Effect Of Acidic Treatment On Metal Adsorptions Of Sugarcane Bagasse Based Activated Carbon

[1]M.D. Irfan Hatim, [2]M.A. Umi Fazara

[1]School of Bioprocess Engineering
Northern Malaysia University College of Engineering
Kompleks Pusat Pengajian KUKUM
02600 Jejawi, Perlis.
[2]School of Environmental Engineering
Northern Malaysia University College of Engineering
Kompleks Pusat Pengajian KUKUM
02600 Jejawi, Perlis.
irfan@kukum.edu.my

ABSTRACT

This paper discusses the technical feasibility of commercial sugarcane bagasse based activated carbon (SBAC) and chemically treated SBAC for Cu (II) removal. A batch wise process using simulated wastewater was developed. SBAC with particle size 1mm-2mm containing 4.8 wt % ashes was treated with a mixture of aqueous hydrofluoric acid (HF) and nitric acid (HNO_3). The ash content was reduced to 0.3 wt % respectively. Modified adsorbent were physically and chemically characterized by scanning electron microscopy (SEM), BET surface area analysis and Boehm's titration. The BET analysis shows that chemically modified SBAC can reach the surface area of 1120 m^2/g from non- treated SBAC that is 837 m^2/g. Equilibrium results on adsorption of Cu^{2+} showed that chemically treated SBAC increased the adsorption capacity up to 39.06 mg Cu/g, which was 50% higher than the untreated carbon. Thus, this revealed that the adsorption capacity of metal ions increased on the chemically treated SBAC compared to non-treated SBAC, suggesting that surface modification of a carbon adsorbent by acidic treatment generates more adsorption sites on their solid surface for metal adsorption.

Keywords: Sugarcane bagasse activated carbon (SBAC), Ash removal, Adsorption, Copper ions, Hydrofluoric acid, Nitric acid.

1. INTRODUCTION

It has been found by many researchers that agricultural by products such as sugarcane bagasse, rice husk, almond shell, coconut shell, olive stone are suitable raw material for the production of activated carbon. In the tropics like Perlis, sugarcane (*Saccarhum officinarum*) constitutes a major raw material for the production of sugar. During processing however, a number of by products are generated i.e., sugarcane bagasse, filter mud, molasses and material of the sugar industry, which is obtain after the pressing of the sugar-cane juice. Bagasse is usually burned to supply energy that is needed for evaporation of water in the crystallization process of sugar. Nevertheless, a fair amount of surplus bagasse still remains. Several investigators highlighted the possible use of sugarcane bagasse as activated carbon precursor. Review done by investigator shows that, the possibility of using sugarcane bagasse for producing activated carbon production and concluded the product from this material could be technically inferior to the product produced from coconut shell in many applications.

Almost all activated carbon contain ash and becomes one of the drawbacks of sugarcane bagasse based activated carbon. Ashes do not contribute to the porosity, and hence its presence should be as low as possible, because it adds to the sample weight and not the

adsorption capacity (Chermisinoff et al., 1980). The amount of ash in sugarcane bagasse based activated carbon varies from 3 to 5% and it is relatively high if compared to coconut-shell-based activated carbon that is around 0.3%. The presence of ash in activated carbon limits its applications. This ash can dissolve; depending on the solvent used and will contaminate the solvent. Besides, the dissolved ash can alter the pH of a solution (Jankwoska et al., 1991). In food and pharmaceutical industries, if the ash is not completely removed, it dissolved into the product this can lead to contamination of food and medicine. Activated carbon is also widely used as decolorization agent in sugar industry. Thus, the leachable ash is undesirable since it can cause uneven distribution of heat in the boiler during sugar crystallization (Smisek et al., 1970).

At present, quite a few researchers done towards modifying activated carbon to achieved zero ash content. One of the methods used to remove the ash is through acid leaching process. Most recent studies showed that, a UK bituminous coal containing 5.0 wt% ash can be reduced to 0.2 wt% using acid hydrofluoric leaching process (Karen et al., 2003). Hydrofluoric acid is able to dissolve aluminosilicate compounds under ambient conditions and in a single leaching step. This surface modification of activated carbon is recognized as an attractive approach for enhancement of heavy metal removal especially copper. Copper is introduced into water bodies from metal cleaning and plating, petroleum, refining and agriculture activities. Prolonged oral exposure of excess quantity of copper may result in liver damage and acute poisoning to human body. Removal of copper by activated carbon has gained industrial importance recently including palm shell based activated carbon. Attractiveness of sugarcane bagasse activated carbon comes from its properties such as high porosity, large surface area, favorable pore size and high mechanical strength. For that reason, modifications through acid treatment will be done in order to improve its properties and automatically enhance metal ion adsorption.

