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Combining Activated Carbon Adsorption and CO_2 Carbonation to Treat Fly Ash Washing Wastewater and Recover High-Purity Calcium Carbonate

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Abstract: Fly ash washing wastewater was carbonated with carbon dioxide (CO_2) to remove calcium (Ca) by forming a calcium carbonate ($CaCO_3$) precipitate. An investigation of the factors affecting carbonation showed that Ca removal was highly dependent on the initial pH of the wastewater. The Ca removal was 10%, 61%, 91% and more than 99% at initial wastewater pH levels of 11.8, 12.0, 12.5 and 13.0, respectively. The optimal conditions for carbonation were initial pH of 13.0, carbonation time of 30 min and CO_2 flow rate of 30 mL/min. The Ca concentration in the wastewater decreased to <40 mg/L, while 73 g of $CaCO_3$ precipitate was produced per liter of wastewater. However, heavy metals, specifically Pb and Zn, co-precipitated during carbonation, which resulted in a $CaCO_3$ product that contained as much as 0.61 wt% of Pb and 0.02 wt% of Zn. Activated carbon modified by a quaternary ammonium salt was used to selectively adsorb the Pb and Zn first. The Pb- and Zn-free water was then carbonated. By combining adsorption with carbonation, the Ca concentration in the treated wastewater was decreased to about 28 mg/L, while the Na, Cl and K were retained. The wastewater thus treated was ready for NaCl and KCl recovery. In addition, the precipitate had a Ca content of more than 38 wt% and almost no heavy metals. The average particle size of the precipitate was 47 μm, with a uniform cubic shape. The quality of the precipitate met the requirements for the industrial reuse of $CaCO_3$. In summary, adsorption and carbonation combined were able to remove pollutants from wastewater while recovering useful resources.

Keywords: fly ash; washing wastewater; Ca removal; CO_2 carbonation; precipitate

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1. Introduction

As one of the main technologies for municipal solid waste disposal, incineration is renowned for its capacity to reduce volume and mass [1]. However, the generation of bottom ash and fly ash, particularly the latter, is one of the disadvantages of incineration. Municipal solid waste incineration (MSWI) fly ash includes materials collected from the flue gas treatment system (e.g., electrostatic precipitators, bag filters) and particulates settled at the bottom of flue and chimneys [2]. Because it contains heavy metals, chlorides and toxic organics, fly ash is designated as hazardous in many countries [3]. On the other hand, fly ash is rich in resources such as inorganics oxides (CaO, SiO_2 and Al_2O_3) and salts (NaCl and KCl) [4]. Therefore, the question of how to detoxify fly ash and recover resources predominates in current studies.

Washing via water is an effective method to extract soluble chemicals from fly ash. More than 90% of chloride and 30% sulfate were removed by washing with water alone [5]. The removal of sulfate could be raised to 80% when Na_2CO_3 solution was used [6]. Washing by electric-field-enhanced oxalic acid could achieve an even higher removal (95%) for chloride [7]. Acid washing was also able to dissolve heavy metals and, thus, reduce their leaching toxicities [8]. In summary, washing with water or accelerated washing with the addition of acid, alkaline or other reagents (phosphate, carbonate) is a promising method to decontaminate fly ash [9]. The washed fly ash can be reused as a cement admixture, geopolymer precursor, light-weight aggregate, etc. [10].

However, washing results in wastewater that is high in salinity, alkalinity and hardness, as it usually contains high concentrations of Ca, Na, K, Cl, etc. These stem from chemicals such as NaCl, KCl and $CaCl_2$. The Na and Cl concentrations in washing solution can reach as high as 10,000 mg/L. In China, CaO or $Ca(OH)_2$ is often sprayed to incineration flue gas to neutralize acidic HCl and H_2S gases. The resultant neutralization products or residual reactants are gathered in the flu gas treatment system as part of the fly ash [11]. Therefore, fly ash is often highly alkaline. Studies have shown that the Ca compounds found in fly ash include $Ca(OH)_2$, $CaSO_4$, $CaCO_3$, CaClOH, CaO, etc. [12,13]. Most of these chemicals are easily dissolved in water and, thus, released into the aqueous phases, resulting in both alkalinity and hardness in washing wastewater.

In addition, heavy metals are also washed off, although the concentrations of these metals are relatively low and are highly dependent on the washing reagent. For instance, washing by Na_2CO_3 and Na_2HPO_4 actually reduced the concentrations of Pb and Zn in solution by stabilizing them in fly ash [14,15]. Nevertheless, the concentrations of heavy metals can range from a few mg/L to a few dozen mg/L [16].

