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RESEARCH ARTICLE

CO_2 capture analysis of tobacco biochar-$AlCl_3$ composite

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ABSTRACT

In this study, the performance of tobacco biochar-$AlCl_3$ composite for CO_2 capture was investigated. Biochar-$AlCl_3$ composites were prepared at different blend ratios (10:0.4; 10:2; 10:4, wt./wt.) and used for CO_2 capture experiments to determine the optimal Al metal content at which CO_2 adsorption was highest. Biochar composites were produced through slow pyrolysis under inert nitrogen atmosphere in a fixed bed reactor at 600°C for 3h. Properties of biochar-metal composites and raw biochar samples were characterized with SEM-EDS, XRD and FTIR analysis. CO_2 experiments were conducted in TGA under N_2 atmosphere with a flow rate of 50 ml/min at 25°C. The maximum CO_2 adsorption was observed as 59.97 mg g^{-1} for biochar: $AlCl_3$ composite at a ratio of 10:2. Finally, results of study showed that biochar-$AlCl_3$ composites have great potential as a CO_2 capture material due to its low-cost, sustainability and CO_2 capture capacity.

Keywords: Biochar, composite, CO_2 capture, $AlCl_3$

1. INTRODUCTION

Industrialization and increase in population has resulted in excess usage of fossil fuels (coal, natural gas, petroleum). There is increasing worldwide concern in relation between the use of fossil fuels and the fossil fuel derived emissions of greenhouse gases. The global warming is a serious environmental problem and attributed primarily to the increase of the greenhouse gases [1] which is threatening the life. Carbon dioxide (CO_2) is the major component of greenhouse gases and mainly produced from fossil fuel consumption [2]. In recent years, amount of CO_2 liberated by the utilization of fossil fuels has been over 30 gigatonnes [3]. Therefore, a great deal of researchers has intensively studied on CO_2 capture [4]. There are currently available CO_2 capture materials which are usually applied in power plants, cement manufacturing factories where CO_2 release. However, cost of current CO_2 capture adsorbents are still high, making process economically unfavourable. Furthermore, these systems use amine and other alkaline solvents to chemically bind CO_2, but they have negative effects on environment, such as high energy requirements and corrosion of process equipment. Thus, developing highly efficient and cost-effective adsorbents are urgently needed to capture and store CO_2. It is reported that carbon materials have potential to be used in CO_2 capture with high stability, high regeneration ability, and lower energy consumption than conventional chemical systems [5].

Biomass is a clean, renewable source which can be found in high amounts widely. Biochar is a pyrogenic carbon produced by pyrolysis of biomass under inert atmosphere conditions [6]. It has received much attention recently because of its application potential [7]. Biochar is a low-cost carbon material and it can be also used for soil improvement and carbon sequestration. Also, recent studies showed that biochar has the ability to capture CO_2 at levels comparable to well-known adsorbents. Biochar can also be regenerated easily using low level energy due to its physical adsorption behavior.

The CO_2 adsorption performance of biochar is strongly influenced by the modification of surface chemistry [8]. In a previous study, Creamer et al., (2016) used metal oxyhydroxide–biochar composites of cotton wood biochar and reported that CO_2 can be adsorbed at high amounts using metal oxyhydroxide–biochar composites. Tobacco is an important agricultural and industrial product for Turkey.

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According to the data given by Turkey Statistical Institute, the annual production of tobacco was approximately 75 thousand tons at 2014. A great amount of waste tobacco biomass occurs after processing and causes an environmental problem. Therefore, in this study, waste biomass residues from tobacco industry were used to produce biochar and its composites with $AlCl_3$ through one-step slow pyrolysis at 600 ^oC. The tobacco biochar and its composites with various blend ratios of $AlCl_3$ were investigated to determine the potential and efficiency for CO_2 capture process.

