Effects of Calcination Temperature and Chemical Modification on the Adsorption of Cd and As(V) by Biochar Derived from *Pteris Vittata*

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Research Article

Keywords: Phytoremediation, arsenic (As), cadmium (Cd) pollution, biomass, toxic elements

Posted Date: March 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-287389/v1>

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Abstract

Phytoremediation can be applied successfully to solve the serious worldwide issue of arsenic (As) and cadmium (Cd) pollution. However, the treatment of biomass containing toxic elements after remediation is a challenge. In this study, we investigated the effective use of biomass resources by converting the As hyperaccumulator *P. vittata* into biochar to adsorb toxic elements. Plant biomass containing As was calcined at 600 °C, 800 °C, and 1200 °C and its surface structure and adsorption performances for As and Cd were evaluated. Calcination at 1200 °C increased the specific surface area of the biochar, but it did not significantly affect its adsorption capacity for toxic elements. The calcined biochar had very high adsorption capacities of 90% and 95% for As and Cd, respectively, adsorbing 450 mg/g-biochar of both elements. The As adsorption rate was improved by FeCl₃ treatment. However, the adsorption capacity for Cd was not significantly affected by the NaOH treatment. In conclusion, it was found that after phytoremediation using *P. vittata* biomass, it can be effectively used as an environmental purification material by conversion to biochar. Furthermore, chemical modification with FeCl₃ improves the biochar's adsorption performance.

Introduction

Environmental pollution caused by anthropogenic and natural sources is a serious problem. Soil and water pollution caused by toxic elements, especially arsenic (As) and cadmium (Cd), can have grave consequences on human health. Arsenic is ubiquitous in the environment, including in the atmosphere, rocks, water, and organic matter^{1,2}. Such health hazards caused by naturally occurring As have been reported in many Southeast Asian countries. Argos et al. estimated that tens of millions of people in Bangladesh and India suffer from health hazards caused by As ingested orally from drinking water and consuming food³. Arsenic ingestion can cause acute symptoms such as vomiting, diarrhea, muscle spasms, dysphagia, skin erosion, and death after coma⁴. As a chronic disease, inflammation of the mucous membranes of the eyes, nose, and throat is observed, and as the disease progresses, skin disorders such as black pigmentation and depigmentation keratosis appear, and the disease becomes more serious causing peripheral neuritis and cancer⁴.

Cd is released into the environment by the mining of zinc and other metals, and health hazards are often reported in river basins adjacent to these mines and smelters⁵. Many cases of health hazards caused by Cd have been confirmed in Asia, and soil and water contamination have been reported in Thailand⁶ and China⁷. Acute diseases caused by Cd in humans include nausea, vomiting, and abdominal pain, and chronic diseases, including tubular disorders, osteomalacia, and itai-itai disease⁸. Therefore, soil and water pollution caused by these toxic elements is a health hazard and an environmental problem that needs to be addressed promptly. To address these pollution problems, we focused on phytoremediation, an environmental remediation method using plants.

Phytoremediation is a method used for the removal of toxic substances from soil and groundwater using the material absorption capacities of plants⁹. In particular, research on methods using hyperaccumulator plants, which are plants that accumulate specific elements at high concentrations¹⁰, is being actively conducted using *Pteris vittata* L.¹¹, *Thlaspi caerulescens*¹², and *Alyssum lesbiacum*¹³, which accumulate As, Cd, and nickel (Ni), respectively. The advantages of phytoremediation include lower cost than treatment using heavy machinery, lower environmental burden because it does not involve modification of the surrounding environment, and applicability to a wide range of lands¹⁴. However, while valuable metals such as Ni can be reused after accumulation¹⁵, the use of biomass with high concentrations of other toxic elements has not been studied, and incineration is the only option. Therefore, in this study, the conversion of biomass into biochar was conceived as a method to utilize the biomass after phytoremediation.

