied Adsorbents

revealed that pre-treatment with HCl was a more efficient method compared to post-treatment.

In a study conducted by Liu et al, the researchers investigated the use of modified walnut shell biochar (WSC) and wood powder biochar (WPC) for the adsorption of methylene blue (MB) in the liquid phase.[21] The biochars were modified using $ZnCl_2$, KOH, H_2SO_4, and H_3PO_4. The modified biochars exhibited a mesoporous structure, with WSC having larger pore sizes compared to WPC. Alkaline modification, specifically with KOH, resulted in the highest SSA. The presence of oxygen-containing functional groups on the biochar surface provided more adsorption sites for MB, thereby enhancing the adsorption reactions. WPC demonstrated a higher adsorption capacity than WSC, with $ZnCl_2$ being the most effective modification, followed by KOH, H_3PO_4, and H_2SO_4. The maximum adsorption capacities observed were 850.9 mg/g for WPC with $ZnCl_2$ treatment and 701.3 mg/g for WSC with KOH treatment.

The disparity between our study and previous research on biochar modification for increased adsorption of cationic pollutants can be attributed to several factors. Firstly, variations in biochar properties, such as source material, pyrolysis conditions, and modification methods, likely influenced the interaction between biochar and modification methods, leading to different outcomes. Secondly, differences in the methods used for modification, including concentration, duration, and

Table 2. Experimental and predicted responses of Ni removal under BBD

Run order	Initial concentration of Ni (ppm) (A)	pH solution (B)	Adsorbent dose (g/L) (C)	Time contact (min) (D)	Ni Removal (%) by PB		Ni Removal (%) by ACB		Ni Removal (%) by ALB	
					EXP[a]	PRE[b]	EXP	PRE	EXP	PRE
1	90	3	5	40	15.22	13.7	9.7	9.2	5.2	5.0
2	60	5	2.5	60	29.67	28.6	24.7	22.8	22.8	22.8
3	30	5	5	60	36.33	37.9	29.0	29.7	28.3	29.8
4	60	5	7.5	60	31.33	30.8	22.8	22.8	17.8	17.9
5	90	5	2.5	40	22.00	21.1	16.4	17.6	14.1	13.6
6	60	3	5	20	16.17	16.1	9.7	9.7	4.7	5.4
7	60	3	5	60	24.45	24.4	18.2	18.2	16.3	17.1
8	60	3	7.5	40	27.67	28.5	22.5	22.9	17.8	17.4
9	60	5	5	40	33.00	31.9	27.8	25.7	24.2	21.3
10	60	5	5	40	31.50	31.9	25.8	25.7	21.3	21.3
11	60	7	5	60	46.00	44.4	41.3	39.9	36.5	36.4
12	90	5	5	20	22.00	22.8	17.9	18.6	13.0	13.3
13	60	5	5	40	29.83	31.9	24.2	25.7	19.5	21.3
14	60	5	7.5	20	38.00	38.3	33.0	33.1	27.8	28.7
15	60	5	5	40	33.00	31.9	28.7	25.7	23.5	21.3
16	60	7	2.5	40	31.50	34.1	25.8	27.4	21.3	21.8
17	60	3	2.5	40	14.17	16.4	7.8	8.2	4.5	4.1
18	90	5	7.5	40	27.56	27.5	20.9	20.2	20.1	19.6
19	60	7	7.5	40	39.83	41.1	35.8	37.4	31.2	31.7
20	90	7	5	40	25.00	24.6	19.3	19.2	14.1	13.9
21	30	5	2.5	40	34.00	33.1	25.0	26.3	17.0	16.5
22	60	5	2.5	20	21.50	21.3	19.5	17.8	12.8	13.7
23	60	7	5	20	28.00	26.4	23.0	21.6	18.2	18.1
24	30	5	5	20	36.00	36.8	30.0	32.3	27.0	27.6
25	60	5	5	40	33.50	31.9	26.2	25.7	21.2	21.3
26	30	5	7.5	40	46.00	45.9	39.3	38.9	29.0	28.5
27	90	5	5	60	19.78	21.4	13.3	16.0	8.4	9.5
28	30	7	5	40	51.00	50.6	45.7	45.5	38.8	38.2
29	30	3	5	40	32.67	31.2	22.3	21.9	15.7	15.2

[a] and [b] are the values obtained from the batch experiments and predicted by the model, respectively.

type of modifying agents, can significantly affect biochar properties and adsorption performance.

