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REMOVAL OF CADMIUM USING ALKALINE-TREATED ACTIVATED CARBON FROM LEUCAENA LEUCOCEPHALA BIOMASS

Water contamination that caused by heavy metals is a very common phenomenon in the industrial age. One of the popular way to treat metal contaminated water is by adsorption process using activated carbon as the adsorbent. This paper works on producing activated carbon by chemical means with impregnation ratios of NaOH:char (w/w) was predetermined at 1:1 (ACT1-1), 2:1 (ACT2-1) and 3:1 (ACT3-1) under activation temperature of 700°C. Considering the *Leucaena leucocephala* is a wildly, easy and fast grown species, with the availability throught the year, it was chosen to be used as the precursor. The properties of these activated carbons and its potential for cadmium removal from aqueus solution was analyzed. It was found that the highest surface area was recorded at 662.76 m²/g. Four parameters were studied which are contact time, the effect of pH, initial concentration of adsorbate and temperature. The equilibrium time was achieved in 40 min treatment at initial concentrations of 30 mg/l. The adsorbent exhibited good sorption potential for cadmium at pH 8.0 and equilibrium temperature of 30°C. Based on the results, this study had proved that activated carbon from *Leucaena leucocephala* biomass have the good potential to be used for removal of cadmium from wastewater.

Keywords: Activated carbon; Cadmium; Leucaena leucocephala; Adsorption

1. Introduction

Heavy metal contamination of water is a serious problem hapenning in industrialization nations due to many factors, mainly through anthropogenic actions. It is not only harmful to human health but contamination of water could also be harmful to the aquatic life. As for cadmium, despite the permissible maximum intake per day at 0.003 gL^{-1}, it is an important metal used in manufacturing of nickel-cadmium batteries, plastic stabilizers, anti-corrosive metal coatings, alloys, coal combustion as well as pigments [1,2]. Commonly found in cations, various techniques to clean wastewater from the heavy metals were used including chemical precipitation, adsorption, ion exchange, membrane filtration, reverse osmosis, coagulation, electrochemical treatment and biosorption processes [3,4].

Considering capital cost and availability, adsorption process is a popular way used to treat wastewater from the heavy metals. Various abundantly available natural materials, waste and agricultural activities residue could be utilised as the adsorbent [5]. Biomass such as sawdust and wood particles could act as an adsorbent [6]. However, conversion of these materials into activated carbon (AC) is more favourable as it can adsorb pollutants efficiently from the water [7].

Activated carbon can be defined as an excess of amorphous carbon materials prepared in such a way exhibit a high degree of porosity with enlarged surface area [8]. Activated carbon is a highly demanded product due to its various potential applications. Their well-developed porosity and rich surface functional group is the main advantage of this material [9]. There are many applications of activated carbon in wide areas, but most were in environmental and health care such as in drinking water filter [10]. Other than that, activated carbon is commonly utilized for various liquid and gas phase adsorption in industry apart from controlling the environment [8]. Production of activated carbon usually starts with crushing of the biomass into particles before being carbonized at temperature between 300-500°C in inert atmosphere. The carbonized material or also called char will be further activated using physical or chemical activation. In physi-

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cal activation, samples were heated between 700-900°C in inert gasses atmosphere such as CO_2 and N_2. On the other hand, chemical activation involves mixing of char with activating agent before heated. Chemical activation was favoured due to higher surface area created on the activated carbon as compared to physical activation [11]. Due to high cost to produce activated carbon, cheap raw materials such as agriculture waste, industrial residue as well as fast growing trees were utilised as the precursor of the activated carbon production [12,13]. *Leucaena leucocephala* is one of a wild, fast growing tree species that for the time being have no value for mass production of any other material. It can easily grow without specific silviculture techniques.

Leucaena leucocephala is also commercially known as Petai Belalang. It is a small leguminous tree originated from Central America. The Portuguese and Dutch brought them to Taiwan in the seventeenth century. *Leucaena leucocephala* is able to withstand dry areas as well as poor soil conditions. This is due to its high nitrogen fixation ability [13]. *Leucaena leucocephala* can be easily found and it is widely grown all over Malaysia. The abundance of *Leucaena leucocephala* tree offer an opportunity to utilizing this biomass in various field. The present research focuses on the potential use of *Leucaena leucocephala* biomass for removal Cd ion from aqueous solution. The *Leucaena leucocephala* biomass were converted into activated carbon using alkaline treatment method, to ensure higher surface area formed during the activation process. Surface analyser was used to identify the success of the activation process. Activated carbon was tested for Cd removal from water, analysing different parameters including contact time, temperature, pH and initial concentration of the adsorbate. Currently, there are very little information available on the utilization of *Leucaena leucocephala* biomass based activated carbon for water purification, thus this work will contribute some insight on this topic of interest.