The initial objectives of the present work were to study the effect of hydrofluoric acid and nitric acid treatment on the characteristics of the sugarcane bagasse based activated carbon to enhance the adsorption performance. The copper adsorption equilibrium and kinetics were determined. Langmuir and Freudlich isotherm equations were employed to quantify the adsorption equilibrium. In order to characterize the physico-chemical characteristics of the material, techniques such as scanning electron microscopy (SEM) and BET surface area analysis and Boehm's method were done.

2. EXPERIMENTAL

2.1 Raw Material

The sugarcane bagasse based activated carbon sample was obtained from The Pacific Activate Carbon Company located in Kedah, Malaysia. The carbon prior to the experiment was sieved in order to restrain influence of the particle size on the adsorption capacity; all carbon granules were within range of 1.00-2.00 mm. Selected activated carbon was kept in a sealed plastic container.

2.2 Leaching Method

The samples have been leached by single and acids blend i.e. nitric Acid (HNO_3) mixed with hydrofluoric acid (HF) of molarities ranging from 0.1M to 2M. For a typical operation 100 ml of acid blends and 30 g of sample were charged into 250 ml flask and covered by parafilm. The suspension was stirred for 120 minutes at 240 rpm and room temperature 28^0C. After that the sample was filtered out using a filter paper and washed extensively by distilled water

until the pH of filtrate was that of the distilled water. The sample then dried in oven for overnight. The experiments were performed in a Teflon beaker.

2.3 Ash Content Determination

The ash contents were determined based on ASTM D 2867-95. The calculation of percentage of ash content and ash removal are as follows:

Percentage of ash content = $\dfrac{\text{(mass of ash) x 100}}{\text{(mass of dry sample)}}$

Percentage of ash removal = $\dfrac{\text{(ash before treatment – ash after treatment)}}{\text{(ash before treatment)}} \text{ x 100}$

2.4 Surface Properties

2.4.1 Physical Analysis

Physical analysis that are implemented basically to excess the characteristics of palm shell based activated carbon after deashing process using acid pre-treatment. SEM (Scanning Electron Microscope) equipped with Energy Dispersive Spectrometers (EDS) is used to visualize the surface morphology and structure of commercial and modified activated carbon. The surface area of commercial and chemically modified activated carbon is determined by Sorptomatic 1990 Series.

2.4.2 Chemical Analysis

Chemical analysis is done to investigate the surface chemistry of commercial and chemically treated SBAC. Samples were contacted with four types of bases of increasing strength; NaOH, Na_2CO_3, $NaHCO_3$, $NaOC_2H_5$. 1 g of SBAC was neutralize by adding 50 cm^3 of basic solution with a concentration 0.1 N during 48 hours stirring. Solutions were filtered . 10 cm^3 of filtrate were titrated by 0.1N HCl in the presence of helianthine for $NaHCO_3$ and Na_2CO_3 and phenolphtaline for NaOH and $NaOC_2H_5$.

The quantity of neutralized base is given by:

$$C(meq/g) = \left[N_{base} - \left(N_{HCl} \times \frac{V_{HCl}}{10} \right) \right] \times 50 \qquad (1)$$

2.5 Adsorption Equilibrium

Copper solutions with different concentrations were prepared from $Cu(NO_3)_2$ respectively. The solution pH was adjusted by adding HCl or NaOH and the ionic strength was kept at 0.15 M by adding sodium nitrate. Two pH systems were tested that are pH 3 and pH 5. The range of concentrations for copper (II) varied from 10 mg/L to 500 mg/L. A 100 ml volume of copper solution was added to 125-ml flasks. One g of activated carbon was then added to each flask. The flasks were covered using Parafilm and placed on the orbital shaker at 240 rpm and room temperature 28^0C for 24 h. The final samples were filtered and analyzed using Ionized Coupled Plasma (Varian) Spectrophotometer equipment. The final pH of the solution was

also measured. The copper adsorption equilibrium and kinetics were determined. Langmuir and Freudlich isotherm equations were employed to quantify the adsorption equilibrium.