Because of its high concentration of salts and heavy metals, washing wastewater often does not meet the requirement for direct discharge, and treatments are necessary. Chemical precipitation, membrane treatment, ion exchange and electro-deionization have all been used to treat wastewater with high salinity [17,18]. Crystallization is another technology widely used for wastewater treatment. It has been employed to recover useful and valuable substances, remove heavy metals and soften water while reclaiming pure distilled water [19,20].

Fly ash washing wastewater contains a high concentration of NaCl and KCl. KCl is a valuable fertilizer. Attempts have been made to separate NaCl and KCl from fly ash washing wastewater by crystallization [21]. This research is part of a project that uses mechanical vapor recompression (MVR) and cooling crystallization processes to recover NaCl and KCl in a fly ash washing facility in Shanghai. However, a high concentration of Ca in washing wastewater is problematic. It is advisable to remove Ca to less than 40 mg/L to ensure the smooth operation of the crystallization process. At present, chemical precipitation and ion exchange are used to remove Ca to the required concentration. $NaCO_3$ is added to precipitate Ca as $CaCO_3$, and ion exchange is used as a polishing step to ensure low Ca concentration. However, chemical precipitation consumes a large amount of reagent, while ion exchange is also relatively expensive to operate. An alternative to removing Ca is urgently needed.

Therefore, this study aimed to carbonate fly ash wastewater with CO_2 and investigate the impact of wastewater pH, the flow rate of CO_2 gas and the carbonation time on the Ca removal efficiency. At the same time, the behavior of heavy metals (e.g., Pb, Zn) during carbonation was also studied. Activated carbon was used to adsorb heavy metals. The quality of the precipitate from carbonation with and without the adsorption pretreatment was compared. The morphology and the chemical and crystalline composition of the precipitate were studied in detail to reveal the behavior of Ca and other anions and cations to present a more comprehensive picture of the carbonation process. The ultimate goals were to optimize the conditions for carbonation and to investigate the combination of adsorption with carbonation to produce high-purity $CaCO_3$ products.

2. Materials and Methods

2.1. Fly Ash Washing Wastewater

The raw fly ash washing wastewater was from a fly ash washing facility in Shanghai, with a pH of approximately 11.8. Table 1 lists qualities of the wastewater.

Table 1. Quality of raw wastewater.

Parameters	Concentration (mg/L)	Heavy Metal	Concentration (mg/L)
Na^+	22,764	Pb	14.50
Ca^{2+}	11,731	Zn	10.20
K^+	19,712	Cd	12.29
Cl^-	66,721	Ni	3.03
SO_4^{2-}	878	Cu	0.57
Mg^{2+}	0.33	Cr	0.07
CO_3^{2-}	1800		
Total organic carbon (TOC)	52.5		

2.2. Activated Carbon and Other Chemicals

Activated carbon used in this study was a coal-based granular activated carbon with a particle size of 12 × 40 mesh (1.4 × 0.38 mm). DDA (dimethyldiallylammonium chloride) with a purity of 50 wt% was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). CO_2 gas was from Shanghai Jiangnan Gas Co., Ltd. (Shanghai, China), with a purity of 99.99%.

2.3. Procedures of Carbonation

During carbonation treatment, CO_2 was injected via an aerator (pore size 10 μm) into a beaker containing 100 mL of fly ash washing wastewater. Changes in pH were monitored via an on-line pH monitor (FK-pH6.0, FULLKON, Shanghai, China) with a precision of ±0.02. The effects of initial pH, flow rate of CO_2 gas and carbonation time were investigated. Initial pH of the wastewater was adjusted to 12.0, 12.5 or 13.0 by NaOH solution (1 mol/L). CO_2 flow rates were set at 30, 60 and 100 mL/min. The flow rate was controlled via a flow rate regulator with gauge (Shanghai Regulator Factory, Shanghai, China). Durations of carbonization were set at 5, 10, 15, 20, 40 and 60 min. After aeration for a predetermined period of time, wastewater was filtered through 0.45 μm filter. Filtrate was analyzed for concentration of anions and cations. Precipitate from carbonation was washed with deionized water until the conductivity of the water was close to that of the deionized water (about 0.14 μs/cm), and then dried at 105 °C via a drying oven (Heratherm, Thermo Fisher Scientific, Waltham, MA, USA) for 24 h for later analysis.

2.4. Activated Carbon Tailoring and Adsorption

Activated carbon was added to two columns 1.5 m long and 15 cm in diameter. For one of the columns, 10 L of DDA (10 wt%) solution was pumped cyclically for 12 h to load DDA onto activated carbon. Fly ash washing wastewater was then pumped through both columns for adsorption. Effluent was collected every 4 h and analyzed for concentrations of heavy metals.

