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Research Article

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The effectiveness of coconut shell activated carbon on the adsorption of heavy metal using different activating agents.

Ali L Yaumi, Bintu G Mustafa, Umar A Isah, Gutti Babagana, Faith A Ojih

Department of Chemical Engineering, Faculty of Engineering, University Of Maiduguri, Borno State, Nigeria.

Abstract The effect of chemical activation on the adsorption of metals ions (Al^{2+}, Cu^{2+}, Ni^{2+}, $Mg^{2+}$and Fe^{2+}) using waste Nigerian based coconut shell was investigated. Coconut shell was carbonized at 400 ˚C and activated at 400, 500, 600 and 650 ˚C using four activating agents. The produced activated carbon was characterized which revealed that increase in carbonization temperature leads to a decrease in both the ash content and char yield while the moisture content decreases with increase in carbonization temperature and pore volume are in a rise and fall pattern and increase in volatile content. The iodine value increased progressively with activation temperature, and then decreased when the temperature exceeded 600 ˚C, the optimum temperature for the production of activated carbons from coconut shell is approximately 600 ˚C The adsorption of metal ions using coconut activated with H_2SO_4 and HCl was significantly higher than carbons activated with NaOH and $Ca(OH)_{2.}$ This shows that waste coconut activated with H_2SO_4 and HCl can effectively be used to remove metal ions from waste waters and in different metal recovery processes than coconut shell activated with NaOH and $Ca(OH)_2$.

Keywords Coconut shell, adsorption, heavy metals, activated carbon

Introduction

The problems of ecosystem are increasing with development technology. Heavy metal pollution is one of the main problems due to their toxicity to human life, Organic pollutants and its derivatives found in industrial waste waters and as a main components in plastics are considered to have toxic effects on human health even when present in small concentrations [1]. The treatment efforts involved the application of unit processes such as chemical precipitation, coagulation, adsorption, ion exchange, and membrane filtration [2]. Coconut shells have been found to be good material for production of activated carbon. This is because; the carbon cycle of a coconut shell is about a months, and the time it takes to grow into full grown coconut carbon which is considered extremely effective for the removal of impurities in industries.

Activated carbon with their high porosity, are extensively used in industrial purification and chemical recovery [3-4]. Activated carbon is utilized as adsorbent in portable water treatment due to its well-developed pore structure, high internal surface area and good mechanical characteristic [5]. It is also use in pharmaceutical industry and in research laboratories as decolourising agent and catalyst support. Currently, micro porous activated carbons were found to be suitable materials for natural gas storage [6].

Adsorption with activated carbon represents a low cost, highly effective method to remove metal ion from aqueous solution at low concentration [7]. More recently, interest has been shown in the preparation of activated carbon using agricultural by-product (municipal waste) as precursor materials. The production of activated carbon from agricultural by-product as precursor materials has potential economic and environmental impact which convert unwanted agricultural waste to useful high value adsorbent and reduced the importation of activated carbon wherefore increasing our economic base in the country. This is achieved by preparing the activated carbon *via* physical and chemical activation.

Therefore it is necessary to raise the activities of these carbons via physical activation and compare the effectiveness of these different activating reagents in the adsorption of heavy metal ions. The aim of this research is to study the effect of chemical activation on the adsorption of heavy metals using activated carbon produce from coconut shell waste.

Materials and Methods

Sample Collection

The carbonaceous precursor used for preparation of activated carbon (AC) is coconut shell and was collected from Tashan Bama Maiduguri Borno state. Sample was washed gently with water to remove mud and other impurities present on the surface and then sundried. Commercial activated carbon prepared from coconut shell was obtained from chemical engineering laboratory university of Maiduguri. Activating agents are hydrochloric acid, sulphuric acid, Calcium hydroxide, and sodium hydroxide.

Synthesis of Activated Carbon

Carbonization

Known weight of waste coconut shell waste was cut into small sizes, washed, and dried. Then carbonized in a pyrolytic reactor at about 400–500˚C for 2 h after which the charred products were allowed to cool at room temperature. The charred material was pulverized (crushed) using mortar and pistol and sieved.

