Optimization of Pyrolysis Conditions to Synthesize Adsorbent from Paper Mill Sludge

Parmila Devi and Anil K. Saroha

Abstract—**Pyrolysis temperature is the key factor influencing the biochar yield. Experiments were performed to study the effect of pyrolysis temperature and additive dose on biochar yield. It was observed that biochar yield decreased with an increase in pyrolysis temperature and maximum yield was obtained at 300 °C. Conversely, surface area of the biochar increased with an increase in temperature and maximum surface area was obtained at 700 °C. The biochar was impregnated with different dosage of $CaCO_3$ to analyze the effect of $CaCO_3$ as an additive dosage on biochar properties. Addition of $CaCO_3$ significantly affects the surface area and pore volume of the biochar, although it does not lead to significant change in biochar yield. Batch experiments were performed to explore the potential of raw and impregnated biochar as an adsorbent for the removal of pentachlorophenol (PCP). A removal efficiency of 86% and 97% was obtained with raw biochar and 3% $CaCO_3$ impregnated biochar respectively.**

Index terms—**Adsorption, biochar, optimization, pyrolysis**.

I. Introduction

Decline in traditional routes of disposal of sludge has put an economic and environmental burden on paper mills. Currently, landfilling is the most popular method for disposal of sludge because once sludge is lanfilled, it do not need further processing. But landfilling of paper mill sludge has number of environmental concerns. Sludge undergoes degradation and decomposition reactions resulting in generation of greenhouse gases (CH_4, N_2O) and toxic leachate. Additionally, landfilling of sludge is a costly affair as it may cost some mills over $1,000,000 annually [1]. Therefore, there is a need to find some cost effective and environmentally clean alternative for sludge disposal. Thermo-chemical treatment has been found as the simple, viable and flexible alternative for the disposal of the sludge. Thermo-chemical conversion technologies including combustion, pyrolysis and gasification have attracted increased interest since they offer a simple way to convert waste into fuels, adsorbent and chemicals [2].

Some studies have been reported in the literature on pyrolysis of paper sludge [2]-[4], to obtain value-added products such as biochar, biofuels and adsorbents. Several researchers have used the char obtained from the pyrolysis of paper sludge as adsorbent for water treatment applications [5]-[8]. The adsorbents obtained from paper sludge have been used in the adsorption of metals, dyes, and organics from effluent. It is widely agreed that the sorption capacity of the biochar varied with raw material used as well as the time temperature profile used in pyrolysis process. Variability in time and temperature profile resulted in biochars with significantly different bulk and surface characteristics [9]. Several parameters impact the mechanism and kinetics of pyrolytic reactions such as composition of the substrate, heating rate, pyrolysis temperature, and, additive dosage. By understanding the influence of these parameters on the process, optimum pyrolytic conditions can be determined, which will reduce the undesirable side reactions and promoting the formation of desired products.

In the present study, the effect of various parameters such as pyrolysis temperature, residence time and additive dosage is optimized to obtain maximum yield of the biochar. The biochar was treated to obtain maximum adsorption capacity adsorbent for removal of pentachlorophenol from effluent.

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II. Materials and Methods

A. Preparation of Raw Material

Pulp and paper mill sludge was used as raw material for biochar production. Prior to the pyrolysis experiments, raw sludge samples were dried for 3 days in sunlight and then oven dried for 48 hrs to bring the moisture content up to 8–10%. Dried sludge samples were then ground in grinder to obtain the particle size of 0.25 mm – 1.75 mm. Ground sludge samples were kept in air tight containers till further use.

B. Pyrolysis of Paper Mill Sludge

The experimental set up for paper mill sludge pyrolysis is shown Fig. 1. To optimize the pyrolysis process, 20 g of dried paper sludge of particle size (0.25mm – 1.75mm) was inserted in a tube. The nitrogen gas was passed continuously through the tube containing paper mill sludge to maintain oxygen limited conditions throughout the experiment. Pyrolysis was carried out at different temperatures (300 °C-700 °C) to study the effect of pyrolysis temperature on biochar yield. Experiments were carried out for 2 hrs. at the heating rate of 10°C/min. Once the temperature is optimized, sludge was pyrolyzed with different dosage of $CaCO_3$ (1-3 %), to enhance the adsorption capacity of biochar by enriching the basic functional moieties on biochar surface. The resultant biochar was allowed to cool at room temperature and weighted to find out the biochar yield. Experiments were carried out for 2 hrs. at the heating rate of 10°C/min. Once the temperature is optimized, sludge was pyrolyzed with different dosage of $CaCO_3$ (1-3 %), to enhance the adsorption capacity of biochar by enriching the basic functional moieties on biochar surface. The resultant biochar was allowed to cool at room temperature and weighted to find out the biochar yield.