Additionally, the behavior of metal ions in solution, influenced by factors such as pH, ionic strength, and the presence of competing ions, may have interacted differently with the modified biochar in our experimental setup. Lastly, the modification methods used in our study may have influenced the dominant adsorption mechanism differently compared to previous studies, affecting the overall adsorption outcome. These factors emphasize the complexity of biochar modification and the importance of considering specific conditions and mechanisms when evaluating modification methods. Numerous studies have reported the successful effects of using modified biochars, specifically those treated with acids and bases, for the removal of anions. These modifications have been found to greatly enhance the effectiveness of biochars in removing various polluting anions from aqueous solutions. In a study conducted by Hu et al researchers investigated the efficacy of modified biochar as an adsorbent for removing nitrate from aqueous solutions.[20] The biochar underwent separate treatments with H_2SO_4 and NaOH, followed by preparation at a temperature of 600 °C. The acid modification resulted in a significantly higher SSA compared to both the unmodified and alkali-modified biochars. Conversely, the alkali-modified biochar exhibited lower adsorption capacity and SSA, which could be attributed to surface precipitation, as indicated by results of XRD analysis. The functional groups C-OH and C-H played a crucial role during the adsorption process. Batch experiments revealed that the acid-modified biochar demonstrated excellent absorbability (12.75 mg/g) under neutral solution and room temperature conditions. The maximum adsorption capacity of the acid-modified biochar was found to be 34.20 mg/g, approximately 2.4 times higher than that of the unmodified biochar. Furthermore, it was observed that lower pH values created positive charge conditions, thereby enhancing the adsorption capacity. In another study conducted by Xu et al, the effectiveness of acid-modified biochar derived from corn straw in removing toxic Cr(VI) from water was examined.[19] The results of batch experiments revealed that the acid-modified biochars, namely those modified with HNO_3, H_2SO_4, and H_3PO_4, exhibited higher removal efficiency for Cr(VI) compared to untreated biochar. This improvement was attributed to the increased presence of oxygen-containing functional groups (-COOH and -OH) in the acid-modified biochars, which acted as electron donors (e^-) and hydrogen ions (H^+) to facilitate the reduction of Cr(VI) to less toxic Cr(III). Notably, the HNO_3^- modified biochar displayed the highest efficiency in removing Cr(VI) among the acid-modified biochars.

To optimize the removal of Ni using different adsorbents under various factors, the data was fitted with different models (linear, quadratic, and cubic). Analysis of variance (ANOVA) was conducted for all three adsorbents, and it was found that the reduced cubic model provided the best fit (Table 3). The F test was used to determine the relationship between the mean squares of the model and the error. Table 3 presents the ANOVA results for predicting the response level of the reduced cubic model and the efficiency of Ni removal by different adsorbents. The significance of the model (probability values > F less than 0.05) and the non-significance of the lack of fit (LOF > 0.05) test indicate the suitability of the fitted models. Each model was evaluated using three factors: R^2, adjusted R^2, and predicted R^2 in the ANOVA tables (Table 3). The high values of R^2 and adjusted R^2 in the reduced cubic equations for the study of Ni removal by all three adsorbents demonstrate the strong predictive power of the model for the test conditions.[16] Furthermore, the values of R^2 and adjusted R^2 are closely aligned, indicating a relatively high and acceptable correlation between the observed and predicted values.

Equations 3 to 5 present the relationships between the dependent variables and the removal of Ni (fitted to the reduced cubic model) in the treatments of PB, ACB, and ALB, respectively. In these equations, A, B, C, and D represent the initial concentration of Ni, the pH of the solution, the adsorbent dose, and the contact time of the solution with the adsorbent, respectively.

$$\text{Removal of Ni by PB} = -72.87407 - 0.60012A + 26.39881B + 7.46574C + 2.63348D + 0.23403AB - 0.021481AC - 0.00106481AD - 0.25833BC - 0.76670BD - 0.074167CD - 2.16060B^2 - 0.00545320D^2 - 0.026968AB^2 + 0.082743B^2D \quad (3)$$

$$\text{Removal of Ni by ACB} = -133.45123 - 0.38345A + 48.16824B + 13.63611C + 2.84110D + 0.18495AB - 0.032963AC - 2.59444BC - 0.9420BD - 0.076667CD - 4.18419B^2 - 4.02936 \times 10^{-3} D^2 - 0.024190AB^2 + 0.23611B^2C + 0.10035B^2D \quad (4)$$

$$\text{Removal of Ni by ALB} = -251.95948 + 1.65498A + 67.72970B + 37.46708C + 2.88876 D - 0.059051AB - 0.42959AC - 2.4537 \times 10^{-3}AD - 3.45417BC - 0.94696BD - 0.099750CD$$