Chemical Impregnation

The carbonised waste coconut shell was weighed and poured in different beakers containing known quantity of dilute Hydrochloric acid, Sulphuric acid, Calcium hydroxide, and Sodium hydroxide (H_2SO_4, HCl, NaOH, and $Ca(OH)_2$). The concentrations of the acid used were already determined before this study. The content of the beakers were thoroughly mixed until a paste of each was formed. The pastes of the samples were then transferred to a stainless steel and the stainless steel was placed in a Muffle furnace and was heated to 400 ˚C for 1 h. The activated samples were then cooled at room temperature, washed with distilled water to a pH of 6-7, and dried in an oven at 105 ˚C for 3 h. The final products were sieved to same particle size kept in an air tight container, ready for use. Different concentrations (ranging from 0.025 M–0.5M) of each activating agents were prepared and used to activate waste coconut shells before the adsorption of the metal ions.

Preparation of activated carbon

Coconut shell was first washed and dried in an oven at 110 ˚C for 1 h, carbonization was carried out using electric muffle furnace which allows limited air supply and the sample weighing 200 g was introduced into the furnace. The charred produced was allowed to cool down to room temperature, pulverized to a workable size with mortar and pestle, the pulverized char was filtered with mechanical filter. The next step was activation of the sample in an oven using H_2SO_4, HCl, NaOH and $Ca(OH)_2$. A carefully weighed 25.0 g sample was put in a beaker containing 500 cm^3 of 1 M solution of activating agent. The content of the beaker was thoroughly mixed and heated in an oven until it's formed a paste. The paste was transferred into a crucible, the crucible was placed in a furnace, it was fired at 400˚C for 2 h. After allowing the activated sample to cool down to room temperature. It was washed with distilled water and dried in an oven at 400, 500, 600 and 650 ˚C for 1 h. The final product was kept in an air tight container ready to use.

Characterization of Activated Carbons

The waste Nigerian based coconut shells, used in this work were characterized using the ASTM method [8]. Bulk density is an important parameter of powdered solids. The American Water Work Association (AWWA) has set a lower limit on bulk density at 0.25 gm/ml for, activated carbon to be of practical use. The bulk density, dry density and porosity were calculated using the following expressions:

Bulk density = (Mass of wet sample)/(Mass of Volume)

Dry density = (Mass of dry sample)/(Volume of cylinder)

Porosity (η) =(Volume of void)/(Total volume)

Iodine Number

Iodine number is defined as the number of milligrams of iodine absorbed by one gram of activated carbon powder. Iodine solution is prepared by dissolving 13 grams of iodine in 50 cm^3 of glacial acetic acid and then diluting up to the mark in a 1000 cm^3 volumetric flask.

Iodine number = (Difference in concentration in mg)/(Weight of activated carbon in g)

Determination of moisture content

Thermal drying method was used in the determination of moisture content of the samples. The percentage moisture content (%MC) was computed as follows:

Moisture content = (Loss weight on drying)/(Initial sample weight)×10

Determination of ash content/volatile matter

The standard test method for ash content-ASTMD 2866-94 was used. The ash content was calculated using the equation.

Ash content = (Ash weight(g))/(Oven dry weight)×100

Volatile mater was calculated using the equation:

Volatile matter = (weight of volatile component)/(oven dry weight)×100

Adsorption Experiment

Six metal ions (Al^{2+}, Mg^{2+} Cu^{2+}, Ni^{2+}, Pb^{2+} and Fe^{2+}) frequently found in industrial and municipal wastewater were chosen for this study. All metal ions in solutions were made by dissolving a known quantity of each salt containing these metals in distilled water in the ratio 1: 1000. Two gram of the activated carbons activated with the four activating agents was added separately to the six mixtures containing each metal ion in solution, stirred for 30 min and filtered with a filter paper to get the filtrate. The amount of metal ions in solution (i.e., Zn^{2+}, Cr^{3+}, Pb^{2+}, Ni^{2+}, and Fe^{2+}) was determined using conduct metric method from the filtrate after adsorption using waste Nigeria coconut shell activated carbon. As described in the work of Banjonglaiad *et al*. 2008, at low concentrations, conductivity is linearly related to the different metal ion concentrations so that if just one metal is present its concentration is readily established through calibration [9]. Hence a calibration curve of concentration versus conductivity was first prepared for each metal ion. A commercial carbon was also used as control.