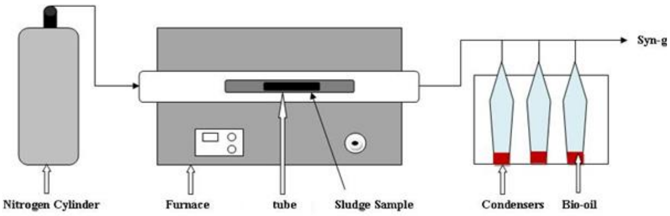

Fig. 1. Experimental set up for pyrolysis of paper mill sludge

C. Analysis

Biochar yield is calculated by equation 1:

$$\text{Biochar Yield } (wt\ \%) = \frac{w_c\left(\frac{100-x}{100}\right)}{w_{rm}\left(\frac{100-y-x}{100}\right)} * 100 \qquad (1)$$

where w_c and w_{rm} is the weight of char and raw material respectively. X and y is the % ash and % moisture.

D. Adsorption Experiments

Batch adsorption experiments were carried out with biochar pyrolysed at 700 ^oC and $CaCO_3$ impregnated biochars. Prior to the experiments, biochar samples were washed three times with distilled water and then dried in an oven at 70^{o}C for 24 hrs. Biochars were then sieved to 0.250 - 1.0 mm and store in air tight plastic container till further use. Biochar samples were assigned with different labels i.e. 700 BC, 1% $CaCO_3$, 2 % $CaCO_3$ and 3 % $CaCO_3$ according to pyrolysis temperature and dosage of $CaCO_3$ impregnated during pyrolysis. Adsorption experiments were performed at neutral pH and the PCP concentration range of 0-50 mg/L. This range was selected based on the PCP concentrations found in industrial wastewaters. In the adsorption studies, a known amount (1 g/50 mL) of biochar (particle size 1000-250 µm) was added to each flask followed by agitation for specified times to a maximum of 24 hrs. The contact time and conditions were selected based on preliminary experiments which demonstrated that equilibrium was established in 24 h. No further uptake of PCP was observed between 24 and 72 h. Solutions were then filtered and concentration of the PCP was measured using the UV-VIS spectrophotometer. All the measurements were carried out at the wavelength of 320 nm. Amount of PCP removed/adsorbed was calculated using this equation:

$$qe = \frac{(C_o - C_e) * V}{W} \qquad (2)$$

where qe is the amount (mg/g) of PCP adsorbed, C_o and Ce are the initial and equilibrium PCP concentrations (mg/L) in solution, V is the PCP volume (L), and W is the biochar weight (g).

III. Result and Discussion

A. Optimization of Pyrolysis Conditions

1) Effect of temperature

Pyrolysis temperature is the key factor influencing the biochar yield. To study the effect of temperature, biochar yield, sludge was pyrolyzed at different temperatures (300-700 ^oC) by maintaining the heating rate 10^{o}C/min with a nitrogen sweep rate of 1 LPM. The pyrolysis time was kept constant (i.e. 2 hrs) throughout the pyrolysis experiments. It was observed that biochar yield decreased with increase in pyrolysis temperature and maximum yield was observed at 300 ^oC (Fig. 2). Conversely, surface area of the biochar increased with increase in temperature and maximum surface area obtained at 700 ^oC. At higher temperatures, micro-pore volume increased significantly due to dissociation of cellulose and hemicelluloses. Breakdown of complex compounds creates the void between the particles, resulted in increase in total surface area of the biochar produced [1]. Decrease in the biochar yield is due to the decomposition of the initial feedstock and secondary reactions during the sludge pyrolysis [10].

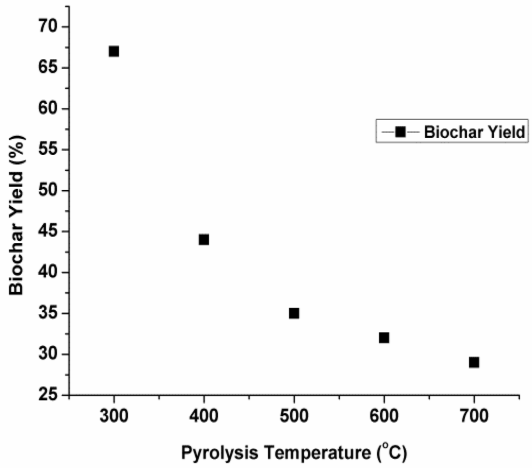

Fig. 2. Effect of temperature on biochar yield
(Temperature-300-700 oC, Residence time- 2 hrs., Heating rate- 10 oC/min, Nitrogen sweep rate- 1LPM)

