

## Biomass-Derived Activated Carbon: A Viable Material for Remediation of $Pb^{2+}$ and 2, 4-Dichlorophenol (2, 4 DCP) through Adsorption

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### ABSTRACT

Carbon has been one of the magnificent elements which have revolutionized material science. From carbon we obtain the best porous absorber (activated carbon) with excellent properties for large spectrum of industrial applications. Activated Carbon (AC) is the common term used for a group of absorbing substances of crystalline form, having a large internal pore structures that make the carbon more absorbent. This paper presents the surface properties of coconut shell derived-activated carbon and its sorptive applications. Some of the physic-chemical properties of the carbon were characterized in terms of porosity having value of 0.13, iodine number of 334.23 mg/g, surface area of 327.52 m<sup>2</sup>/g and surface acidity value of 0.31 mmol H<sup>+</sup>/g. The coconut shell activated carbon was subjected to various treatment conditions of (40oC, 60oC, 80oC) temperatures, (30 minutes, 1 hour, 2 hours) treatment time and (1 M, 2 M, 3 M) concentrations of HNO<sub>3</sub>. Surface acidity was determined on each of the treated activated carbon to establish the optimum condition of the acidic treatment. The highest surface acidity value of 3.06 mmol H<sup>+</sup>/g was obtained at treatment condition of 80oC, 2 hours and using 3 M concentration of the acid while the lowest value of 0.89 mmol H<sup>+</sup>/g occurs at 40oC, 2 hours and 1 M concentration. The adsorbent with the highest surface acidity was used to check the effect of the acidic treatment on the absorption of lead Pb and 2,4-Dichlorophenol (2,4-DCP).

### Keywords:

Activated carbon; coconut shell; surface acidity; adsorption

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## 1. Introduction

Recently, carbon has been one of the magnificent elements which have revolutionized material science. From carbon we obtain the best porous absorber (activated carbon) with excellent properties for large spectrum of industrial applications. Activated Carbon (AC) is the common term used for a group of absorbing substances of crystalline form, having a large internal pore structures that make the carbon more absorbent [1]. These properties are obtained when a char is subjected to controlled gasification by oxidizing gases, or when a raw material impregnated with dehydrating

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agents is subjected to carbonization. Generally, the raw materials for the production of AC are those with high carbon but low inorganic contents such as wood, lignite, peat and coal [2]. Besides that, a lot of agricultural waste and by product have successfully converted to AC for examples macadamia nutshell [3], paper mill sludge [4] and peach stones [5]. In Malaysia there are potential raw materials resources to produce the activated carbon. In this research, a local agricultural waste which is coconut shells was used to produce an activated carbon due to its availability and inexpensive material with high carbon and low inorganic content. AC is used primarily as an adsorbent to remove organic compounds and pollutant from liquid and gas streams. The market has been increasing constantly as a consequence of environmental issues, especially water and air purification. Furthermore, as more and more countries are becoming industrialized, the need for activated carbon to comply with environmental regulation will grow at faster rate. Liquid phase applications represent the largest outlet for AC. In these applications, AC is used in the purification of a variety of liquid streams, such as those used in water treatment and the processing of food, beverages and pharmaceuticals. The growth of the activated carbon market in the last two decades in the most industrialized region will very probably continue in the near future as more developing areas of the world will realize the importance of controlling water and air pollution. This demand can be satisfied considering the large number of raw material available for the production of AC, the variety of activation processes described, and the available forms of AC. Thus, continuous research has to be implementing to develop the high quality of AC for specific uses. This research article proposes a promising approach towards utilization of biomass waste material such as coconut shell for the remediation of toxic pollutants.

## **2. Materials and Methods**

### **2.1 Collection of Sample**

The coconut shell used for this work was purchased from a coconut oil producer in Uselu market, Benin City. Dirt was removed from samples after which they were washed and sun dried for 24hrs. The samples were crushed into smaller sizes to enhance its entrance into the muffle furnace. The samples were further oven dried at 105°C to remove excess moisture content followed by carbonization muffle furnace at temperature of 600°C for 2hrs and the powdered obtained was kept in a closed container prior to the activation process.