Biochar refers to the carbonized material produced by heating biomass at 250 °C or higher under oxygen-free or oxygen-limited conditions¹⁶. An important feature of biochar is that it possesses certain organic carbons, called fused aromatic ring structures, which are similar to charcoal. These structures are formed during pyrolysis and are key to the properties related to mineralization and adsorption. In addition, biochar has a large specific surface area and high cation exchange capacity and is stable in the environment because of its resistance to degradation¹⁷. Because of these characteristics, biochar is an effective adsorbent for the restoration of environments contaminated by various substances, including heavy metals. It has been reported that biochar derived from *Ginkgo biloba* adsorbed up to 93.22 mg/L of Pb(II) and 22.58 mg/L of Cu(II) at an initial concentration of 100 mg/L¹⁸. Oil-palm empty fruit-bunch derived biochar and rice husk derived biochar adsorbed a maximum of 18.9 mg of As(III) and 19.3 mg of As(V) per unit weight, respectively, in a solution containing an initial concentration of 50 mg/L¹⁹. Rapeseed straw-derived biochar adsorbed 32.74 mg/g of Cd(II) in 40 mL of CdCl(II) solution with an initial concentration of 1.25 g/L²⁰. Furthermore, these studies have reported that the chemical modification of biochar can improve the adsorption of toxic elements. Thus, calcination temperature and post-calcination chemical treatment of biochar have been shown to improve heavy metal adsorption capacity, indicating that they are promising environmental purification materials. However, there are no reports on the use of hyperaccumulators as purification materials.

In this study, biochars of As-accumulated *P. vittata* biomass were prepared and their heavy metal adsorption properties for As and Cd were evaluated to effectively utilize them after their initial use for environmental remediation. *P. vittata* is known to accumulate As in its inorganic form, which is known to evaporate at temperatures below 200 °C²¹. Therefore, the As that was accumulated in the biomass during the biochar production process evaporates, and it will be relatively easy to collect and obtain a clean biochar. In addition, the biochars were chemically modified with FeCl₃ and NaOH to improve their heavy metal adsorption capacities.

Results And Discussion

Evaluation of surface structure and specific surface area of biochar

SEM images of untreated biochars of *P. vittata* and those chemically modified by FeCl_3 and NaOH that were calcined at 600 °C, 800 °C, and 1200 °C are shown in Figs. 1 to 3, respectively.

The leaf biochars at each calcination temperature (Fig. 1) showed an increase in the number of particles on the surface of the grain as the firing temperature increased. On the other hand, there was no significant difference in the surface structure of the biomass as the calcination temperature was changed. Furthermore, in the case of chemical modifications of leaf biochars, the FeCl_3 -treated sample (Fig. 2) was found to have crystalline particles attached to the surface. In the NaOH-treated sample (Fig. 3), some of the layered structures on the biochar surface were detached. In addition, cracks on the biochar surface were observed in all the FeCl_3 - and NaOH-treated samples.

Granular materials were identified on the surface of the non-treated biochar calcined at a temperature of 1200 °C, and they indicated that the functional groups on the surface of *P. vittata* leaves were decomposed and basic surface oxides were formed. Sasaki et al. reported that surface functional groups decompose and basic oxides are formed when carbon is heated in a vacuum or inert air stream at temperatures greater than 1000 °C²³. Leaves contain more chloroplasts than stems, and thus have a large quantity of sugars, which explains the presence of granular material in the biochars of leaves calcined at 1200 °C.

The adhesion of crystalline particles was observed on the chemically modified biochar surfaces of samples in the case of FeCl_3 modification probably caused by the precipitation of Fe in the FeCl_3 on the surface, either directly or as complexes. Fe^{3+} ions generated when FeCl_3 is dissolved in water are known to be reduced to Fe in the presence of activated carbon in the aqueous phase²⁴, which explains the modification of Fe on the biochar surface. A porous structure caused by exfoliation of the surface structure was observed on the biochar surface treated with NaOH. Li et al.²⁰ reported that the specific surface area of biochar was increased as a result of NaOH treatment. Therefore, it was considered that the surface of the biochar was eroded by the corrosive effect of NaOH resulting in the exfoliation of the surface structure and the generation of pores. In addition, the granular material identified in the leaf biochar calcined at 1200 °C disappeared after the NaOH treatment. This suggests that the granular material was composed of alkali-soluble substances. In addition, the cracks observed on the chemically modified biochar surface could be due to physical crushing by the agitator during the modification procedure.