3. RESULTS AND DISCUSSIONS

3.1 Effect of Acid Treatment and Molarity

The choice of acid blend used depends on the composition of the ash. Sugarcane bagasse based activated carbon composes of both mineral and non-mineral species mainly silicates. HNO_3 are effective in removing the mineral species whereas HF is more effective in dissolving silicates, which is present in large quantity. Figure 1 illustrates the ash removal by treatment with single acid that is HF and HNO_3. Single treatment with HF exhibit good removal compared to HNO_3 treatment. The optimum ash removal is at 2 M HF that is approximately 91%. The huge increase in the amount of removal using HF could be attributed to its ability to dissolve silicate and its compounds such as aluminosilicates that is present in a large quantity in the ash. This result was expected according to the well-known capability of HF to extract aluminosilicates from coal (Steel et al., 2001). The treatment using acid mixture of HF and HNO_3 at different molarity has been summarized graphically in Figure 2. The optimum condition for the mixture to remove the ash is at 1.8 M HF and 0.2 M HNO_3 that is at 95.24%, slightly higher than single acid treatment between SBAC and HF. This strongly proves that HNO_3 adsorbs mineral species in preferentially pyrite.
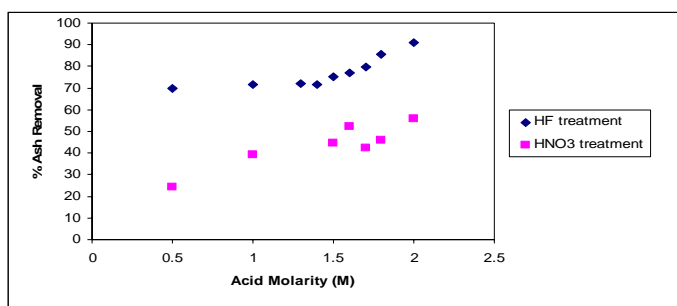

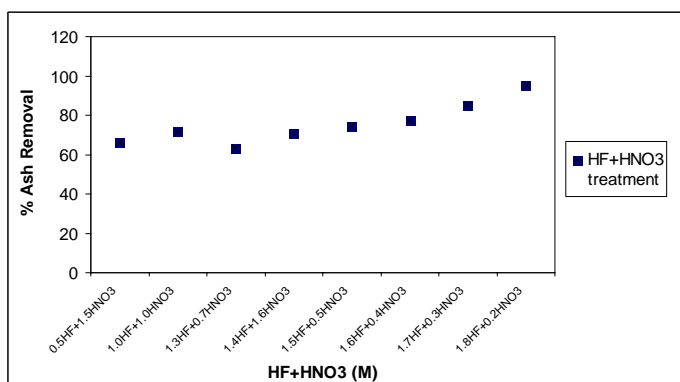Figure 1: Percentage of ash removal : treatment with single acid

Figure 2: Percentage of ash removal : treatment with acid mixture

3.2 Surface Area Analysis

Table 1: Summary of specific surface areas and micropore volume of PSAC samples

SBAC sample	S_{BET} [a] $(m^2\,g^{-1})$	V_m [b] $(cm^3\,g^{-1})$
Untreated SBAC	837.594	0.2947
SBAC treated with:		
1.5 HF + 0.5 HNO$_3$	876.481	0.3112
1.6 HF + 0.4 HNO$_3$	885.189	0.3177
1.7 HF + 0.3 HNO$_3$	1109.65	0.3969
1.8 HF + 0.2 HNO$_3$	1120.52	0.3978

a = Specific surface area
b = Micropore volume

The surface area of commercial and chemically modified activated carbon is determined by Sorptomatic 1990 Series. Since mixture of 1.8 HF and 0.2 HNO$_3$ exhibit the highest ash removal that is 95.24%, the higher surface area obtained. The purpose of the analysis is to study the relationship between ash content and surface area. The BET analysis showed in Table 2 indicates that, chemically modified SBAC can reach the surface area of 1120 m^2/g from untreated SBAC that is 837 m^2/g. Therefore, it indicates the ash has block some of the pores. This reflect to the higher adsorption capacities of Copper (II) on treated SBAC. Treatment of the SBAC with HF did not effect the micropore structure because fluorine was not fixed on the surface. In addition, HF is a weak acid. As we scroll through the results, when the concentration of HNO3 decreased, the surface area and micropore volume of SBAC becomes higher. This is due to the destruction of the pore walls by the oxidant treatment.

3.3 SEM Micrographs

(a)   *(b)*   *(c)*
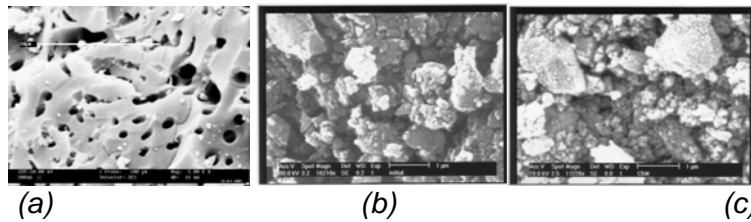
Figure 3: SEM micrographs of the sample surface
(a) SBAC pore network (b) untreated SBAC (c) treated SBAC

From the SEM micrograph shown in Figure 2 on the activated carbon samples. It demonstrates the pore network of the activated carbon. The untreated SBAC shows blockage on the pores. It does not contribute to the porosity, and hence its presence should be as low as possible.

