Carbon dioxide capture using various metal oxyhydroxide-biochar composites

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Abstract

Innovative and cost-effective methods are needed to capture and store CO₂ to reduce anthropogenic impact on global warming. This work produced and characterized aluminum hydroxide, magnesium hydroxide, and iron oxide-biochar composites, and evaluated their ability to capture CO₂ at room temperature and atmospheric pressure. Biomass feedstocks were treated with metal ions of a variety of concentrations, and were then pyrolyzed at 600 °C. Characterization experiments showed that the process not only turned the biomass into biochar, but also converted the metal ions into metal oxyhydroxide nanoparticles onto the carbon surfaces with the biochar matrix. As a result, the composites, particularly the ones with optimal metal to biomass ratios, had higher CO₂ capture capacity than the unmodified biochar. All the composites had relatively large surface area and captured CO₂ mainly through physical adsorption. Although Fe₂O₃-biochar composites had the highest surface area, the AlOOH-biochar composite showed the largest sorption. Thus, both the characteristics of the metal oxyhydroxides and the surface area contributed to the CO₂ capture capacity. The maximum adsorption capacity (71 mg g⁻¹ at 25°C) by AlOOH-biochar is comparable to commercial adsorbents. The samples had between 90-99% desorption at 120 °C, so they required low cost regeneration. All these results suggested that biochar-based composites could be a high efficiency and cost-effective adsorbent for CO₂ capture.

Keywords: engineered biochar; biochar nanocomposites; CO₂ capture; CO₂ adsorption; carbon sequestration

1. Introduction

As a greenhouse gas, carbon dioxide (CO₂) is one of the major contributors to global warming and is significantly produced from anthropogenic sources. To reduce greenhouse gas emission, CO₂ capture technologies are retrofitted to power plants post combustion in the electric-power sector [1]. Unfortunately, current CO₂ capture technologies have high energy penalties [2] and the most robust technology, amine scrubbing [3], has significant negative human and environmental drawbacks [4]. It is therefore necessary to develop effective CO₂ sorbents that are inexpensive and renewable, for use in large-scale post combustion technologies.

Physical adsorbents, such as carbon materials, have potential to capture CO₂ with higher stability, higher regeneration, and lower energy consumption than conventional chemical processes [5-7]. Many of the adsorbents for CO₂ capture, however, are relatively high priced and thus, there are needs for the development of cost-effective ones. Biochar is a low-cost carbon material that can be produced by low temperature pyrolysis of waste biomass [8-10]. Biochar is often used as soil amendment for soil improvement and carbon sequestration [11-13]. Recently, Creamer et al. [14] showed that biochar has the ability to capture CO₂ at levels comparable to well-established adsorbents. In comparison to other commonly used CO₂ capture adsorbents, biochar is more cost-effective because of following advantages: (1) it can be produced from waste organic materials; (2) its production is performed at relatively low temperature; (3) the material can also be regenerated at a low energy, due to its physical adsorption behavior [14].

Recent development of the biochar technology showed that biochars can be modified (i.e., engineered biochars) to enhance their sorption ability to various chemical compounds [15-17]. Previous studies have used metal oxyhydroxide-biochar composites to capture contaminants in aqueous solutions. For example, Zhang et al. [18] used MgO-biochar composite to remove phosphate and nitrate from solution. Yao et al. [19] used Mg oxyhydroxide biochar to remove phosphate in solution. In both studies, there was a strong correlation between the Mg content and the removal P from solution, which can be explained by the electrostatic interactions between the P and the Mg oxyhydroxide particles on biochar surfaces. Zhang and Gao [20] used a AlOOH /biochar composite to successfully remove arsenic and methylene blue from solution. In this case, the aluminum in biochar served as a precursor for the formation of AlOOH nanoparticles, which increased bonding affinity of the sorbent to the contaminants. Similarly, an AlOOH and mesoporous carbon composite was synthesized in a study by Chang et al. [21]; this stable framework had high surface area and showed to be capable of rapid CO₂ capture. Other metal oxyhydroxide-biochar composites, such as Fe₂O₃-biochar composite, which possessed ferromagnetic properties due to the presence of iron oxide [22, 23], have also been synthesized and showed enhanced sorption to various contaminants.

Previous studies have shown that frameworks with open metal sites tend to have a high affinity for CO₂ [5]. The basic nature of carbon and metal oxide frameworks enhances the selectivity of the material toward CO₂ over CH₄ and N₂, two other components in flue gas. Further, the addition of polar basic groups produces a reversible bond with CO₂ [5]. Metal oxyhydroxides are generally basic, so tend to bond with CO₂, an acidic gas, when polar surfaces are in contact. It is thus expected that the biochar-

based composites should also capture CO₂. Nevertheless, only few studies have investigated the sorption of CO₂ on metal oxyhydroxide-biochar composites [24].