The specific surface areas of biochars at each calcination temperature are listed in Table 1. The specific surface areas of the leaf biochar were 6.57 m²/g and 4.31 m²/g at 600 °C and 800 °C, respectively, with no significant difference. However, at 1200 °C, it was 34.54 m²/g, nearly 5 to 7 times higher. The results showed that the specific surface area of the biochars increased with high-temperature calcination. In

addition, the specific surface areas of the Fe-modified leaf biochar were 160 m²/g, 114 m²/g, and 129 m²/g for calcination temperatures of 600 °C, 800 °C, and 1200 °C, respectively, displaying a maximum increase of almost five times compared to that before modification. The specific surface areas of the NaOH-modified biochar were 73.79 m²/g, 31.92 m²/g, and 65.38 m²/g at 600 °C, 800 °C and 1200 °C, respectively. In the case of the NaOH-modified biochar, the highest specific surface area was observed at 600 °C. Therefore, the increase in the specific surface area of the biochar was higher with FeCl₃ treatment than that of NaOH treatment. Considering the observation of the surface structure by SEM, it can be inferred that the specific surface area of the FeCl₃-treated sample increased because of the adhesion of Fe to the surface and the formation of pores by physical breaking of the biochar surface. In the case of the NaOH-modified biochars, exfoliation of the surface structure was also observed, which may be the reason for the increase in the specific surface area. Surface cracks were observed in both FeCl₃- and NaOH-treated biochars, suggesting that the adhesion of Fe to the surface is a more significant factor in increasing the specific surface area.

Table 1
Specific surface area (m²/g) of biochars at each calcination temperature and after chemical modification.

	Calcination temperature		
Treatment	600 °C	800 °C	1200 °C
No treatment	6.57	4.31	34.54
FeCl ₃ -treated	160.83	114.78	129.35
NaOH-treated	72.23	31.92	65.38

Reported examples of biochar from other biological resources are rapeseed straw biochar calcined at 600 °C (19.13 m²/g) by Li et al.²⁰, cotton stalk biochar calcined at 600 °C (224 m²/g) by Zhang et al.²⁵, and rice straw biochar calcined at 800 °C (36.4 m²/g) by Basta et al.²⁶. In comparison to these studies, the surface areas of the *P. vittata* biochars in this study were similar under similar calcination conditions. The specific surface area of FeCl₃-modified biochar was reported by Cope et al. for rice husk at 550 °C (77.3 m²/g)²⁷ and Li et al. for rapeseed straw at 600 °C (6.82 m²/g)²⁰. NaOH-modified sawdust at 700 °C (423.28 m²/g) was reported by Chen et al.²⁸, and rapeseed straw at 600 °C (43.18 m²/g) was reported by Li et al.²⁰. The surface areas of the FeCl₃-modified biochars of this study using *P. vittata* exceeded the values reported in previous studies. In addition, the NaOH-modified biochars of this study had surface areas similar to those of the rapeseed straw biochar. Therefore, FeCl₃ modification of biochar has a greater effect on the increase in specific surface area compared to previous studies.

Evaluation of As and Cd adsorption capacities of *P. vittata* biochar

Figure 4 shows the adsorption isotherms of As(V) and Cd for the biochars calcined at 600 °C, 800 °C, and 1200 °C. Biochars tended to adsorb more Cd than As. The adsorption of Cd was particularly pronounced in the initial concentration range of 1–150 mg/L. At low initial concentrations (10 mg/L), calcination temperature of biochar did not have an effect on the adsorption of As. However, Cd adsorption increased in biochars that were calcined at high temperatures (800 °C and 1200 °C). At initial concentrations of above 100 mg/L, the adsorption capacities of the samples calcined at 600 °C and 800 °C were higher. The quantity of toxic elements adsorbed per unit weight of biochar at an initial concentration of 1000 mg/L was approximately 450 mg/g-biochar at any calcination temperature. The best adsorption values were 451.69 mg/g-biochar at 800 °C for As and 454.65 mg/g-biochar at 600 °C for Cd. Furthermore, Figs. 5 and 6 show the adsorption isotherms of As and Cd for the FeCl₃- and NaOH-modified biochars, respectively. It was confirmed that Cd tended to be adsorbed more readily than As, even in chemically modified biochars. The best adsorption by biochar at the initial concentration of 1000 mg/L were 458.40 mg/g-biochar at 800 °C for FeCl₃ modification and 455.38 mg/g-biochar at 1200 °C for NaOH modification. Adsorption capacity increased by approximately 2% in the case of FeCl₃ modification, while it was not significant in the case of NaOH modification.