2. MATERIALS AND METHODS

2.1. Materials

For this study, tobacco waste (TW) residues provided by a local company were used as a low-cost CO_2 capture material. TW was thus dried in oven at 70°C for 4 h. Dried residues were grounded with a kitchen type blender. Grounded samples were sieved and a particle size below 250 µm was used in experiments to prevent mass and heat transfer limitations. Aluminium chloride was purchased from Sigma-Aldrich Chemistry.

2.2. Preparation of Biochar/Metal Oxyhydroxide Composite

The biochar and its composite with different ratios of $AlCl_3$ were prepared according to procedure of a previous work by Creamer et al. (2015). Three different $AlCl_3$ amounts (0.2, 1 and 2 g) were solved in 60 mL of deionized (DI) water. 5 grams of tobacco waste was added into the solution and mixture was stirred. Raw biomass and its composites with $AlCl_3$ were placed in a tubular furnace (Magmatherm MT) and pyrolysed under inert N_2 atmosphere at 600 ^oC for 3 h. At the end of pyrolysis, samples were taken and washed with DI water several times to remove excess metal and impurities. Then, the product composite samples were dried at 60 °C in a vacuum oven and stored in sealed containers in desiccator until usage. The four biochar samples are labeled as TW0, TW02, TW1 and TW2 based on added $AlCl_3$ amount.

2.3. Characterization of Samples

The main characteristics of raw biochar and composites are given in Table 1. Composite samples and raw biochar were characterized for their metal content and crystal structure. Energy dispersive X-Ray spectroscopy (EDS) at 1000x magnification was used and Al content of biochars were determined. The elemental compositions of samples are shown in Table 1. Scanning electron microscope (SEM) imaging analysis of samples was conducted at 5000x and 8000x magnification to investigate distribution of Al on surface of composites. To detect and verify the existence of surface functional groups, FT-IR spectra of the biochar samples were taken with a Perkin Elmer-2000FTIR spectrometer. The spectra were recorded from 4000 to 650 cm^{-1} at a resolution of 1 cm^{-1}.

2.4. Carbon Dioxide Capture in TGA

CO_2 mass measurements were carried out using a Simultaneous DTA-TG Analyser (Shimadzu, Japan). For each experiment, about 20 mg sample was used. At first, temperature was ramped from room temperature to 120 ^oC with a heating rate of 20 °C min^{-1} under inert nitrogen gas and held for 20 min at this temperature to remove moisture and potential volatile components. Then sample was cooled to 25 ^oC with 10 °C min^{-1}. The inert gas flow rate was 50 mL min^{-1} for both heating and cooling. When the thermal equilibrium established, the CO_2 gas was fed at a rate of flow rate of 50 mL min^{-1} for 3 h.

2.5. Regeneration in TGA

TW1 biochar sample was selected to evaluate the efficiency of regeneration, since it showed the best CO_2 gas adsorption capacity in TGA experiments. Regeneration experiment study was conducted using a Simultaneous DTA-TG Analyzer (Shimadzu, Japan). After the CO_2 passed at 25^oC for 3 h, the gas switched to N_2 and the temperature was ramped to 120^oC again for 2 h with a heating rate of 20°C min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Biochar

In order to determine elemental content of samples, EDS analysis was conducted at 1000x magnification. Fig 1 shows images obtained by SEM and results of EDS analysis. Location of elements on the surface of samples can be seen from images. EDS data analysis confirmed the presence of Al metal for each sample. As presented in Fig 1a-d, content of Al was gradually raised related with the biochar-metal ratios. The Al metal on the surface of the biochar samples can be identified with clear peak.