2.5. Chemical Analysis

Concentrations of Ca, sulfate, carbonate, and bicarbonate and total alkalinity were measured by Standard Methods of China, GB 7476-87, HJ/T 342-2007 and SL 83-1994 [22], respectively. Heavy metals Pb, Cr, Zn, Cd, Ni and Cu were measured via ICP-OES (Optima 8000, PerkinElmer, Waltham, MA, USA). TOC was measured by a multi N/C 3100 analyzer (Analytikjena, Jena, Germany).

2.6. Characterization of Precipitate

X-ray diffraction (XRD, Rigaku UItima IV, Tokyo, Japan) analysis was conducted with 2θ ranging from 5° to 90° at a 40 kV accelerating voltage and a 30 mA current with a CuKα radiation source. The chemical composition, particle size distribution and morphology of the precipitates were determined by an X-ray fluorescence spectrometer (XRF, ZSX Priums IV, Rigaku, Tokyo, Japan), a laser particle size analyzer (Malvern Mastersizer 2000, Malvern, UK) and a scanning electron microscope (Zeiss Gemini 300, Oberkochen, Germany).

3. Results and Discussion

3.1. Carbonation

3.1.1. Effects of Initial pH

The main purpose of the carbonation of fly ash washing wastewater is to remove Ca by forming $CaCO_3$ precipitation. When CO_2 is introduced into the wastewater, it is absorbed and exists as dissolved CO_2, carbonic acid, carbonate or bicarbonate. The speciation is highly dependent on the aqueous pH [23].

The pH of the raw washing wastewater in this research was 11.8. To investigate the effects of pH, initial pH was adjusted to 12.0, 12.5 and 13.0, respectively. The CO_2 flow rate was 30 mL/min. The changes in pH and the Ca removal efficiency at pH 11.8, 12.0, 12.5 and 13.0 as carbonation progressed are shown in Figure 1a–d. The introduction of CO_2 led to a rapid drop in pH at an initial pH 11.8 (Figure 1a). The pH declined from the original 11.8 to 6.7 after only 10 min. This could have been due to the low buffering capacity of the raw wastewater. The Ca removal efficiency peaked at 10.3% at 10 min. As carbonation continued, Ca removal efficiency actually decreased to about 4.9% at 60 min. This means that the direct carbonation of wastewater for the Ca removal was not effective. Raising the initial pH of the wastewater was necessary.