The adsorption rates of As and Cd on the biochars with and without chemical modification at each initial concentration are shown in Fig. 7. While the specific surface areas of unmodified biochars were much larger at 1200 °C than at 600 °C and 800 °C, the adsorption rate of As(V) was only about 90% at any initial concentration. However, the adsorption rate of the FeCl₃-modified biochars significantly improved at all initial concentrations at all calcination temperatures. In particular, it was shown that the adsorption rate in the low concentration range of 1 to 10 mg/L of initial concentration, which was not observed for unmodified biochars, was improved when biochars calcined at 800 °C and 1200 °C were used as feedstock. Although some improvement or decrease in adsorption performance was observed for biochars modified with NaOH, no significant change in the overall Cd adsorption properties was observed for biochars prepared at any calcination temperature as feedstock. The unmodified biochars showed a very high adsorption rate of about 97–98% under an initial Cd concentration of 1 to 10 mg/L, from which the adsorption rate decreased as the initial concentration increased, and the adsorption rate remained at approximately 90% for biochars at any calcination temperature at an initial concentration of 1000 mg/L. In the case of chemical modification with NaOH, the adsorption rate of the biochars calcined at 600 °C improved in the initial Cd concentration range of 1 to 10 mg/L, but the adsorption rate slightly decreased at higher concentrations compared to untreated biochars. In the case of biochars calcined at 800 °C and 1200 °C, the adsorption rate at low concentrations was lower than that of the unmodified samples, but it was slightly higher than that of unmodified samples for initial Cd concentrations of 100 to 250 mg/L.

Because the specific surface area was evaluated using the monolayer adsorption model with the Brunauer–Emmett–Teller (BET) equation by nitrogen adsorption, it was not affected by the functional

groups and the chemical state of the biochar surface. In contrast, the adsorptions of As(V) and Cd were not affected by the specific surface area suggesting some sites on the biochar surface specifically bind arsenate regardless of the calcination temperature. The adsorption of As(V) was not affected by the specific surface area. On the other hand, Cd showed an extremely high adsorption capacity at low initial concentrations of 1 to 10 mg/L, while the adsorption rate decreased by 90% at an initial concentration of 1000 mg/L. This is because oxygen-containing functional groups, such as hydroxyl (-OH) and carboxyl (-COOH) groups, have high affinity and bind preferentially to cations such as Cd, but as the number of oxygen-containing functional groups decreases with increasing concentration, the ratio of binding by surface π -electrons increases. Therefore, this is a two-step adsorption mechanism.

The specific surface area of the FeCl₃-modified *P. vittata* biochar was larger than that of the unmodified biochar, and the As adsorption capacity improved. The specific surface area of the biochar calcined at 600 °C was the largest among the three types, but the increase in As adsorption capacity by FeCl₃ modification was the highest for the biochar calcined at 1200 °C. However, the increase in the amount of As adsorbed by Fe-modification was the highest when the biochar calcined at 1200 °C was used as the raw material probably because the Fe³⁺ ions were attracted to the π -electrons or oxygen-containing functional groups on the surface of this biochar than in the other two types²⁹. The leaf biochar calcined at 1200 °C before modification has a larger specific surface area than those calcined at 600 °C and 800 °C, and in this case, the adsorption by π -electrons is stronger because the oxygen-containing functional groups on the surface are less due to the high-temperature calcination. Therefore, it is suggested that the π -electrons of the biochar calcined at 1200 °C attracted more Fe³⁺ ions present in the aqueous solution, which increased the attachment of the reduced Fe particles to the biochar surface or they caused the formation of complexes with oxygen-containing functional groups resulting in an increase in As adsorption and specific surface area. In addition, the reason for the improved arsenate adsorption at low initial concentrations of 1 to 10 mg/L in the case of FeCl₃ modification is that the biochars calcined at 800 °C and 1200 °C had a sufficient amount of Fe that was adsorbed on to their surfaces, which may have resulted in the formation of a high-affinity complex between Fe and arsenate. In the biochar calcined at 600 °C, Fe was less modified than in the other two conditions, which may have caused the difference in the adsorption behavior after modification. On the other hand, it was confirmed that the adsorption performance tended to decrease at initial concentrations of above 100 mg/L compared to that at lower concentrations because the complex formation by Fe has high affinity, but the number of adsorption sites is limited, and hence the adsorption rate may have decreased due to the increase in arsenate present in the surrounding area.