The overarching objective of this work was to determine the effectiveness of metal oxyhydroxide-biochar composites for the capture of CO₂. Specifically, this research aimed to 1) produce and characterize metal oxyhydroxide-biochar composites of three metals(aluminum, iron, and magnesium); 2) assess and model CO₂ capture kinetics onto the composites; 3) optimize the production of the composites for CO₂ capture; and 4) recognize the governing mechanisms for CO₂ sorption onto the composites.

2. Experimental

2.1. Materials

Cottonwood (CW) trees are commonly found in the southern regions of the United States. For this study, raw cottonwood feedstock was obtained from Gainesville, FL and was then dried and milled into ~2mm fractions. Three metal salts, aluminum chloride, iron chloride, and magnesium chloride hexahydrate were purchased from Carolina Biologicals.

2.2. Biochar/metal oxyhydroxide composite production

The biochar-based composites were produced using procedures suggested in previous studies [18, 20, 22], which all produced large quantities of biochar/metal oxyhydroxide composites using one-step pyrolysis. Varying amounts of AlCl₃, FeCl₃, and MgCl₂ hexahydrate were dissolved in solution with 60mL of deionized (DI) water. 5 grams of cottonwood was mixed into the solution and stirred until it was saturated. The

mixture was dried completely at 60 °C and then pyrolyzed at 600 °C in a tube furnace under nitrogen flow for 3 hours. The resulting biochars were then rinsed with tap water for 40 minutes and rinsed with DI water for 20 minutes to remove excess metal and impurities. The biochar samples were then dried, and stored in sealed containers. The samples were labeled by abbreviations representing the metal and feedstock: AlCW (aluminum and cottonwood), MgCW (magnesium and cottonwood), FeCW (iron and cottonwood). The unmodified cottonwood biochar was labeled as CW(0).

2.3. Properties of biochar/metal oxyhydroxide composites

All the biochar samples were characterized for surface area, pore volume, crystal structure, metal content, and material structure. Surface area analysis was performed with a Quantachrome Autosorb-1 analyzer using the N₂ adsorption method. To qualitatively approximate the size of particles, SEM analysis was performed at 8,000x and 5,000x magnification. Once the particles on the surface of the composite are detected, EDS (Energy Dispersive X-ray spectroscopy) at 1000x magnification was used to confirm that these particles are metal compounds. In order to classify the crystalline forms of the metal oxyhydroxides on the samples, X-ray diffraction (XRD) analysis was performed using a computer-controlled X-ray diffractometer. XRD data along with the Scherrer method was used to further calculate particle size. The concentration of metals (aluminum, iron, and magnesium) in the biochar was determined with the AOAC method using inductively coupled plasma with atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 2100 DV).

2.4. CO₂ capture

Adsorption kinetic measurements were performed with a Thermogravimetric Analysis (TGA) instrument at a flow rate of 50 mL/min following the procedures of Shafeeyan, Daud, Houshmand and Arami-Niya [25]. Because CO₂ capture is most effective under high flow conditions [26], this low flow rate may underestimate the total adsorption capacity of the biochar for CO₂. About 20 mg of sample was placed on the TGA balance. Nitrogen gas was first used to purge potential volatile components out of the sample and chamber at 120 °C at 50 mL/min. The temperature was then lowered to 25 °C and CO₂ flows through at a rate of 50 mL/min for 3 hours. Baseline mass measurements were taken once CO₂ starts to flow through the TGA. To mitigate instrument and buoyancy influences, a blank run was performed under identical test conditions. The CO₂ adsorption kinetic measurements for each of the 21 samples were measured by TGA and the results are modeled using a 2nd order adsorption kinetic model.

2.5. Regeneration

For selected biochar samples, after the CO₂ passed through the TGA at 25°C for 3 hours, the gas switched to N₂, and the temperature was elevated to 120 °C again for 3 hours. The remaining mass of CO₂ was divided by the mass of CO₂ captured after 3 hrs at 25 °C to calculate the efficiency of regeneration.