### **2.2 Activation**

The carbonized sample was soaked in 2M KOH solution in a ratio of 1:20 of weight of carbonized sample to volume of KOH solution for 12 hours. The mixture was filtered through a clean white silk and was allowed to drip dry for three days. This was later activated in a muffle furnace at a temperature of 400°C for 3 hours. The activated carbon was allowed to cool at room temperature, washed and was kept in a tightly closed container before the characterization processes.

### **2.3: Determination of Porosity**

2.0 gram of the activated carbon was transferred into a measuring cylinder (10 ml) and the volume of the particle was recorded. This sample was placed into a beaker containing 20 ml of distilled water and boiled for 5 minutes (to displace air in the container). The content was filtered, superficially dried and weighed. The increase in weight of the sample divided by the density of water

gave pore volume. Porosity was calculated by dividing the pore volume of the particle with the total volume of particle [6].

## 2.4 Determination of Surface Area

The Iodine number was first determined and the surface area was calculated from a mathematical relation between surface area and iodine number as reported by [7]. 10 ml of 5% by weight HCl was added to 1g of activated carbon in a conical flask and was allowed to boil gently for 30 seconds to remove any impurities. After the solution was cool at room temperature, 100 ml of 0.1N iodine solution was added into the flask. The content was shaken vigorously for 30 seconds and was filtered quickly into a beaker. 20 ml of the filtrate was titrated against 0.1N sodium thiosulphate using starch as indicator. Similarly, the quantity of sodium thiosulphate needed to titrate the blank was determined. All titration were carried out in triplicate and the average titre value obtained in each case was calculated. The iodine number was defined as the quantity of iodine adsorbed in (mg/g carbon) as residual iodine concentration [8].

$$\text{Iodine number} = \frac{(A - B)}{B} \times \frac{VM}{W} (126.91)$$

A = Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used for blank

B = Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used for activated carbon

V = Volume of iodine solution used

M = Molarity of iodine solution used

W = Weight of activated sample

Surface Area = (0.9946) I.N – 4.91[7].

I.N = Iodine number

## 2.5 Determination of Surface Acidity

In determining the surface acidity, 0.1N NaOH solution (100 ml) and 5 gram of the activated carbon were mixed in a conical flask. The mixture was shaken for 4 hours with a conical flask shaker to ensure that the solution had come to equilibrium. The solution was back titrated with standard 0.1N HCl solution using a pH indicator. The surface acidity of the activated carbon was calculated from the titre value [9].

Surface Acidity =  $\frac{\text{The volume of NaOH used (ml)} \times 0.1\text{N (the normality of the NaOH solution)}}{\text{the volume of HCl used} \times 0.1\text{N (the normality of NaOH solution)}}$  [9].

## 2.6 Surface Acidic Treatment

The Surface acidic treatment was carried out in three different conditions; temperature of heating, duration of heating and concentration of HNO<sub>3</sub> used. 1:20 of the weight of activated carbon to volume of HNO<sub>3</sub> was adopted for all the treatment conditions. 5 gram of the Activated carbon was weighed and dissolved in 100 ml of 1M HNO<sub>3</sub>. This was heated in a thermostatic hot plate at 40°C for 30 minutes. The mixture was allowed to cool at room temperature and filtered through a Whatmann filter paper, washed and kept tightly closed in a small plastic bottle.

The same process was repeated for all conditions of temperatures; 40°C, 60°C and 80°C, all conditions of concentrations of HNO<sub>3</sub>; 1M, 2M and 3M for 30 minutes treatment time. Similarly, the whole treatment process and conditions were done for 1 hour and 2 hours treatment times

respectively. After all treatments, a total twenty seven (27) acid treated activated carbon were obtained based on different treatment conditions. Each sample was labeled based on their treatment conditions. E.g. 1M/40°C/30mins, 2M/40°C/30mins, 3M/40°C/30mins etc. Surface acidity test was conducted on the 27 samples as describe in section 2.4.3 to identify which treatment condition was more effective.