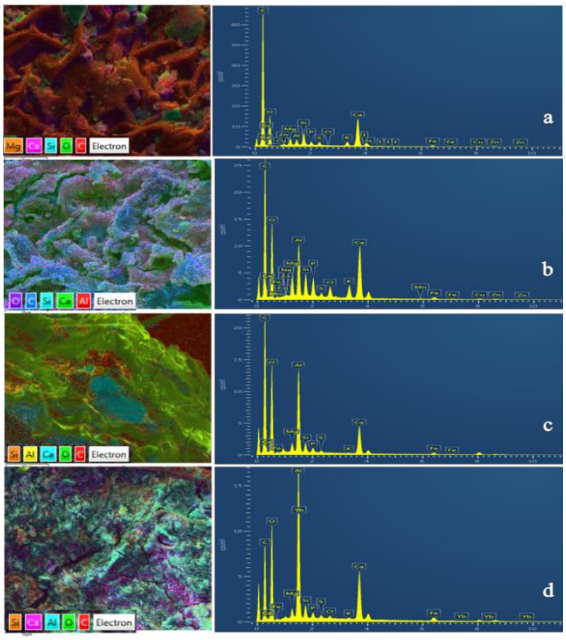

Fig 1. SEM-EDS analysis of representative biochar samples: (a) TW0 (b) TW02, (c) TW1, (d) TW2

Table 1. Elemental analysis of various biochar- $AlCl_3$ composites and raw biochar sample

Sample	*C*	*O*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*K*	*Ca*	*Sc*	*Fe*	*Cu*	*Zn*
TW0	64.85	24.88	0.82	**0.55**	1.15	0.37	0.34	0.03	0.62	4.98	0.1	0.47	0.32	0.33
TW02	53.08	30.73	1.53	**3.23**	1.33	1.23	0.26	0.76	1.13	5.48	-	0.56	0.25	0.29
TW1	53.1	35.84	0.68	**5.63**	0.61	0.33	0.14	-	0.03	3.14	-	0.49	-	-
TW2	41.95	37.93	0.77	**10.49**	0.97	0.45	0.24	0.22	0.11	5.71	1.16	-	-	-

- below detection limit

Elemental compositions of samples obtained by EDS analysis are tabulated and shown in Table 1. As can be seen from the table, various amount of Al metal successfully loaded into the biochar. Al metal content increased from 0.55 wt% for TW0 to 10.49 wt% for TW2.

XRD analysis was used to observe the crystallinity and type of metal oxyhydroxides present in samples. Fig 2 shows the wide angle XRD patterns of various $AlCl_3$-biochar samples. Apparently these samples had similar diffraction peaks, which could be indexed as the diffraction pattern of AlOOH. The XRD results confirmed that the metal oxyhydroxide particles in all the samples were highly crystalline.

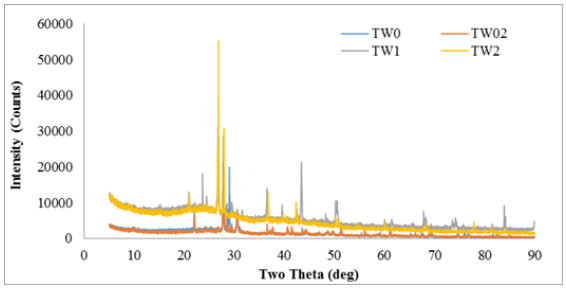

Fig 2. Wide angle XRD patterns of various biochar- $AlCl_3$ composite and raw biochar samples

In order to compare the nature of the functional groups present on the surface of the samples, FTIR analysis was performed. Fig 3 shows the results of FTIR measurements taken for tobacco biochar-$AlCl_3$ composite samples (TW0, TW02, TW1 and TW2). In spectrum of raw biochar (TW0), several peaks were observed at 3312, 1784, 1554, 1411 and 1316 cm^{-1} which can be attributed to O-H stretching vibration (alcohol), C=O group moieties, C=C aromatic groups [9, 10].

Biochar composites with metal optimization caused some changes in the spectra of samples (TW02, TW1 and TW2). At least six different peaks are found between 1519 and 1270 cm^{-1}. Karge (1992) [11] stated that $Al_xO_y^{n+}$ gives rise to a typical band at about 1450 cm^{-1}. FTIR results confirmed the presence of the Al metal in biochar composites.

3.2. Measurements of CO_2 Adsorption

A performance test of the CO2 adsorbing for each composite sample was carried out under the same conditions and results are shown in Fig 4.