3. Results and Discussion

3.1. Biochar Characterization

Due to the nature of biochar, the samples were highly carbonaceous. When the feedstock was modified with the salt (AlCl_3 , MgCl_2 , or FeCl_3), the concentration of each respective metal increased (Table 1), indicating the metals were successfully loaded into the biochar. For the biomass treated with MgCl_2 , the percent of metal in the compound ranged from $<0.1\%$ in the unmodified cottonwood biochar to 5.74% in $\text{MgCW}(40)$, which had a solution mixture ratio of 40:1 ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O} : \text{H}_2\text{O}$). The surface area ranged from $99 \text{ m}^2/\text{g}$ to $290 \text{ m}^2/\text{g}$ in $\text{MgCW}(20)$. There was no significant correlation between the concentration of magnesium metal in the MgCW samples to the surface area ($r^2=0.22$) nor the pore volume ($r^2=0.27$).

For FeCW , the surface area of the metal biochar composite ranged from $99 \text{ m}^2/\text{g}$ in the unmodified cottonwood biochar to $750 \text{ m}^2/\text{g}$ in $\text{FeCW}(10)$, which had the highest concentration of iron. The percent of iron in the biochar ranged from <0.1 in $\text{CW}(0)$ to 3.7% in $\text{FeCW}(10)$. The pore volume was also highest ($.39 \text{ cm}^3/\text{g}$) in $\text{FeCW}(10)$. The correlation between the iron concentration and surface area in the FeCW samples was high ($r^2=0.87$) and the correlation with pore volume was slightly lower ($r^2=0.77$).

The percent of metal in the compound ranges from $<0.1\%$ in the unmodified cottonwood to 0.8% in the aluminum sample that had a ratio of 4:1 ($\text{AlCl}_3 \cdot \text{H}_2\text{O}$). There was a relatively high correlation between the metal ratio in solution and the surface area of AlCW samples ($r^2=0.78$). As the concentration of metal in the solution increases, the surface area tended to increase, although there were only small amounts of aluminum in the composite. The highest surface area was attributed to the samples with highest concentration of aluminum in solution. $\text{AlCW}(3)$ delivered a value of $370 \text{ m}^2/\text{g}$ and similarly, $\text{AlCW}(4)$ had a surface area of $367 \text{ m}^2/\text{g}$. There was a low correlation between

the percent of aluminum in AICW biochar metal composite and the surface area ($r^2=0.37$), as well as with the with pore volume ($0.47 \text{ m}^2/\text{g}$).

SEM images show that the MgCW sample was made up of few oblong particles, perhaps carbon, which are decorated with particles of varying size; some particles had dimensions of less than 100nm (Figure S1, Supporting Information). Mono-dispersed particles with sizes less than 100nm were also found on the surface of the FeCW. The morphology of the AICW sample appeared euhedral, with an angular stacking morphology. In order to determine whether the particles were composed of metal compounds, EDS was used at 1000x magnification. Figure 1 shows the location on the SEM image where the EDS data were taken. The imaging makes it possible to identify iron oxide particles on the surface of the carbon framework (Figure 1c). In Figure 1a, $\text{Mg}(\text{OH})_2$ particles can be seen on the surface of the carbon framework. Boehmite particles can be seen on the surface of the carbon framework (Figure 1b). EDS elemental analysis confirmed that the presence of iron, magnesium, and aluminum in each representative FeCW, MgCW, and AICW sample, was much higher than that of the unmodified (CW) sample (Figure 1a, 1b, and 1c).

XRD testing was used to determine the crystallinity and type of metal oxyhydroxides present in the samples. FeCW and MgCW samples had the strongest peaks (Figure 2). FeCW had d-spacing at 4.85, 2.96, 2.5, 2.1, 1.6, and $1.5 \text{ \AA}$ which match the iron oxide (Fe_2O_3) diffraction patterns in the literature [27]. MgCW had the diffraction d-spacing at 4.8, 2.7, 2.4, 1.8, and $1.6 \text{ \AA}$, which match the reported diffraction patterns for Brucite ($\text{Mg}(\text{OH})_2$) [27]. AICW had d-spacing at 6.2, 2.3, 1.9, and $1.4 \text{ \AA}$, which match the reported diffraction patterns for Boehmite (AlOOH) [27]. As observed

by their well-defined peaks, the metal oxyhydroxide particles on MgCW and FeCW samples were highly crystalline.