Table 3. Analysis of variance of BBD for the Ni removal

Sources of Variation	Sum of Squares	Degree of Freedom	Mean Square	F-value	Probability > F
Adsorbent of PB					
Model	2241.67	14	160.11	52.39	< 0.0001*
Residual	42.78	14	3.05		
Lack of fit	33.72	10	3.37	1.48	0.3733ns
Pure error	9.05	4	2.26		
Cor total	2284.45	28			
$R^2 = 0.981$; Adjusted $R^2 = 0.962$; Predicted $R^2 = 0.893$; CV = 5.78%					
Adsorbent of ACB					
Model	2258.73	14	161.34	47.07	< 0.0001*
Residual	47.98	14	3.43		
Lack of fit	35.52	10	3.55	1.14	0.4892 ns
Pure error	12.47	4	3.12		
Cor total	2306.71	28			
$R^2 = 0.979$; Adjusted $R^2 = 0.958$; Predicted $R^2 = 0.904$; CV = 7.61%					
Adsorbent of ALB					
Model	2079.35	17	122.31	53.03	< 0.0001*
Residual	25.37	11	2.31		
Lack of fit	11.06	7	1.58	0.44	0.8373ns
Pure error	14.31	4	3.58		
Cor total	2104.72	28			
$R^2 = 0.987$; Adjusted $R^2 = 0.969$; Predicted $R^2 = 0.900$; CV = 7.7%					

* Significant, ns: not significant.

$$- 5.75405 \times 10^{-3}A^2 - 6.09813B^2 - 1.90192C^2 + 8.83333 \times 10^{-4}A^2C + 0.030359AC^{\wedge 2} + 0.32792B^2C + 0.098863B^2D \quad (5)$$

The adequacy of the equations (Eqs. 3-5) and the corresponding values for each adsorbent can be observed in Table 2. It is evident that the predicted values closely align with the results obtained from the batch experiments, indicating a strong correlation ($R^2 = 0.99$, 0.99, 0.99 for PB, ACB, and ALB, respectively). This demonstrates the high predictive capability of the BBD model in estimating the Ni removal values.

Effect of Variables on Ni Removal

To investigate the impact of various factors on the removal of Ni by the studied adsorbents, their effects were examined across all three adsorbents. Interestingly, these factors demonstrated similar trends across the adsorbents. However, for the purpose of this discussion, we will specifically focus on the effects of these factors on the ACB adsorbent. The effects of each factor individually (represented in a 1D diagram) and their combined effects (illustrated in a 3D diagram) on Ni removal in the presence of the ACB adsorbent can be observed in Figure 4.

The findings demonstrate that an increase in the initial concentration of Ni results in a linear decrease in Ni removal. Conversely, elevating the pH of the solution, extending the contact time, and increasing the amount of adsorbent used significantly enhance Ni removal. The 3D diagram, illustrating the combined effects of these variables in the presence of the ACB adsorbent, confirms the direct influence of solution pH, contact time, and adsorbent dosage on Ni removal.

Furthermore, it was observed that increasing the initial concentration of Ni in all cases leads to a reduction in Ni removal in aqueous solutions.

The pH of the solution emerged as a critical factor in the adsorption process, as changes in pH alter the ionic state of metals in aqueous solutions. pH variations also impact the ionization of the adsorbent surface, consequently affecting the adsorption process.[22] The increasing pH of the solution promotes the deprotonation of functional groups, particularly hydrophilic groups, on the adsorbent surface. This results in the creation of more negatively charged sites, leading to an increase in Ni adsorption.[23] At lower pH levels, hydrogen ions compete with Ni metal ions for adsorption sites, resulting in reduced Ni removal efficiency. As the pH increases, the concentration of hydrogen ions decreases, facilitating the adsorption of Ni ions. Usman et al reported that increasing pH enhances the negative surface charge of biochar due to the deprotonation of carboxyl and hydroxyl functional groups.[24] In a study by Krishnan et al on the adsorption of Ni from aqueous solutions using AC derived from sugarcane bagasse pith, it was found that the optimal pH range for Ni adsorption is between 5 and 7.5.[25] According to their findings, at higher pH levels, the increased negative charge density on the adsorbent surface, combined with the positive charge of Ni ions, facilitates chemical adsorption. Conversely, at lower pH levels, the increased positive charge density on the adsorbent surface leads to repulsion between Ni ions, reducing the adsorption process, with physical adsorption accounting for the smallest percentage.[25]