### 2.7 Adsorption of lead (Pb)

The treated sample with the highest surface acidity value and the untreated sample were used to study the effect of surface acidity of the coconut shell activated carbon on the adsorption of Lead. AAS was used to detect the concentration of the lead after adsorption.

### 2.8 Adsorption of 2, 4-Dichlorophenol (2, 4-DCP)

The treated sample with the highest surface acidity value and the untreated sample were used to study the effect of surface acidity of the coconut shell activated carbon on the adsorption of 2, 4-DCP. UV-Vis spectrophotometer was used to calibrate the curve for standard concentrations of 2, 4-DCP ranging from 1ppm to 20ppm. The UV-Vis spectrophotometer was also used to detect the absorbance values of the 2, 4-DCP after adsorption. The concentrations were extrapolated from the standard calibration curve.

### 2.9 Adsorption Procedure

The acidic treated activated carbon that shows highest surface acidity test and the untreated activated carbon were used as the adsorbent. 1.0g of the adsorbents were mixed with 100 ml of 20mg/L (20ppm) lead, 100 ml of 20mg/L 2,4-dichlorophenol and 100 ml equimixture of 20mg/L lead and 20mg/L 2,4-dichlorophenol in a separate conical flask respectively. The flask was shaken with a conical flask shaker for 3 hours to ensure equilibrium adsorption. The adsorbents were then separated from the solution by filtration through a whatman filter paper. The residual concentrations of the lead and the 2, 4-DCP was analyzed with AAS and UV-Vis spectrophotometer respectively. The equilibrium adsorption capacity ( $q_c$ ) is defined as the amount of adsorbate per gram of adsorbent and calculated by

$$q_c = \frac{(C_1 - C_2)V}{m} \quad (\text{mg/g})$$

C1 = Concentration of adsorbate before adsorption (mg/L)

C2 = Concentration of adsorbate after adsorption (mg/L)

V = Volume of the solution

m = Mass of the adsorbent (g), [10]

## 3. Results and Discussion

### 3.1 Physioco-chemical Properties of the coconut shell Activated Carbon

The Physioco-chemical properties of the untreated adsorbent are represented on table 1 with results showing a porosity of 0.13 which was determined from the pore volume. A larger pore volume means high porosity and in turn better adsorption capacity. Iodine number of the untreated adsorbent was determined to be 334.23 mg/g which gives an estimated value of the Surface area. Iodine number is an indication of the pore volume availability in the activated carbon of interest [11].

The surface area was calculated to be 327.52 m<sup>2</sup>/g. Generally, the larger the surface area of the adsorbent, the better the adsorption performance [12]. Since the coconut shell activated carbon has not been subjected to form of acidic treatment, however, the surface acidity was determined to be very low at 0.31 mmol H<sup>+</sup>/g which is a very negligible value compared to the various values after various treatment conditions as shown in **Table 2** and also shows the surface acidities of the adsorbent at various treatment conditions of 30 minutes. It reveals that for 30 minutes treatment, 3 M HNO<sub>3</sub> at treatment temperature of 40°C gave the highest surface acidity value of 2.47 mmol H<sup>+</sup>/g and lowest acidity value of 1.13 mmol H<sup>+</sup>/g at treatment temperature of 60°C and 2 M HNO<sub>3</sub>. The surface groups play a key role in the surface chemistry of activated carbon and adsorption is depended upon their surface chemistry [13].

**Table 1**

Characteristics of the untreated coconut shell activated carbon

S/no	Parameters	Results
1	Porosity	0.13
2	Iodine Number (mg/g)	334.23
3	Surface Area (m <sup>2</sup> /g)	327.52
4	Surface Acidity (mmol H <sup>+</sup> /g)	0.31