Although the specific surface area of *P. vittata* biochar modified with NaOH was larger than that before modification, the Cd adsorption capacity improved only at the initial Cd concentration of 100–250 mg/L probably because of the decrease in carboxyl groups (-COOH) associated with NaOH modification. It has been reported that the modification of biochar with NaOH results in the formation of lactones by dehydration condensation of the surface functional group COOH with the hydroxyl group (-OH) of NaOH and an increase in OH²⁰. The *P. vittata* biochar calcined at 600 °C before modification had the highest

amount of -COOH, and that calcined at 1200 °C was considered to have the strongest binding by π -electrons on the biochar surface. However, NaOH modification caused a decrease in -COOH, which is a surface functional group, and the presence of surface functional groups seems to have changed significantly.

Methods

Calcination of biochar

P. vittata plants purchased from FUJITA Co. Tokyo, Japan. The raw material for biochar was *P. vittata* grown in a field trial in Miyagi Prefecture. The concentration of As in *P. vittata* has been confirmed to be approximately 20 mg/kg²². All field experiments are in compliance with local and national regulations. The harvested *P. vittata* was dried naturally, divided into leaves and stems. Then, only the leaves were packed in stainless steel containers and subjected to calcination in an electric furnace under N₂ atmosphere. During the calcination process in the electric furnace, the temperature was increased to below 150 °C for 3 h, from 150 to 600 °C at 100 °C/h, and for 600 °C and above at 200 °C/h. When the desired temperature was reached, it was maintained for 5 min to complete calcination. The biochar was calcined at final calcination temperatures of 600 °C, 800 °C, and 1200 °C, and the obtained calcined biochars were used in the experiments.

Chemical modifications with FeCl₃ and NaOH

The calcined biochars were chemically modified using FeCl₃ and NaOH. A quantity of 1.4 L of 1000 mg/L FeCl₃ solution was prepared and transferred to a 2 L beaker. The pH was then adjusted to 6 using 1 M HCl and NaOH. As a pretreatment, 7 g of leaf biochar was finely ground until more than 90% of it passed through a 1-mm sieve. The crushed biochar was added to the FeCl₃ solution and stirred with a magnetic stirrer for 24 h. After stirring, the solution containing the biochar was suction-filtered, and the resulting FeCl₃-modified biochar was washed with Milli-Q water to remove the unreacted Fe. Then, it was dried in a dryer at 60 °C for 24 h. The above modification procedure was based on the method described by Sadeh-Zadeh and Seh-Bardan¹⁹.

The procedure for chemical modification with NaOH was based on the method described by Li et al.²⁰. A quantity of 140 mL of 2 M NaOH solution was prepared and transferred to a 200 ml beaker. As a pre-treatment, 7 g of biochar from leaves was finely ground until more than 90% of it passed through a 1-mm sieve. After grinding, the biochar was added to the NaOH solution and stirred vigorously for 12 h in a hot stirrer set at 100 °C with a magnetic stirrer. After stirring, the solution containing the biochar was filtered by suction. The resulting NaOH-modified biochar was washed three times with Milli-Q water and three times with 0.01 M NaHCO₃. Then, it was dried in a dryer at 60 °C for 24 h.

Evaluation of physical properties of biochars

Structural observations using scanning electron microscopy (SEM) and measurements of specific surface areas on a total of nine biochar samples including calcined and chemically modified with FeCl_3 and NaOH after calcination were performed

Structural observation by SEM (JSM-6360, JEOL, Japan) was performed on the fractions of the samples that passed through a 1-mm sieve to evaluate the differences in structure due to calcination temperature and chemical modification.

A vacuum superheating pretreatment system (BELPREP-vac III, Microtrac Bell, Japan) and a specific surface area measurement system (BELSORP-mini II, Microtrac Bell, Japan) were used to measure the specific surface area. The sample biochars were crushed into small pieces using a mortar, set in the BELPREP-vac III, and heated at 130 °C for 3 h in vacuum to remove water and other substances adsorbed on the sample. After pretreatment, the sample was set in BELSORP-mini II, and the specific surface area was measured using the nitrogen adsorption method. The BET method was used to analyze the specific surface area of the obtained adsorption/desorption isotherms.