3.4 Boehm's Method

Numerous studies on surface functionalities of carbon are already described in the literature. The differences of the surface functionalities on untreated and treated SBAC are determined by Boehm's titration and are listed in Table 2. The four bases used in the tittration are regard as approximate probs of acidic surface functionalities according to the scheme NaOH (carboxyl, f-lactonic and phenolic) , Na_2CO_3 (carboxyl and f-lactone) $NaHCO_3$ (carboxyl), $NaOC_2H_5$ (carbonyl).

Table 2: Surface acidic functionalities of SBAC by Boehm's titration

Acidic surface groups concentration	Concentration (meq/g)	
	Untreated	Treated
Carboxylic	3.75	4.25
Lactones	0.00	0.00
Phenolic	0.00	0.00
Carbonyl	0.00	0.00

Table 2 showed the acidic surface fuctionalities groups concentration for untreated and treated SBAC (mixture of 1.8 HF and 0.2 HNO_3). It indicates that, additional acidic group that is carboxyl groups may be formed by HNO_3 treatment. The influence of surface functional group on the acidic behavior are the most reliable in explaining why the adsorption capacity of the treated SBAC is higher than untreated SBAC.

3.5 Adsorption Equilibrium

The amount of metal adsorbed was calculated using Langmuir Isotherm that can be described as:

$$q_e = \frac{Q^o b C_e}{1 + b C_e} \qquad (2)$$

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^o b}\right) + \left(\frac{1}{Q^o}\right) C_e \qquad (3)$$

Equation (2) is in non-linear form while equation (3) is in linear form. q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g). C_e is the equilibrium concentration of solute in the bulk solution (mg/l), Q^o is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption.

The Freudlich equation in linear form may be written as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

In this equation K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and *1/n* is the constant indicative of the intensity of the adsorption.

Table 3: Langmuir and Freudlich isotherms for adsorption of Cu (II) on SBAC samples

SBAC	Untreated SBAC			Treated SBAC		
Langmuir constant		pH 3	pH 5		pH 3	pH 5
	Q^o	19.66	32.57	Q^o	26.57	39.06
	b	0.0043	0.0313	b	0.0113	4.223
	r^2	0.9462	0.9515	r^2	0.9486	0.9896
Freudlich constant		pH 3	pH 5		pH 3	pH 5
	K_F	1.211	2.195	K_F	1.0471	5.495
	1/n	0.449	0.5001	1/n	0.5289	0.427
	r^2	0.9904	0.9914	r^2	0.9809	0.9698

Units: Q^o: mg/g; *b*: $(mg/l)^{-1}$; K_F: $(mg/g)/ (mg/l)^{1/n}$

From the data presented both the Langmuir and Freudlich isotherms could be used to fit the data and estimate model parameter. From the adsorption of Cu^{2+}, it was revealed that, the adsorption capacity of metal ions increased on the chemically treated SBAC (treated with mixture of 1.8 HF and 0.2 HNO_3) compared to untreated SBAC. The ultimate uptake of metal ions (Q^o) reached 26.57 mgg^{-1} and 39.06 mgg^{-1}, at pH 3 and pH 5 for treated SBAC. The pH of the solution influenced the adsorption capacity of copper (II) that is almost doubled at higher pH. This is observed that less competition for the adsorption sites between metal and hydrogen ions at higher pH of the solution.

4. CONCLUSION

The ash content was reduced to 0.5wt% respectively. Hydrofluoric acid is able to dissolve aluminosilicate compounds under ambient conditions and in a single leaching step. Hydrouflouric acid is also able to penetrate further into the coal matrix and dissolve most of the other mineral compounds. Modified adsorbent were physically and chemically characterized by scanning electron microscopy (SEM) and BET surface area analysis and Boehm's titration. Under optimum conditions, 95 % of ash was removed. In addition, to its low ash content (< 0.5 %), the treated activated carbon showed enhanced surface area and micropore volume The BET analysis shows that, chemically modified SBAC can reach the surface area of 1120 m^2/g from non- treated SBAC that is 837 m^2/g. From the adsorption of Cu^{2+}, it shows that the adsorption capacity of metal ions increased on the chemically treated SBAC compared to non-treated SBAC, suggesting that surface modification of a carbon adsorbent by acidic treatment generates more adsorption sites on their solid surface for metal adsorption.

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