Results and Discussions

Characterization of activated carbon

Characterization properties of activated carbon obtained by different activating agent is shown in table 1.

Table 1: Characterization properties of activated carbon obtained by different activating agent

Reagent	Carbonisation Temperature (˚C)	Bulk Density (g/cm^3)	Dry Density (g/cm^3)	Ash Content (g/cm^3)	Moisture Content (%)	Porosity (%)	Volatility (%)	Char yield (%)
NaOH	**400**	0.16	0.55	6.08	1.79	5.29	9.48	53.96
$Ca(OH)_2$	**500**	0.61	0.66	8.65	1.98	8.51	17.18	61.25
HCl	**600**	0.68	0.69	10.23	2.45	10.10	23.43	66.25
H_2SO_4	**650**	0.77	0.79	12.01	3.18	13.44	32.55	72.41

The parameters determined are: the ash content, moisture content, pore volume, volatiles content. The American Water Work Association (AWWA) has set a lower limit on bulk density at 0.25 gm/ml for activated carbon to be of practical use. Increase in carbonization temperature leads to a decrease in both the ash content and char yield while the moisture content decrease with increase in carbonization temperature and pore volume are in a rise and fall pattern and increase in volatile content.

Iodine value of the activated carbon

The activation temperature is a very influential parameter on the pore structure of activated carbon, which determines the adsorption capacity. The variation in iodine values of activated carbon product was investigated as a function of activation temperature. Coconut shell was used as raw material and activation time was fixed at 1 h. As shown in Figure 1, the iodine value increased progressively with activation temperature, and then decreased when the temperature exceeded 600 ˚C. At higher temperature (600 ˚C), the pore walls between adjacent pores were probably destroyed and the micro pores were destructed, which led to the decrease in iodine value of the activated carbon. Thus, it can be concluded that the optimum temperature for the production of activated carbons from coconut shell is approximately 600 ˚C.