Evaluation of As and Cd adsorption capacities of biochars

Nine types of biochars were evaluated for their ability to adsorb As(V) or Cd. The samples that were chemically modified with FeCl_3 were evaluated only for As, and those chemically modified with NaOH were evaluated only for Cd.

The biochar samples were finely ground until more than 90% passed through a 1-mm sieve. After grinding, the samples were dried in a dryer at 115 °C for 3 h. After drying, the samples were placed in a desiccator and allowed to cool for 24 h. Then, three empty 50-mL centrifuge tubes were prepared for each sample. In each centrifuge tube, 50 mL of As(V) ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) or Cd (CdCl_2) solution was prepared at concentrations of 1, 10, 100, 150, 250, 500, and 1000 mg/L. A quantity of 0.1 g of pretreated biochar was added to each centrifuge tube. The centrifuge tubes were sealed and shaken for 24 h at 100 rpm in a shaker at 25 °C with a lateral shaking width of 4–5 cm. After shaking, the supernatant was collected from the centrifuge tube and diluted to 10 mL with Milli-Q water by adding nitric acid to achieve a final concentration of 5% (v/v). The test solution was then filtered through a 0.45 μm membrane filter and used as the sample for measurement. The As and Cd concentrations in the test solution were then quantified using high frequency inductively coupled plasma atomic emission spectrometry (iCAP6000, Thermo Fisher Scientific, USA).

Data analysis

The obtained measurement data were checked for significant differences using ANOVA using the statistical analysis software R (version 4.0.2).

Declarations

Acknowledgements

This publication is the result of work sponsored by JSPS KAKENHI Grants-in-Aid for Scientific Research (A) (Grant Number: 19H01158) and the pilot project of the Center for Asian and Pacific Studies, Seikei University.

Author contributions

K.S: Conceptualization, Methodology, Validation, Investigation, Writing – Original Draft, Visualization, Project administration, Funding acquisition. K.I: Investigation, Data Curation. Y.I: Investigation. H.O: Resources, Writing – Review & Editing. S.S: Writing – Review & Editing, Supervision.

Additional Information

There are no conflicts of interest to declare.

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Figures

Figure 1

Surface structure of *P. vittata* biochar by SEM observation. Left column: Magnification 250×; Right column: Magnification 1000×; (a) calcination temperature: 600 °C; (b) calcination temperature: 800 °C; (c) calcination temperature: 1200 °C.

Figure 2

Surface structure of FeCl₃-treated *P. vittata* biochar by SEM observation. Left column: Magnification 250x; Right column: Magnification 1000x; (a) calcination temperature: 600 °C; (b) calcination temperature: 800 °C; (c): calcination temperature: 1200 °C.

Figure 3

Surface structure of NaOH-treated *P. vittata* biochar by SEM observation. Left column: Magnification 250x; Right column: Magnification 1000x; (a): calcination temperature: 600 °C; (b) calcination temperature: 800 °C; (c) calcination temperature: 1200 °C.

Figure 4

As(V) and Cd adsorption isotherms for biochars at various calcination temperatures. (a) calcination temperature: 600 °C; (b) calcination temperature: 800 °C; (c): calcination temperature: 1200 °C.

Figure 5

As(V) adsorption isotherms for FeCl₃ and non-treated biochars at various calcination temperatures. (a) calcination temperature: 600 °C; (b) calcination temperature: 800 °C; (c): calcination temperature: 1200 °C.

Figure 6

Cd adsorption isotherms for NaOH and non-treated biochars at various calcination temperatures. (a) calcination temperature: 600 °C; (b) calcination temperature: 800 °C; (c) calcination temperature 1200 °C.

Figure 7

Adsorption rates of As(V) and Cd on biochars with and without chemical modification at each initial concentration. (a) As(V) adsorption of without chemical treatment; (b) Cd adsorption of without chemical treatment; (c) As(V) adsorption of FeCl₃ treatment; (d) Cd adsorption of NaOH treatment.