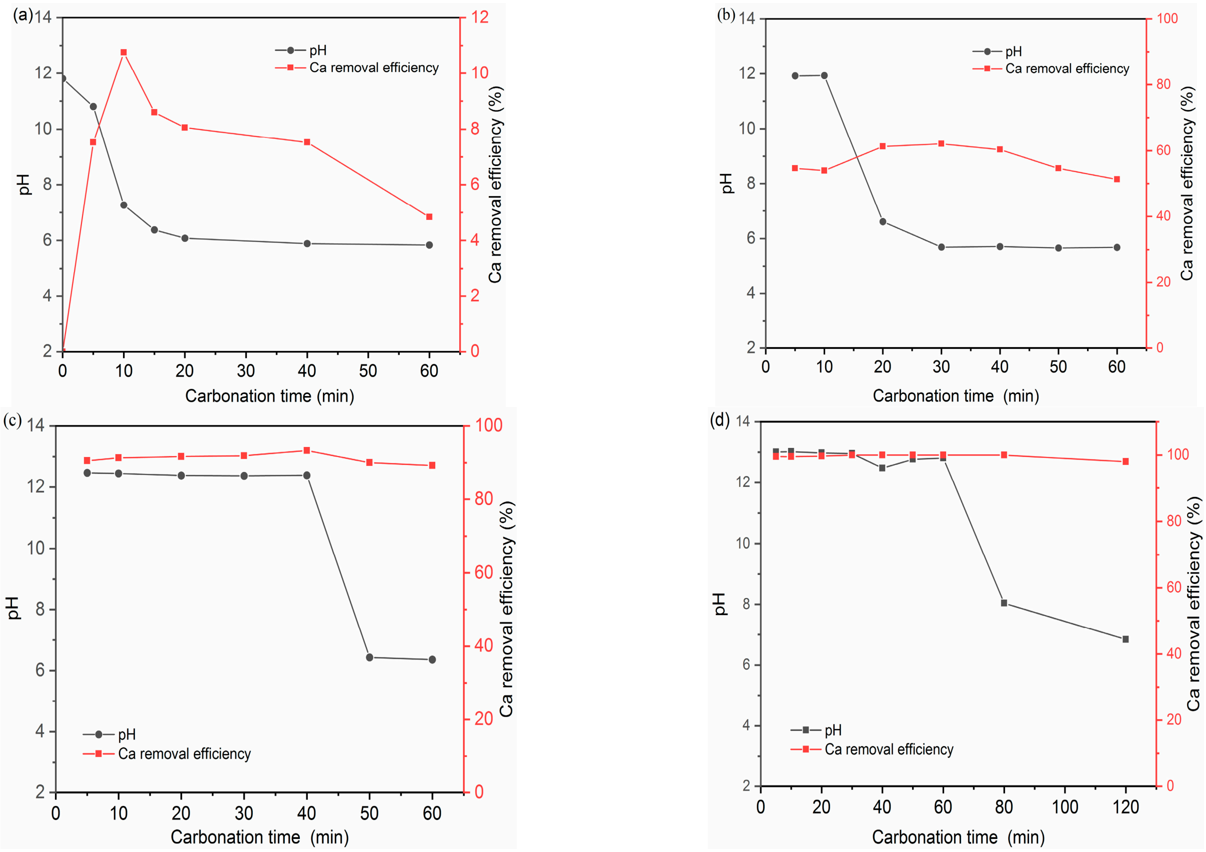

Figure 1. Changes in wastewater pH and Ca removal efficiency at different initial pH: (**a**) pH = 11.8; (**b**) pH = 12.0; (**c**) pH = 12.5; (**d**) pH = 13.0.

When the initial pH was adjusted to 12.0 (Figure 1b), the Ca removal efficiency rose to 54% after 5 min of carbonation and reached 61% at 20 min. The pH remained at 12.0 for 10 min, decreased to about 6.7 after 20 min, and then stabilized at about 5.6 after 30 min. The Ca removal efficiency was stable at around 60% until about 40 min, and then dropped to 50% after 60 min. Comparing this with the results shown in Figure 1a, the Ca removal efficiency was improved significantly by increasing the initial pH of the wastewater from 11.8 to 12.0.

The initial pH was further raised to 12.5 and 13.0 (Figure 1c,d). The Ca removal increased quickly to 90% and 99% after only 5 min of carbonation. At a pH of 12.5, the Ca removal maximized at 93% at 40 min, while at a pH of 13.0, the Ca removal reached almost 100% at 30 min. The Ca concentration in the effluent decreased to 820 mg/L and less than 40 mg/L. The standard method used to analyze Ca concentration has a detection limit of 40 mg/L. The Ca removal remained high even after the pH started to drop. For the initial pH of 12.5, the Ca removal only slightly dropped, to about 88%, after 60 min. At a pH of 13.0, the Ca removal remained greater than 99% after 120 min, even though the pH had already dropped to about 6.2.

A large amount of precipitate was produced during carbonation. Figure 2 shows the mass of the precipitate produced per liter of wastewater (unit: g/L) at different initial pH and different carbonation times. At the original pH of 11.8, a maximum of 4.2 g/L of precipitate was produced, and this was in accordance with the low Ca removal. The mass of the precipitate increased with the increase in the initial pH. The maximum mass values at 12.0, 12.5 and 13.0 were 35 g/L, 60 g/L and 73 g/L, respectively. In addition, at pH 12.5 and 13.0, as the carbonation time extended, the mass of the precipitate remained stable. This corresponded well with the Ca removal results in Figure 1. These results show that the precipitate did not dissolve simultaneously with the pH decline. That is, the re-dissolution of the precipitate lagged behind the pH change. This may have been because it took time for the carbonic–carbonate balance to shift sufficiently for the precipitate to dissolve when the pH started to change. That is, the kinetics of the reaction are also important. During the experiment, the precipitate was separated from the aqueous phase after the carbonation finished. The time of contact between the acidic water and the precipitate was limited.

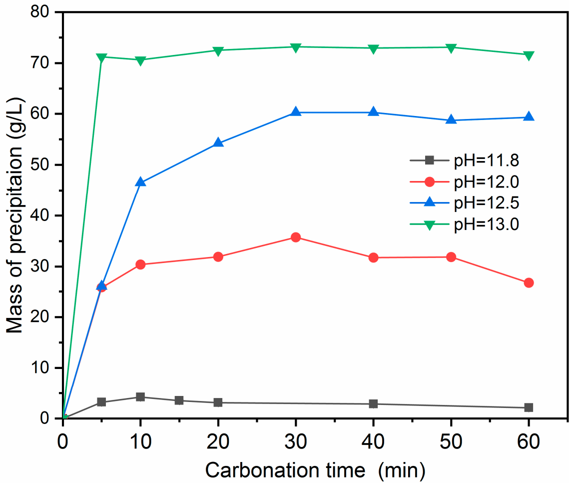

Figure 2. Mass of precipitate per liter of wastewater at different initial pH and carbonation times.

Overall, to achieve high Ca removal, it is important to maintain a high-pH environment. Adjusting the pH to 13.0 is advisable. At this pH, the Ca concentration in the effluent decreased to less than 40 mg/L and a high amount of precipitate was also produced.