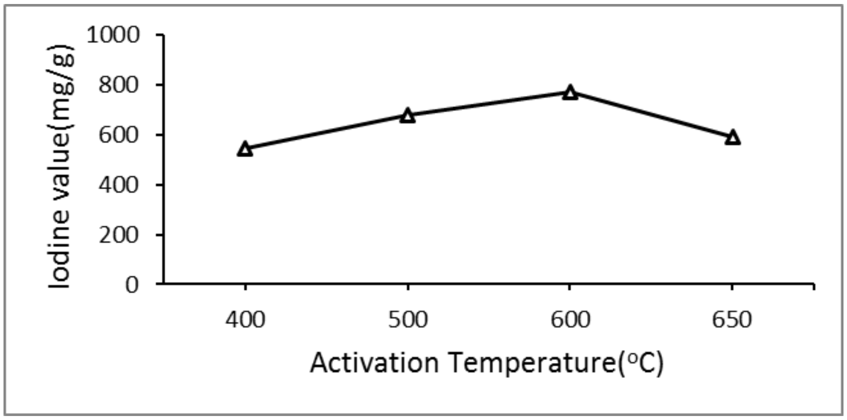

Figure 1: Effect of activation temperature on iodine value of activated carbon

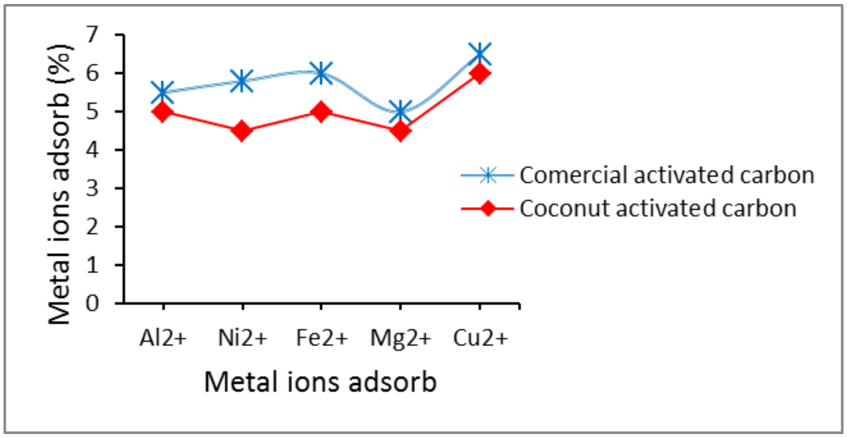

Figure 2: Adsorption of metal ions before activation of local adsorbents and Commercial Activated carbon.

It was observed from figure 2, that commercial activated carbon had the highest adsorption followed by coconut shell carbon within 30 min of adsorption. This result was expected because the commercial activated carbon was activated whereas coconut carbon was not activated. This shows that activation of the coconut carbon using four different activating agents was necessary for effective adsorption of the metal ions. Similarly in the work of F. T.

Ademiluyi *et al* (2012) [10], Adsorption of Metal Ions before Activation of Adsorbents and Commercial Activated Carbon using inactivated waste bamboo, inactivated waste coconut shell, inactivated waste palm kernel shell, and commercial activated carbon. It was observed that commercial activated carbon had the highest adsorption followed by activated carbon from bamboo, then palm kernel shell and lastly coconut within 30 minutes of adsorption.

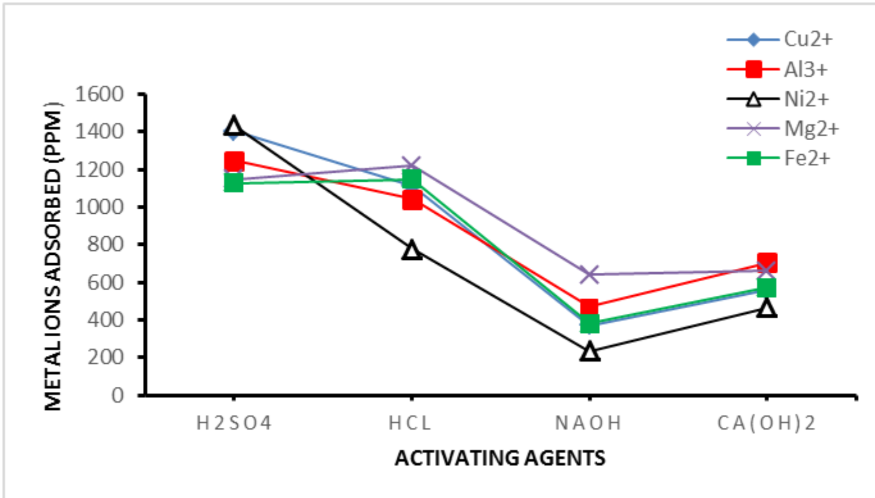

Figure 3: Adsorption metal ions using different activating agents.