In this work, the pyrolysis of MgCl_2 treated biomass introduced $\text{Mg}(\text{OH})_2$ particles on the biochar, which is unlike the results of Zhang et al. [18] that indicate the presence of MgO particles on the biochar surface. The discrepancy might due to differences in the pyrolysis and rinsing processes. In particular, the rinsing of the samples in this study was much more intense and with higher volume of water, which leads to the conversion of MgO into $\text{Mg}(\text{OH})_2$. Yao et al. [19, 28] observed both MgO and $\text{Mg}(\text{OH})_2$ particles on biochar surfaces after pyrolyzing Mg-enriched feedstocks. The presences of AlOOH and Fe_2O_3 particles on the AlCW and FeCW samples are analogous to the results obtained in previous studies [20, 22], probably because these two metal oxyhydroxides are more stable than the MgO when they are in contact with water. Because SEM revealed the presence of particles in the nano range for all samples (Figure S1, Supporting Information), the Scherrer formula was used to further approximate the size. The representative MgCW, FeCW, and AlCW samples had particle sizes of about 23 nm, 36 nm, and 3 nm, respectively, which is similar to the findings of previous studies [18-20, 22, 28].

The characterization results showed that the synthesis method used in this work successfully produced iron, aluminum, and magnesium oxyhydroxide-biochar composites at a variety of metal concentrations and with extensive surface area. Depending on the needs, these biochar-based composites may be used as adsorbents for various applications.

3.2. CO₂ capture kinetics

Figure 3(a, b, and c) illustrates the capture kinetic curve for each of the optimal metal concentrations in the metal-biochar composites (i.e., had the highest CO₂ capture of its kind) and show that the amount of CO₂ captured tends to level off after 30 minutes. The sorption kinetics of all the biochar samples were fitted with the second order kinetics model that followed the procedures of Creamer et al. [14]. Table 2 gives the best-fit parameters for the model along with the correlation coefficient (R^2). The values for the equilibrium amount of the adsorbed CO₂ (q_e) ranged from 27 to 63 mg g⁻¹ for MgCW, 54 to 67 mg g⁻¹ for FeCW, and 63 to 71 mg g⁻¹ for AlCW. Unmodified cottonwood biochar has a q_e of 58 mg g⁻¹, lower than any of the optimal metal-biochar composites. The sample that best captures CO₂ was AlCW(4), which showed a 22% improvement compared to CW(0). MgCW(.01) and FeCW(.1) showed 9% and 16% improvement, respectively. The kinetics constant (k) ranged between 15 to 29 x10⁻⁵ for MgCW, 16 to 22x10⁻⁵ for FeCW and 2.4 to 19 x10⁻⁵ for AlCW. The R^2 values are above .88 for aluminum, above .93 for iron, and above .97 for magnesium.

The maximum sorption of carbon dioxide was recorded for each biochar sample. AlCW, MgCW, and FeCW samples each had an optimal metal concentration at which CO₂ adsorption was highest. All of these adsorption values were higher than that of the unmodified biochar, CW(0); however, AlCW samples, in general, had the highest adsorption. The CO₂ capture capacity of AlCW(4) is comparable other adsorbing composites that are considered for large-scale applications (Table S1, Supporting Information).

3.3. Governing Mechanisms

The adsorption of CO₂ onto the each biochar composite was all highly reversible (Figure S2, Supporting Information). The representative AICW sample had the highest percent regeneration of CO₂ (99%); whereas, MgCW(.01) had 96% and FeCW(.1) had the lowest regeneration of CO₂ (90%). These results suggested that physical adsorption could be the main mechanism governing the capture of CO₂. Easy regeneration is an advantage of the biochar/metal oxyhydroxide composites in the real-world applications for CO₂ capture. In the case of physical adsorption, it is important to have both high surface area and abundant adsorption sites to enable surface bonding.

Figure 4 demonstrates that the adsorption of carbon dioxide onto aluminum oxide modified biochar was poorly correlated to surface area ($R^2=0.08$), indicating that large surface area of the adsorbent may not guarantee the high adsorption of CO₂. Figure 5 shows that, for AICW samples, as the concentration of aluminum increased, the adsorption of CO₂ increased as well, confirming that the metal oxyhydroxides played an important role in the CO₂ capture. Pierre-Louis et al [29] reported that AlOOH particles have strong sorption ability to CO₂, which is mainly controlled by surface adsorption process.

Galinsky et al. [30] found iron oxides incorporated in conductive membrane has excellent redox ability to capture CO₂, under high temperatures; however, iron oxide has not been studied extensively as a CO₂ capture material at low temperatures. In this work, nanosized Fe₂O₃ particles may contribute to the enhanced CO₂ capture by some of the FeCWs through surface adsorption. Although the surface area of FeCW(5) is much higher than that of the AICW(1), it showed lower CO₂ adsorption capacity. This result

suggests that the interactions between the CO₂ and AlOOH particles were much stronger than that of the iron oxide particles. Further investigations, however, are still needed to understand the binding affinity between CO₂ and Fe₂O₃ particles.