2. Methodology

2.1. Material acquisition

Leucaena leucocephala samples were gathered around Selangor, Malaysia. The raw sample of *Leucaena leucocephala* were air dried for 24 hours before being grind to produce wood particles. The moisture content of wood were maintained below 10% to make sure the sample not attached together or clogging the machines. Samples were cut into smaller size for grind. After grinding, the wood particles were sieved into 1 mm to 2 mm of size. The wood particles were oven-dry to get the specific moisture content.

2.2. Preparing activated carbon

Samples were carbonized in a pyrolyzer in bulk. Chemical activation was chosen for the carbonized *Leucaena leucocephala* biomass. *Leucaena leucocephala* char was impregnated with sodium hydroxide, NaOH. This step was performed using three impregnation ratios as shown in TABLE 1. The carbonized sample was mixed with NaOH in 100 mL of distilled water. Stirring was done in a special vertical stainless steel reactor for 2 h before placed in an oven at 105°C for 24 hours. Activation process was done in muffle furnace. The sample was heated from the room temperature to 700°C and continued heated for 90 minutes under inert, nitrogen gas stream at constant 150 cm^3/min flow rate. After 90 minutes, the nitrogen flow was resumed until the sample cool down to the room temperature. Coding of prepared activated carbon were as in TABLE 1.

TABLE 1

Coding of the prepared activated carbon

No.	Sample name	Description (NaOH:char)
1.	ACT1-1	1:1
2.	ACT2-1	2:1
3.	ACT3-1	3:1

2.3. Surface area measurement

Surface analyser, Tri Star 3000 (Micromeritics, USA) was used to measure the surface area, determined by N_2 isotherms using the Brunauer Emmett Teller equation (BET). The sample was first degassed at 300°C for 2 h to remove impurities. The analysis was done by nitrogen adsorption isotherm at 77 K with the relative pressure range between 10^{-6} to 1 [3].

2.4. Estimation of adsorption capacity

The adsorption capacity of activated carbon was measured using the batch adsorption method. Different parameters were tested including the contact time, initial concentration of adsorbate, pH of solution, and adsorption temperature [4,5] through batch adsorption studies. Approximately 0.5 g of the *Leucaena leucocephala* activated carbon was mixed with 100 ml of the aqueous solutions of cadmium ion in different conical flasks using a temperature-controlled water bath shaker. The mixtures were shacked for pre-determined contact time before filtered using filter paper to obtain the treated solution. Final solution was analysed using Inductively coupled plasma optical emission spectrometry, ICP-OES for the remaining metal ion content. Experiment was done three times to reduce error.

3. Results and discussion

3.1. Characteristics

The pore size distributions of the prepared AC from *Leucaena leucocephala* biomass is 120.20 m^2/g, 483.48 m^2/g and 662.76 m^2/g for AC from chemical activation with NaOH:char

ratio ACT1-1, ACT2-1 and ACT3-1, respectively. Observation of the analysed data show that the surface area of the AC increased as the NaOH:char ratio was increased from 1 to 3. The differences between the BET values of ACT1-1 and ACT2-1, ACT2-1 and ACT3-1 were of approximately 600 m^2/g^{-1}, showing a surface area incerement with increasing of the NaOH:char ratio. As observed, the increase in the NaOH:char results in an increase of the BET. However, it showed a decrement in the AC yields. The highest surface area are formed in the highest activation temperature and ratios. For chemical ratio ACT3-1 were resulted in highest surface area for activation temperature 700°C which are 662 m^2g^{-1}. This trend is similar from the previous study by Cazetta, Vargas, Nogami, Kunita, Guilherme, Martins, Silva, Moraes and Almeida [5] that also used NaOH as activation agent. As chemical amount were increased, larger pores began to collapse and smaller micro-pores began to develop which in turn increased the surface area of the activated carbon [6]. Therefore, the increment of the impregnation ratio results in increment in the surface area of activated carbon.