3.1.2. Effects of CO_2 Flow Rates

The CO_2 flow rate may affect the formation of precipitation particles [24]. The initial pH of the raw water was adjusted to 13.0 and the flow rates were set at 30, 60 and 100 mL/min. Figure 3a shows the variation of the pH and Ca removal with carbonation time at different CO_2 flow rates. The patterns of the changes in the pH and Ca removal over time were similar at different flow rates. The pH was stable at first, and then started to drop as the carbonation continued. As the CO_2 flow rate increased, the time it took for the pH to drop shortened. At flow rates of 30, 60 and 100 mL/min, the pH started to drop after 60, 30 and 20 min, respectively. The Ca removal efficiency was high, at more than 99%, before the pH declined. The concentration of the Ca decreased to less than 40 mg/L under all the flow rates. Overall, it seems that the effect of the CO_2 flow rate on Ca removal efficiency is negligible.

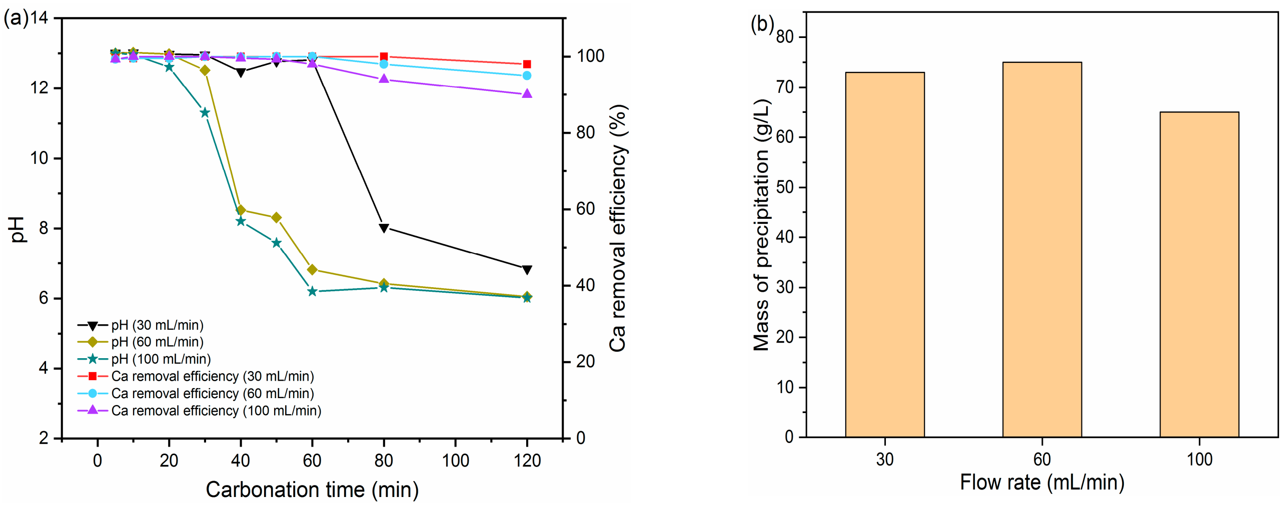

Figure 3. Changes in wastewater pH, Ca removal efficiency and mass of precipitate at different CO_2 flow rates: (**a**) pH and Ca removal efficiency; (**b**) mass of precipitate.

Figure 3b displays the mass of the precipitate after 30 min of carbonation at different flow rates. The mass of the precipitate increased slightly from 73 g/L to about 75 g/L as the flow rate increased from 30 mL/min to 60 mL/min. At a flowrate of 100 mL/min, the mass decreased to about 65 g/L. As shown in Figure 3a, at 100 mL/min, the pH of the wastewater was maintained for only 20 min before it started to decrease. It appears that the higher CO_2 injection caused the pH to drop too fast, which is not conducive to the production of precipitate. González-López et al. [25] also found out that pressure of CO_2 gas, pH and salinity of water affected the dissociation of carbonic acid. A higher CO_2 flow rate can affect the formation of precipitate.

Overall, increasing the CO_2 flow rate did not significantly increase the removal of Ca or the formation of precipitate. For the carbonation of wastewater in this research, a relatively low CO_2 flow rate of 30 mL/min was sufficient.