The results also indicate that as the initial concentration of Ni increases, the efficiency of adsorption decreases. This can be attributed to the rapid occupation of adsorption sites at higher concentrations of Ni ions, which limits

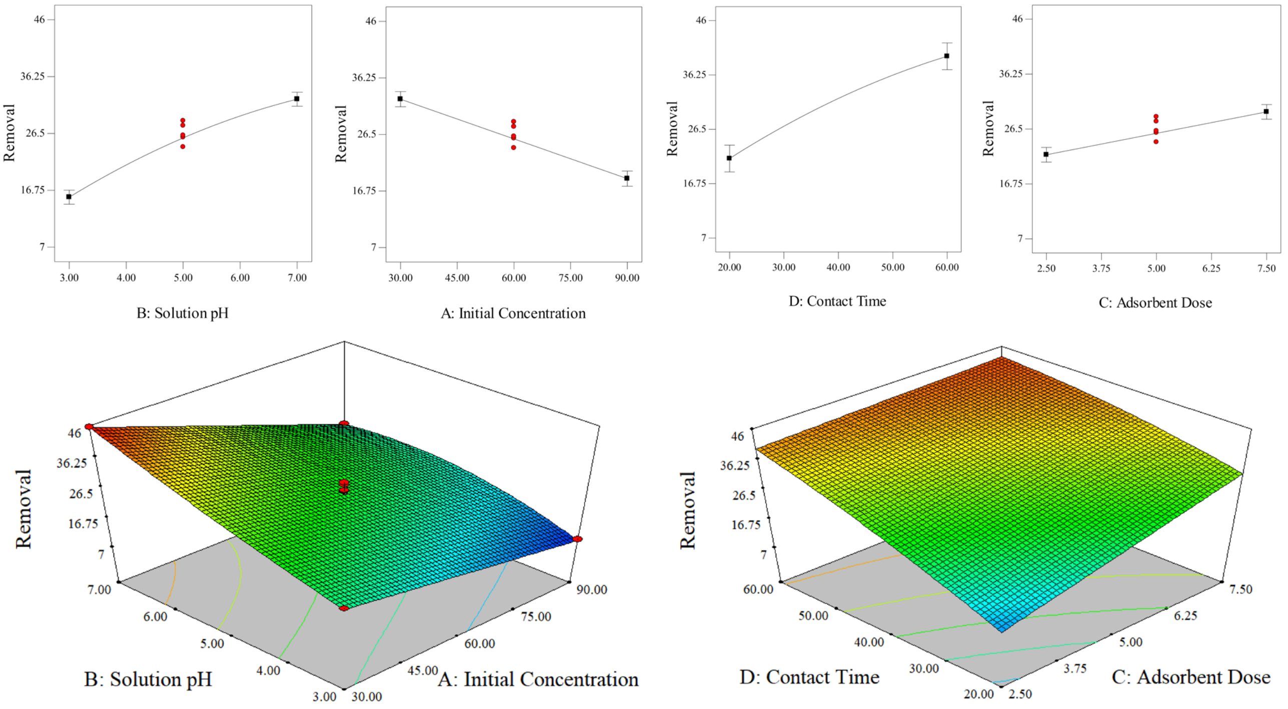

Figure 4. One-Dimensional (1D) and Three-Dimensional (3D) Diagrams Showing the Effects of Independent Variables on Ni Removal Efficiency Under Predefined Conditions, Affected by ACB

the penetration of Ni ions into the adsorbent pores and consequently reduces adsorption efficiency. In contrast, increasing the dosage of the adsorbent improves the efficiency of adsorption. This can be attributed to the fact that a higher dosage of the adsorbent provides a larger SSA for Ni adsorption to take place. Previous studies by Reddy et al on Ni removal using Moringa oleifera bark, and Zafar et al on Ni removal using alkali-treated rice bran, also reported a decrease in Ni removal with increasing Ni concentration.[26,27]