2) Effect of additive dose

Preparation of the high adsorption capacity adsorbent requires the addition of some additive which permits the inter-particle union as well as facilitates the enrichment of desired functional groups on adsorbent surface. In the present study, biochar yield was optimized in presence of alkali as an additive. Calcium carbonate was chosen as principle additive due to its alkaline nature. Additionally, calcium carbonate is used as an additive during paper making process, so paper mill sludge already contains some amount of the calcium carbonate. Different dosage of calcium carbonate was added to study the effect of calcium carbonate dosage on adsorptive properties and yield of the biochar. Biochar yield was not much affected by $CaCO_3$ addition (Fig. 3) while pentachlorophenol adsorptive potential of the biochar was significantly improved. It was observed that the ratio of $CaCO_3$ dosage does not have an effect on the yield of the biochar, but impregnation does have significant impact on surface area and pore volume. Similar results were observed by Liou et al [11].

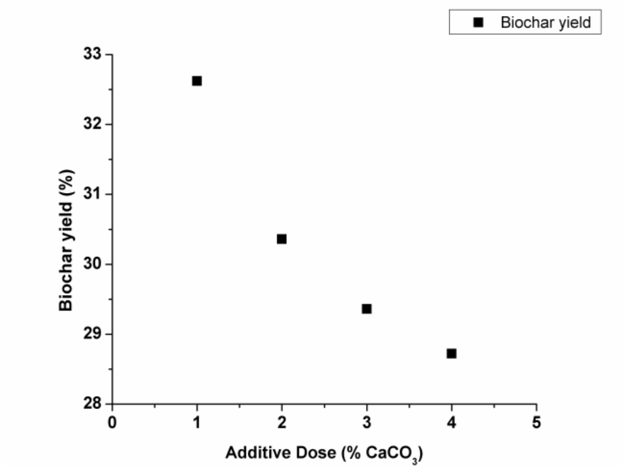

Fig. 3. Effect of additive dosage on biochar yield
(Temperature-700 oC, Residence time- 2 hr., Heating rate- 10 oC/min, Nitrogen sweep rate- 1LPM)

B. Adsorption Studies

Adsorption experiments were carried out with raw and $CaCO_3$ impregnated biochar, to compare the effect of the additive dosage on adsorptive capacity of the biochar (Table I). First experiment was carried out with 700 BC and further experiments were carried out with 1%, 2 % and 3% calcium carbonate containing biochar. Results depicted in the Table I shows that adsorption capacity of the adsorbent increase with increase in pyrolysis temperature (results not shown here). About 86 % of the pentachlorophenol was absorbed with 700 BC. Adsorption capacity increase with increase in additive dosage up to some limit thereafter it starts decreasing. Increase in calcium carbonate dosage increase the adsorption of pentachlorophenol up to 3 %, further addition of the calcium carbonate doesn't make any significant change in amount of the PCP adsorbed. Maximum pentachlorophenol removal (97 %) was observed for 3 % $CaCO_3$ containing biochar. This may be due to the reason that addition of $CaCO_3$ cause enrichment of biochar surface with basic functional groups [12]. Biochar prepared from paper mill sludge was alkaline in nature, while pentachlorophenol is acidic in nature. The adsorbent with basic functional groups have higher potential for removal of pentachlorophenol.

TABLE I: PENTACHLOROPHENOL REMOVAL BY PAPER MILL SLUDGE BIOCHAR

Biochar	% Removal	q_e (mg/g)
700 BC	86.88	1085.71
1% $CaCO_3$	89.92	1104.14
2% $CaCO_3$	91.81	1147.62
3% $CaCO_3$	97.33	1216.67
4% $CaCO_3$	95.04	1188.09

IV. CONCLUSIONS

High adsorption capacity adsorbents were prepared from the paper mill sludge. For adsorbent preparation, optimization of pyrolysis conditions was done to access the effect of pyrolysis temperature, and additive dose on biochar yield. It was observed that pyrolysis temperature is the key parameter affecting the biochar yield and adsorbent surface area. Biochar yield was decreased significantly with increase in pyrolysis temperature. To increase the adsorption capacity of the biochar, sludge was impregnated with different dosage of calcium carbonate. Impregnation of biochar with $CaCO_3$ enrich the biochar surface with alkaline functional groups, hence the adsorption capacity of the biochar improved dramatically. 3% $CaCO_3$ showed maximum adsorption potential for PCP.

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