3.2. Characteristics of Precipitate

The results from the carbonation show that carbonation is able to remove Ca by precipitating it from the aqueous phase. The characterization of the precipitate was carried out via XRD and XRF analyses. The XRD patterns of the precipitate at different carbonation times at an initial pH of 13 are shown in Figure 4. The XRD results reveal a clear transformation in the compositions of the precipitate over the carbonation time. $Ca(OH)_2$ predominated in the precipitate after 5 min of carbonation. It seems that as the pH was raised to 13, the wastewater was a solution saturated with $Ca(OH)_2$. The Ca removal was mainly due to the crystallization of the $Ca(OH)_2$. Only a small amount of $CaCO_3$ was detected at this stage. This shows that it took time for the $CaCO_3$ to form. As the carbonation progressed, the $Ca(OH)_2$ gradually disappeared. After 30 min of carbonation, almost no $Ca(OH)_2$ was detected, and $CaCO_3$ became the dominant crystalline structure. The XRD patterns after 30 min were quite similar, with $CaCO_3$ as the dominant species. NaCl, KCl and $CaSO_4$ were also found in the precipitate. The XRD results reveal that, even though the Ca removal reached 99% as soon as the carbonation started, to recover $CaCO_3$ precipitation, it is important to carbonate for at least 30 min.

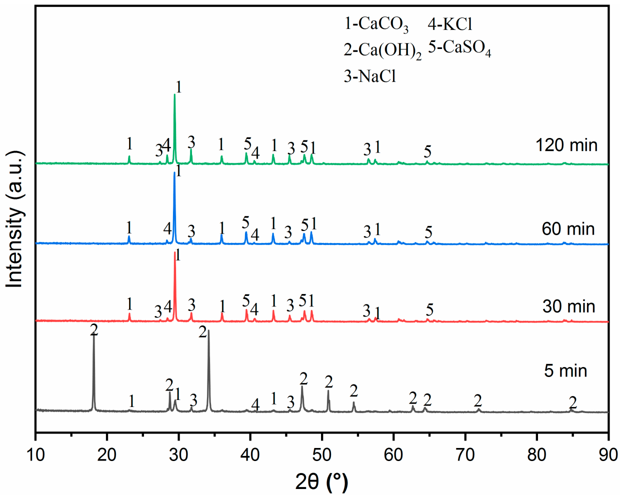

Figure 4. XRD patterns of precipitate at different carbonation times.

Additionally, Table 2 lists the chemical compositions. The dominant elements include Ca, Cl, Na and K. This is in agreement with the results from the XRD analysis. In particular, the Ca contents were more than 30 wt% after carbonation for 30 min, indicating the formation of mainly Ca-containing precipitates. However, the XRF also detected the presence of Pb and Zn, together with small amounts of Fe, S and Si. Comparing the concentrations of heavy metals in the raw wastewater (Table 1) with the contents in the precipitate (Table 2), it appears that although fly ash wastewater contained many heavy metals, only Pb and Zn co-precipitated with $CaCO_3$ during the carbonation. Metals such as Cu, Ni, Cd and Cr remained in the aqueous phase. In particular, the contents of Pb and Zn surpassed the requirements for the industrial use of $CaCO_3$ (Standard of China, HG/T2776-2010 [26]). Therefore, to recover high-quality $CaCO_3$, it is necessary to inhibit the co-precipitation of heavy metals during carbonation.

Table 2. Chemical composition (wt%) of precipitates.

Element (wt%)	Carbonation Time			
	5 min	**30 min**	**60 min**	**120 min**
Ca	35.409	30.197	30.468	30.850
Cl	0.525	1.188	0.724	0.812
Na	0.135	0.401	0.280	0.324
K	0.116	0.244	0.110	0.268
Pb	0.489	0.384	0.612	0.550
Zn	0.020	0.014	0.016	0.016
Fe	0.029	0.023	0.027	0.031
S	0.054	0.082	0.125	0.079
Si	0.160	0.137	0.150	0.161
Cu	ND	ND	ND	ND
Ni	ND	ND	ND	ND
Cd	ND	ND	ND	ND
Cr	0.007	ND	ND	0.006
Mn	ND	ND	ND	ND

Note: ND: not detected.

3.3. *Heavy Metals Removal from Fly Ash Wastewater*

As shown by the characterization of the carbonation precipitate, a significant amount of Pb and Zn co-precipitated, which resulted in a $CaCO_3$ product with impurities. To purify the carbonation product, a quaternary ammonium salt (DDA)-modified activated carbon was used to pre-treat the fly ash wastewater to remove the Pb and Zn.

The speciation of Pb and Zn in the aqueous environment is influenced by the co-existing ions and substances in the water, such as H^+, OH^-, Cl^-, SO_4^{2-} and CO_3^{2-} [27]. Visual Miniteq software 3.1 was used to calculate the predominant species at different pH. The results are shown in Figure S1 in the Supplementary Materials. At pH < 8, Pb and Zn exist mainly as positively charged ions [28]. As the pH increased to around 8, Pb and Zn began to form precipitates, such as $Pb(OH)_2$, $PbCO_3$ and $Zn(OH)_2$. Furthermore, at pH > 11, the precipitates re-dissolved, and the Pb and Zn existed as negatively charged hydroxylated anions, such as $Pb(OH_3)^-$ and $Zn(OH)_3^-$. That is, Pb and Zn existed as negatively charged species at the wastewater pH in this research. Therefore, it is important that the activated carbon used should have a strong capacity for the adsorption of anions.