3.2. Batch adsorption study

3.2.1. Impact of contact time

Batch adsorption studies were performed by using 100 ml of adsorbate cadmium solutions of known initial concentrations which was predetermined between 10 mg/l to 50 mg/l with the mass of adsorbent 0.5 grams in the temperature of 30°C. The graph below shows the effect of contact time for 700°C, activation temperature. This data is crucial as the equilibrium time is one of the parameters to ensure economic wastewater treatment process plant application [8]. Fig. 1 shows the adsorption for activated carbon ACT1-1, ACT2-1 and ACT3-1 at 700°C activation temperature. Time range between 10 minutes until 160 minutes. Ratio ACT1-1 resulted in lower adsorption percentage at equilibrium than other temperature it is because of the lower surface area for the ratio ACT1-1. For ACT2-1 and ACT3-1, almost 100% maximum adsorption percentage were achieved at equilibrium due to the higher surface area for both sample. Larger surface area means more adsorption site available for adsorbate uptake [9]. Longer contact time for adsorbent resulted in higher adsorption percentage. For sample ACT1-1 the maximum adsorption percentage at equilibrium on 160 minutes is 99.79%, for ratio ACT2-1 the maximum adsorption percentage at equilibrium is 99.82% and for ACT3-1 the maximum adsorption percentage at equilibrium is 99.90%.

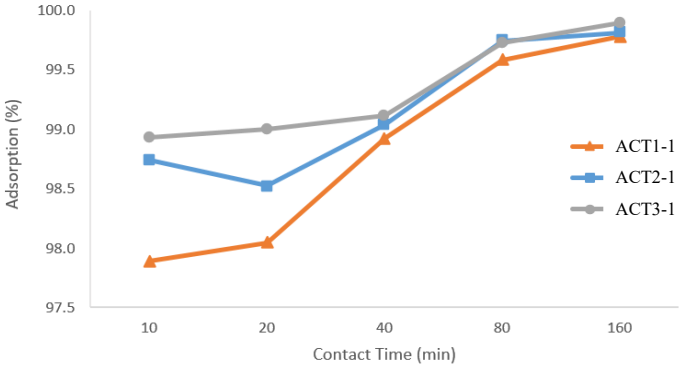

Fig. 1. The adsorption percentage of cadmium removal versus the contact time

3.2.2. Impact of pH

Fig. 2 shows the effect of solution pH on the adsorption percentage. The initial pH were adjusted from pH 3 until pH 8. For pH 3 the percentage of adsorption is lower for ratio ACT1-1. It is because of the acidic content in the solution. Eventhough the surface is positively charged under these conditions, the electrostatic repulsion had lowered the uptake of metal ions [10]. Nevertheless, by increasing pH, the negative charge on the surface of adsorbent can be increased, by enhancing the metal adsorption. ACT2-1 and ACT3-1 gives a higher final adsorption rate than ratio ACT1-1 due to higher surface area for both samples.