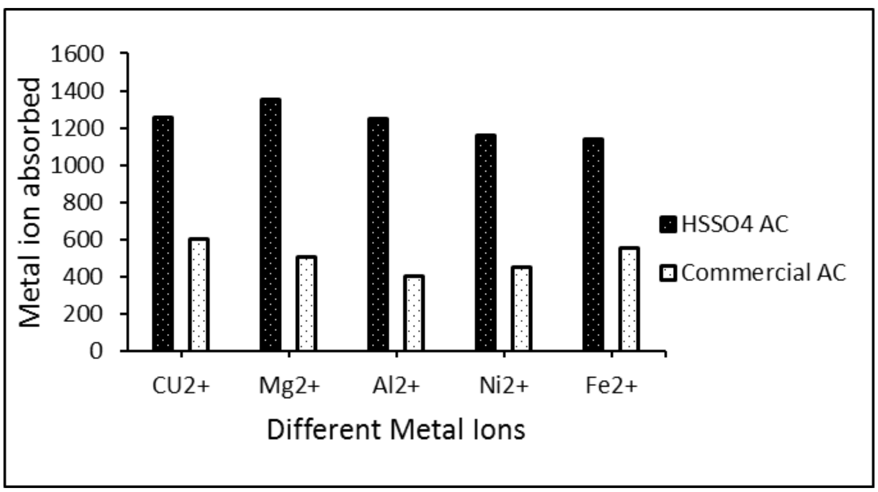

Figure 4: Adsorption of different metal ions using coconut shell activated with H_2SO_4 and commercial activated carbon.

Figure 3, shows the effect of physical activation on the adsorption of metal ions using activated carbon activated with H_2SO_4, HCl, NaOH, and $Ca(OH)_2$. The highest percentage of metal ions adsorbed was obtained from activated carbon activated with H_2SO_4, as an activating agent, it showed high adsorption for all the metal ions than other activating agents. It was observed that the amount of metal ions adsorbed activated with H_2SO_4 and HCl was significantly higher than carbons activated with NaOH, and $Ca(OH)_2$. This shows that adsorption of metal ions require chemisorptions than physical adsorption. Activation with H_2SO_4 and HCl created more reactive sites for adsorption of metal ions. Similarly, in the work of Ramírez *et al*. (2003), petroleum coke was activated with $ZnCl_2$, NaOH and H_3PO_4 [11]. The degree of physicochemical alteration was significantly different for the three carbons obtained after activation with three chemicals. Activated carbon activated with H_3PO_4 being the strongest was able to adsorb mercury, and silver more effective than NaOH and $ZnCl_2$. Also the amount of Iron II ions adsorbed by carbons from coconut, activated with H_2SO_4 and HCI was significantly higher than carbons activated with $Ca(OH)_2$ and NaOH. This means that H_2SO_4 and HCl increase the concentration of surface oxygen groups which reacts easily with metal irons ions than NaOH and Ca $(OH)_2$. Liu *et al*. 2007 similarly studied two step acid- based modification of AC for the adsorption of Chromium (VI) ions using HNO_3 and a mixture of NaOH and NaCl [12]. The result revealed higher of Chromium (VI) adsorption capacity due to the presence of more acidic groups.

Figure 4 shows the adsorption of different metal ions using coconut activated with H_2SO_4 and commercial activated carbon. Coconut shell after activation adsorbed more metal ions than the commercial activated carbon. This shows that coconut activated with H_2SO_4 can effectively be used to remove metal ions from waste streams than activated carbon from NaOH and $Ca(OH)_2$.

Conclusions

The effect of chemical activation using different activating agents on the adsorption of heavy metals ions using activated carbons from waste materials (coconut shell) was investigated. Physical activation had a significant effect on the adsorption of metal ions and on the type of carbonaceous material used. Coconut (*coco nucifera*) shell containing high cellulose (24.35%) and volatile content (72%) proved to be a promising precursor for Activated carbon development. Chemical activation of precursor by sulphuric acid, Hydrochloric acid, Calcium hydroxide and Sodium hydroxide produced activated carbons of various surface characteristics.increase in carbonization temperature leads to a decrease in both the ash content and char yield while the moisture content decrease with increase in carbonization temperature and pore volume are in a rise and fall pattern and increase in volatile content. The iodine value increased progressively with activation temperature, and then decreased when the temperature exceeded 600°C, the optimum temperature for the production of activated carbons from coconut shell is approximately 600°C. The adsorption of metal ions using coconut, activated with H_2SO_4, and HCl was significantly higher than carbons activated with NaOH, and $Ca(OH)_2$

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