Dimethyldiallylammonium chloride (DDA) was chosen to modify the activated carbon first, before adsorption. Liang et al. [29] compared the effects of different quaternary ammonium salts and concluded that modification via quaternary ammonium salt was able to change the surface charge of activated carbon. The change was attributed to the N in the quaternary ammonium, which was positively charged in the pH range of common aqueous environments. The modification enhanced the activated carbon's adsorption of anions by electrostatic adsorption. Among the quaternary ammonium salts investigated, DDA showed the best results.

In this research, original activated carbon and activated carbon modified by DDA were installed in columns for comparison to remove heavy metals. Figure S2 in the Supplementary Materials shows the Pb and Zn breakthrough curves of the activated carbons. The bed volume in the figure is the volume of water processed divided by the bed volume of the column, and it is dimensionless. As shown by the breakthrough curves, DDA modification can greatly enhance adsorption of Pb and Zn. The bed volume that could be operated before Pb an Zn were detected in the effluent was almost four times that of the original activated carbon.

To ensure the quality of the precipitate from the carbonation, the effluents from the DDA-modified activated carbon with Pb and Zn concentrations less than 0.01 mg/L were collected for future carbonation. Table 3 shows the quality of the wastewater after adsorption. The modified activated carbon showed strong selectivity for Pb and Zn, while about 20% of the Cd, Ni, Cu and Cr was also adsorbed. By comparison, the Na^+, K^+ and Cl^- were not affected, while the concentrations of Ca^{2+} and SO_4^{2-} decreased slightly. The activated carbon also showed strong adsorption of TOC, which declined from 52.5 mg/L in the raw wastewater to 10.1 mg/L. Overall, activated carbon adsorption was effective as a pretreatment method, which successfully removed heavy metals and organics.

Table 3. Quality of wastewater after activated carbon adsorption.

Parameters	Concentration (mg/L)	Heavy Metal	Concentration (mg/L)
Na^+	22,350	Pb	<0.01
K^+	18,900	Zn	<0.01
Cl^-	67,230	Cd	9.32
Ca^{2+}	10,750	Ni	2.50
SO_4^{2-}	620	Cu	0.33
CO_3^{2-}	1750	Cr	0.05
TOC	10.1		

3.4. Carbonation after Activated Carbon Adsorption

The effluent from the activated carbon column was adjusted to a pH of 13 and carbonated for 30 min. Figure 5 shows the particle size distribution and SEM images of the precipitate. The particle sizes of the precipitates were predominantly in the range of 40–100 µm, with a median size of 47 µm and a homogeneity coefficient of 1.13. The specific surface area of the particles was 0.48 m^2/g. The particles were classified as microfine particles. As shown by the SEM image in Figure 5b, the resultant precipitate particles were uniformly sized cubes. These cubes were most likely calcite. In their research on calcium carbonate synthesis, Shen et al. [30] also reported that calcite in cubic shapes was produced when $CaCl_2$ reacted directly with Na_2CO_3. An additive (e.g., sodium dodecyl benzene sulfonate) was needed to form spherical vaterite.

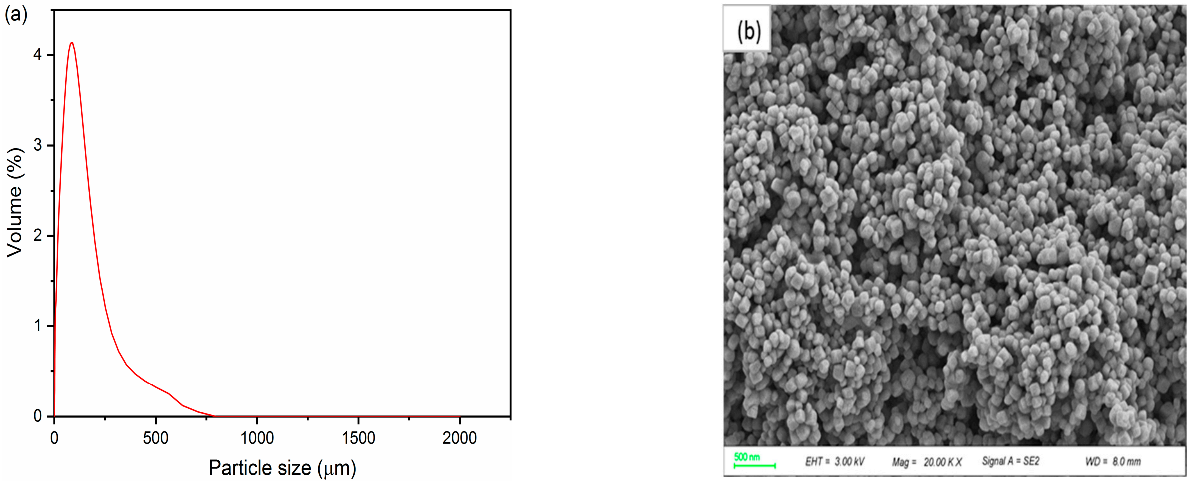

Figure 5. Particle size and SEM analysis of precipitate: (**a**) particle size distribution; (**b**) SEM image.