Desirability Process

A numerical optimization technique was employed to optimize the model and determine the optimal variables for the removal of Ni by the studied adsorbents. The limits for each variable were set within the range relevant to the design, with a focus on achieving the highest Ni removal. The desirability function method was utilized to establish the optimization conditions for each variable and response. Based on the results, 30 solutions were proposed for optimizing Ni removal for each adsorbent. Table 4 presents the top 5 solutions with high desirability for each adsorbent. Based on the software's best prediction and ideal model, PB achieved the highest Ni removal of 53.16%. This was observed at an initial concentration of 30.11 mg/L, pH 6.79, adsorbent dose of 6.71 g/L, and contact time of 41.16 min, with a desirability of 1. ACB, on the other hand, exhibited the greatest Ni removal of 48.85% at an initial concentration of 40.23 mg/L, pH 6.91, adsorbent dose of 6.00 g/L, and contact time of 48.99 min, with a desirability of 1. The highest Ni removal achieved by ALB was 39.6%, observed at an initial concentration of 36.10 mg/L, pH 6.77, adsorbent dose of 4.67 g/L, and contact time of 52.41 min, with a desirability of 1. In a study conducted by Hosseini et al using natural zeolite and RSM for optimized Ni removal, the best results were obtained at an initial Ni ion concentration of 10-15 mg/L, clinoptilolite dosage of 0.37-0.43 g/L, contact time of 56-68 min, and pH of 4.8-6.[28] Similarly, Garg et al investigated the impact of various factors on Ni removal using agricultural waste biomass and RSM.[29] The optimal conditions for the highest Ni removal from an aqueous solution with an initial concentration of 50 mg/L were found to be an adsorbent dose of 1500 mg/L, pH of 7.52, and stirring speed of 150 rpm.

Conclusions

In this study, the efficiency of removing Ni using acidic and alkaline-modified biochars was investigated, considering various adsorption factors. Surprisingly, contrary to expectations, the chemical modification of biochar did not enhance its performance in Ni removal. The decrease in SSA and the lack of improvement in effective functional groups (carboxylate, sulfide, and hydroxide) due to the chemical modification processes were identified as the main reasons for the reduced Ni removal efficiency. This reduction can be attributed to limitations in the chemical process, including the formation of non-removable complexes when acidic or alkaline compounds react with Ni, as well as the formation of new compounds that hinder Ni removal or cause other issues. Technical defects and suboptimal optimization in the chemical modification processes, such as uneven distribution of functional groups, insufficient contact time, or reactor feeding inefficiencies, also contributed to the decrease in efficiency. The study revealed direct effects of pH, contact time and adsorbent dose, as well as inverse effects with initial Ni concentration on Ni removal. The prediction models showed high validity, with the BBM accurately predicting Ni removal. Maximum percentages of achieved adsorption were 53.16% for PB, 48.85% for ACB, and 39.6% for ALB, at specific factors, yielding a desirability

Table 4. Prediction of Maximum Ni Removal Based on Numerical Optimization for Three Adsorbents (PB, ACB, ALB)

Solution	Initial Concentration of Ni (ppm) (A)	pH Solution (B)	Adsorbent Dose (g/L) (C)	Time contact (min) (D)	Ni Removal (%)	Desirability
1 (PB)	30.11	6.79	6.71	41.16	53.16	1
2 (PB)	31.52	6.86	3.93	49.56	51.29	1
3 (PB)	30.93	6.76	6.24	44.32	52.56	1
4 (PB)	33.23	6.93	7.34	47.07	55.17	1
5 (PB)	42.91	6.97	3.54	59.83	51.33	1
1 (ACB)	40.23	6.91	6.00	48.99	45.85	1
2 (ACB)	32.31	6.88	7.06	37.78	49.00	1
3 (ACB)	35.41	6.60	7.42	31.87	45.81	1
4 (ACB)	31.29	6.76	7.11	30.43	47.05	1
5 (ACB)	36.78	6.92	7.03	34.57	46.04	1
1 (ALB)	36.10	6.77	4.67	51.41	39.60	1
2 (ALB)	44.68	6.76	6.68	59.67	39.19	1
3 (ALB)	35.91	6.86	3.93	56.75	41.28	1
4 (ALB)	38.27	6.87	5.01	49.88	39.53	1
5 (ALB)	31.82	6.99	5.21	45.81	41.18	1

score of 1.

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Methodology: Mahboub Saffari, Masomeh Moazallahi.
Project administration: Mahboub Saffari.
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Software: Mahboub Saffari.
Supervision: Mahboub Saffari.
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Competing Interests

The authors declared no conflict of interest.

Ethical Approval

There were no ethical considerations to be considered in this research.

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