Only under high temperatures (200-315 °C) and high pressure conditions, Mg(OH)₂ particles can chemically sorb CO₂ by producing magnesium carbonate [31]. In this work, the adsorption experiment was performed under relatively low temperature and pressure conditions, so the chemi-sorption reaction was not feasible. As the result, when the Mg(OH)₂ particles were incorporated into the biochar framework, it showed little effect in promoting the CO₂ capture by the MgCWs.

4. Conclusions

Biochar, an environmentally friendly, low-cost and sustainable adsorbent can capture substantial amounts of CO₂; this study showed that, after optimization, metal-biochar composites had enhanced CO₂ adsorption ability, which was better than the unmodified biochar. The aluminum hydroxide-biochar composite, AlCW(4), captured more CO₂ than the other metal composites. The CO₂ capture by the biochar-based composites was mainly controlled by the surface adsorption mechanisms with contributions from both carbon surface and metal oxyhydroxide particles. Findings from this work indicated that metal oxyhydroxide-biochar composites can be a promising framework for CO₂ capture with adsorption capacity comparable to commercial, more expensive sorbents.

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Table 1. Summary of the basic properties of biochar-based nanocomposties

	Metal ratio	Surface Area (m ² g ⁻¹)	Pore Volume (mL g ⁻¹)	% Metal in biochar
CW(0)	0	99	0.01	<0.1
MgCW(.01)	0.01	275	0.01	0.2
MgCW(.25)	0.25	244	0.03	1.7
MgCW(1)	1	184	0.1	3.7
MgCW(3)	3	228	0.12	4.5
MgCW(6)	6	197	0.29	5.5
MgCW(20)	20	289	0.25	4.7
MgCW(40)	40	262	0.27	5.7
AlCW(.025)	0.03	256	0.01	0.1
AlCW(.25)	0.25	206	0.03	0.6
AlCW(2.5)	2.5	331	0.3	0.7
AlCW(1)	1	263	0.25	0.8
AlCW(3)	3	370	0.39	0.6
AlCW(4)	4	367	0.37	0.6
FeCW(.01)	0.01	302	0.01	0.2
FeCW(.05)	0.05	NA	NA	0.6
FeCW(.1)	0.1	458	0.04	1.1
FeCW(5)	5	665	0.59	3.3
FeCW(6)	6	654	0.19	2.1
FeCW(10)	10	749	0.33	3.7

Table 2. Summary of the best-fit parameters of second-order kinetics model* for CO₂ adsorption.

	q_e (mg g ⁻¹)	k (g mg ⁻¹ s ⁻¹)	R^2
CW(0)	57.96	0.00019	0.98
MgCW(.01)	63.69	0.00015	0.97
MgCW(.25)	47.69	0.00021	0.97
MgCW(1)	35.35	0.00018	0.99
MgCW(3)	33.83	0.00021	0.99
MgCW(6)	27.79	0.00029	0.99
MgCW(20)	35.05	0.00027	0.98
MgCW(40)	32.33	0.00028	0.98
AlCW(.025)	63.87	0.00015	0.97
AlCW(.25)	62.98	0.00012	0.98
AlCW(1)	69.3	0.000048	0.96
AlCW(2.5)	64.63	0.000035	0.88
AlCW(3)	69.49	0.000024	0.89
AlCW(4)	71.05	0.000041	0.89
FeCW(.01)	64.3	0.0002	0.98
FeCW(.05)	55.61	0.00022	0.95
FeCW(.1)	66.57	0.00018	0.98
FeCW(5)	60.68	0.00017	0.98
FeCW(6)	65.26	0.00016	0.98
FeCW(10)	53.79	0.00021	0.93

*: Governing equation: $q_t = \frac{q_e}{1 + k(q_e - q_t)^2}$, where q_t is the amount of CO₂ adsorbed at time t (sec) and q_e is the amount at equilibrium (mg g⁻¹). k is the second order rate constant (g m⁻¹ h⁻¹).

Figure captions

Figure 1. SEM-EDS analysis of representative biochar samples: a) MgCW, b) AlCW, and c) FeCW

Figure 2. XRD analysis of representative biochar samples.

Figure 3. CO₂ adsorption onto the optimal metal oxyhydroxide-biochar composites.

Figure 4. Correlation between surface area and CO₂ adsorption capacity of AlCW.

Figure 5. Correlation between metal content and CO₂ adsorption capacity of AlCW.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.