Tables 4 and 5 are the chemical compositions and quality of the water after carbonation. According to the XRF analysis results in Table 4, the contents of heavy metals in the precipitate were all negligible. The CA content reached 38.29 wt%. $CaCO_3$ thus formed could be used industrially.

Table 4. Chemical composition via XRF.

Element	Ca	Cl	K	Pb	Zn	Cu	Ni	Cd	Cr	Fe	Mn	S	Si
Content (wt%)	38.29	0.52	0.12	ND	ND	ND	ND	ND	ND	0.006	0.005	0.05	0.15

Note: ND: not detected.

Table 5 lists the quality of the water after adsorption and carbonation. The water still contained high concentrations of Na, K and Cl, while the concentrations of heavy metals all met the standard for discharge. This ensured that the water could be entered into the MVR to recover NaCl and KCl.

Table 5. Quality of wastewater after adsorption and carbonation.

Parameters	Concentration (mg/L)	Heavy Metal	Concentration (mg/L)
Na^+	21,250	Pb	<0.01
K^+	18,920	Zn	<0.01
Cl^-	63,530	Cd	8.23
Ca^{2+}	28	Ni	1.70
$SO_4{}^{2-}$	420	Cu	0.30
$CO_3{}^{2-}$	4250	Cr	0.04
TOC	8.50		

Furthermore, according to Table 5, the carbonate concentration increased significantly due to the introduction of CO_2, which was converted into the liquid or solid phase in the form of carbonate. The ability of carbonation to sequester CO_2 was calculated by comparing the mass of the carbonate in the wastewater with the mass of the carbonate that remained and the carbonate in the precipitate. The carbonation had a carbon sequestration ability of about 80%. Due to its alkalinity, studies have used CO_2 as a reagent not only to detoxify fly ash, but also to sequester CO_2 [31,32]. This research showed that fly ash wastewater also had the potential to sequester greenhouse gas. This is in agreement with the review of technologies for CO_2 mineralization by fly ash conducted by Wang et al. [33]. The review pointed out that the Ca compounds in washing wastewater were in more favorable forms (e.g., $CaCl_2$, $Ca(OH)_2$) for reactions with CO_2 than those in the original fly ash (e.g., CaClOH).

4. Conclusions

The fly ash washing wastewater in this research had high salt contents of NaCl and KCl, which had great potential for recycling. Carbonation can effectively reduce the concentration of Ca in wastewater to less than 40 mg/L. The removal efficiency of Ca exceeded 99% when the pH of the wastewater was adjusted to 13.0. The XRD analysis illustrated that the Ca first precipitated as $Ca(OH)_2$, and it took about 30 min for $CaCO_3$ to become the predominant species. In addition, the CO_2 flow rate also affected the formation of precipitation. A relatively low flowrate was conducive to maintaining a high-pH environment. Overall, the optimal conditions for carbonation are pH of 13.0, carbonation time of 30 min and flow rate of 30 mL/min. However, direct carbonation caused the co-precipitation of heavy metals, which affected the quality of the $CaCO_3$ precipitate. Therefore, it is necessary to remove heavy metals first. With DDA-modified activated carbon adsorption as the pretreatment, carbonation was able to produce not only a $CaCO_3$ with high purity, but also a wastewater that was ready for NaCl and KCl recovery. The Ca content in the $CaCO_3$ thus formed reached more than 38 wt%. The cube-shaped precipitate consisted mainly of microfine particles. In conclusion, the adsorption and carbonation treatment of fly ash washing wastewater can serve as a pretreatment process for subsequent salt recovery. This process not only showed high calcium removal efficiency, but also produced a by-product that was reusable.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16202896/s1. Figure S1. Speciation of Pb and Zn in the fly ash wastewater; Figure S2. Pb and Zn breakthrough curves for original and DDA-modified activated carbons.

Author Contributions: W.C.: conceptualization, project administration, supervision, review and editing; Y.C.: data curation, formal analysis, investigation, draft; Y.W.: visualization, data curation; N.Z.: data curation, investigation. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are contained within the article and Supplementary Materials.

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

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