As seen in Fig 4 a weight loss between 40-85 min for each sample was observed. This loss can be attributed to evaporation of moisture content. Adsorption capacities became gradually higher as the content of Al metal concentration was raised. Thereafter, the adsorption was constantly maintained until 10:2 blend ratio and then substantially decreased at 10:4 blend ratio. Based on these results, TW2 reacted with CO_2 from the starting point at room temperature and the maximum adsorption was observed as 59.74 mg g^{-1} at 165 min. Amounts of adsorbed CO_2 according to raw biomass and blend ratios at 10:0.4; 10:2; 10:4 was determined to be 40.10 mg g^{-1}, 59.02 mg g^{-1}, 59.97 mg g^{-1}, and 44.38 mg g^{-1}, respectively.

These adsorption capacities of different samples were referenced to explain the effect of metal content in tobacco biochar composites.

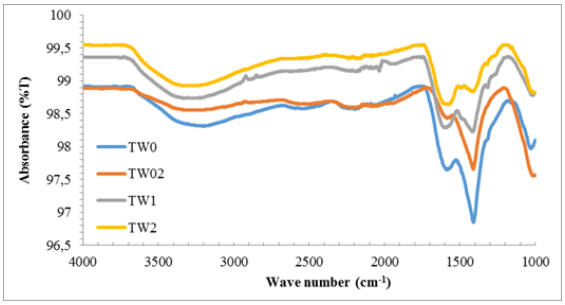

Fig 3. Representative FT-IR spectra of biochar- $AlCl_3$ composite and raw biochar samples

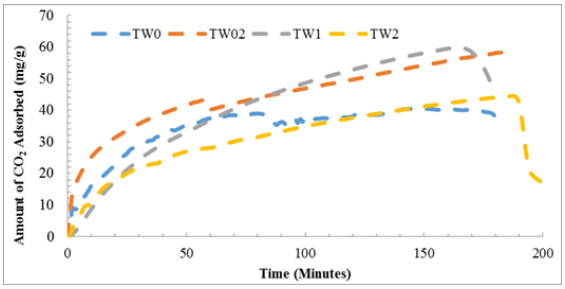

Fig 4. CO_2 adsorption capacities of biochar- $AlCl_3$ composite and raw biochar samples

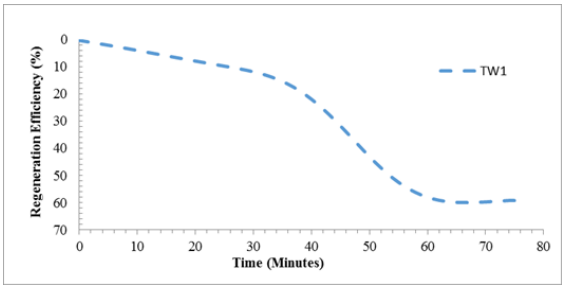

Fig 5. Regeneration efficiency curve of selected biochar sample (TW1) according to temperature under pure N_2 feeding condition

Bhagiyalakshmi et al. (2011) [12] stated that adsorbents for CO^2 capture suffer a high regeneration temperature around 400 to 800 ^oC. As seen in Fig 5, the desorption occurred between 0-60 min at 120 ^oC. Results confirmed that CO^2 is substantially removed from biochar composite and TW1 can be easily regenerated by simple desorption at low temperature.

4. CONCLUSION

In this study, the effect Al metal content on CO_2 capture performance of biochar composites was investigated. In summary, it was found that adsorption capacity of CO_2 can be increased with the increase in Al content up to 10:4 blend ratio. Then a decrease in adsorbed CO_2 amount was absorbed. The Aluminium–biochar composite at 10:2 blend ratio (TW1) has shown the best adsorption capacity as 59.97 mg g^{-1}. The results were comparable with the results given in literature. Therefore, it is concluded that tobacco biochar-$AlCl_3$ composites have a potential for CO_2 capture and can be proposed as a low-cost and high-efficient adsorbent with high adsorption capacity. Furthermore, it can be regenerated at lower temperatures which mean reduced energy needs for re-usage.

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