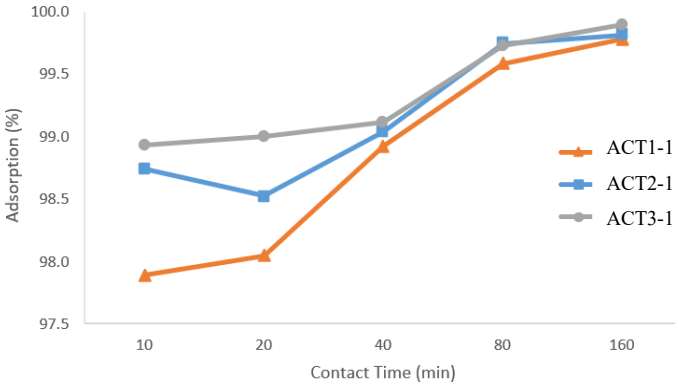

Fig. 2. Impact of pH on removal cadmium from solution

3.2.3. Impact of adsorbate initial concentration

Fig. 3 shows the effect of initial concentration of adsorbate between ratio ACT1-1, ACT2-1 and ACT3-1 for the activation temperature of 700°C. The concentration were prepared between 10 ppm until 50 ppm. For 10 ppm all ratio resulted in same amount of maximum adsorption percentage at equilibrium. It is because at the lower initial concentration of cadmium, pore can adsorb highest amount of metals. However, the graph slightly reduced when the concentration is increase. It can be seen that the maximum adsorption percentage at equilibrium was decreasing for the concentration 20, 30 and 40. And greatly decrease when the concentration up to 50 ppm for both ratios which are 94.81%, 95.26% and 95.76%. To conclude, when the concentration was increasing, the adsorption rate were decreasing. Higher initial adsorbate concentration means less adsorption site available for higher amount of metals in the solution which later results in lower adsorption percentage [11].

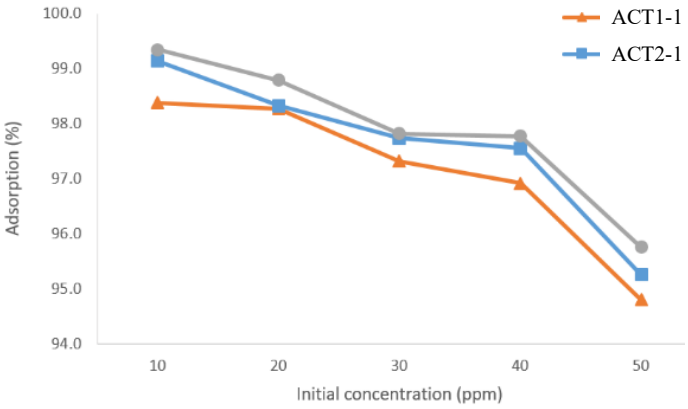

Fig. 3. Percentage of cadmium removal versus initial concentration of adsorbate

3.2.4. Impact of reaction temperature

Fig. 4 shows the effect of temperature for ACT1-1, ACT2-1 and ACT3-1. The temperature were measured at 30°C, 40°C, 50°C, 60°C and 70°C. Fig. 4 shows the adsorption rate is higher at lower temperature of 30°C for all samples. However it slightly decrease when the temperature is increase from 30°C to 40°C. It is keep on decreasing until the temperature 70°C. Between three ratios, ACT3-1 showed higher adsorption rate for the temperature 30°C until 70°C. It is because of the higher surface area for the ratio ACT3-1 sample. The higher surface area resulted in the higher availability of adsorption sites, relatively high compared to the adsorbate ions to be absorbed, thus the cadmium ions were without difficulty adsorbed and removed [12].

5. Conclusion

This study investigates the efficiency of activated carbon made from *Leucaena leucocephala* biomass through chemical activation technique by using sodium hydroxide (NaOH) as the activating agent and its application as adsorption. The adsorption characteristic had been examined at different parameters. For the contact time, the equilibrium adsorption was acquired within 40 minutes for metal ions at initial concentrations of 30 mg/l. The highest adsorption percentage for contact time is by ACT3-1.

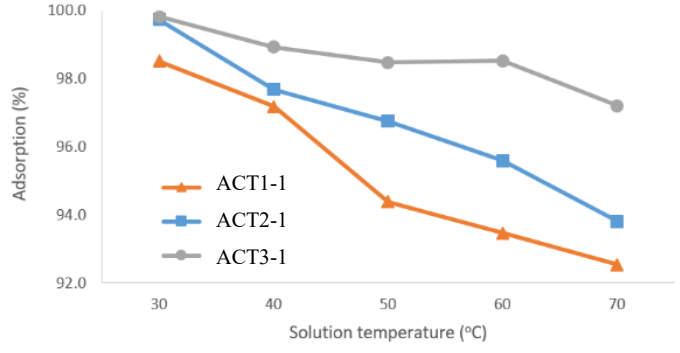

Fig. 4. Impact of temperature on cadmium removal

Other than that, longer time showed higher maximum uptake of metal ions by activated carbon which also dependent on the initial metal ion concentration. An increase in the pH of the adsorbate solution also increase the adsorption where the optimum pH for cadmium removal is 8.0. Batch adsorption experiment of the *Leucaena leucocephala* biomass activated carbon against cadmium ions solution shows excellent performance. Considering all the results analysed, the *Leucaena leucocephala* biomass-based activated made using chemical mean would be useful for producing economic cadmium contained water treatment system.

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