### 3.2: Effect of Acidic Treatment on the Surface Acidity

The effect of acidic treatments on the surface acidity at various treatment time 30mins, 1hr and 2hrs also at temperatures 40°C, 60°C, and 80°C are represented in (**figure 1**). These can be observed that all treatments at 40°C gave higher surface acidity. The surface acidities of all treatment at 60°C and 80°C where at the same area range and are lower. It therefore implies that at 30 minutes duration of treatment, 40°C treatment temperature increases the surface acidic group of the activated carbon much better than at higher temperature as shown in **A (figure 1)**. In reference to **Table 2** at 40°C treatment temperature at 30mins and 3 M HNO<sub>3</sub> also gave the highest surface acidity of 2.60 mmol H<sup>+</sup>/g. The lowest surface acidity occurs at 60°C treatment temperature and 1 M HNO<sub>3</sub>. **B. (figure 1)** explains the effect of 1 hour treatments on the surface acidity and it shows that adsorbents treated with 3 M HNO<sub>3</sub> at the three temperatures gave a good surface acidity. This is not the same in **Table 2** above which shows the surface acidities of the adsorbent at various treatment conditions of 2 hours. It reveals that for 2 hours treatments, 3 M HNO<sub>3</sub> and treatment temperature of 80°C gave the highest surface acidity value of 3.06 mmol H<sup>+</sup>/g and lowest acidity value of 0.89 mmol H<sup>+</sup>/g at treatment temperature of 40°C and 1 M HNO<sub>3</sub>.

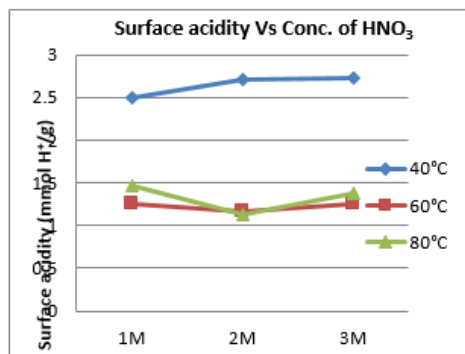
**C. (figure1)** explains the effect of 2 hours treatment on the surface acidity and was observed that all treatments at 3 M HNO<sub>3</sub> gave higher surface acidity, but that of 2 M at 80°C also gave a high surface acidity. It therefore implies that at 2 hours duration of treatment, 3 M HNO<sub>3</sub> is very effective in increasing the surface acidic group of the activated carbon much better than lower concentrations of the acid. It is observed that the overall highest surface acidity of all the treatment condition occurs at 2 hours duration treatment with it surface acidity at 3.06 mmol H<sup>+</sup>/g and the lowest was also observed at 2 hours duration with surface acidity value of 0.89 mmol H<sup>+</sup>/g.

**Table 2**  
Acidic treatment for 30mins, 1hr and 2hr

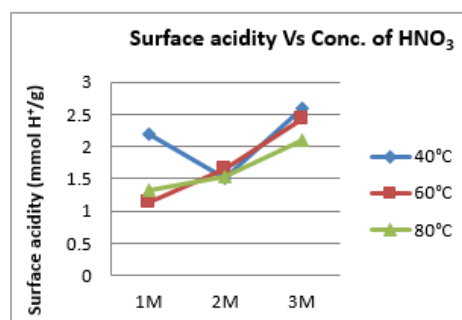
Temperature	Concentration (M)	Surface Acidity (mmol H <sup>+</sup> /G) 30mins	Surface Acidity (mmol H <sup>+</sup> /G) 1hr	Surface Acidity (mmol H <sup>+</sup> /G) 2hr
40°C	1	2.50	2.19	0.89
	2	2.70	1.50	1.02
	3	2.73	2.60	2.64
60°C	1	1.25	1.14	1.15
	2	1.16	1.65	1.66
	3	1.25	2.44	2.54
80°C	1	1.47	1.32	1.84
	2	1.13	1.54	2.99
	3	1.37	2.10	3.06

At 30 minutes duration of treatment (A) 40°C treatment temperature increases the surface acidic group of the activated carbon much better than at higher temperature. B. explains the effect of 1 hour treatments on the surface acidity. It shows that adsorbents treated with 3 M HNO<sub>3</sub> at the three temperatures gave a good surface acidity. C. shows the surface acidities of the adsorbent at various treatment conditions of 2 hours. It reveals that for 2 hours treatments, 3 M HNO<sub>3</sub> and treatment temperature of 80°C gave the highest surface acidity value of 3.06 mmol H<sup>+</sup>/g and lowest acidity value of 0.89 mmol H<sup>+</sup>/g at treatment temperature.

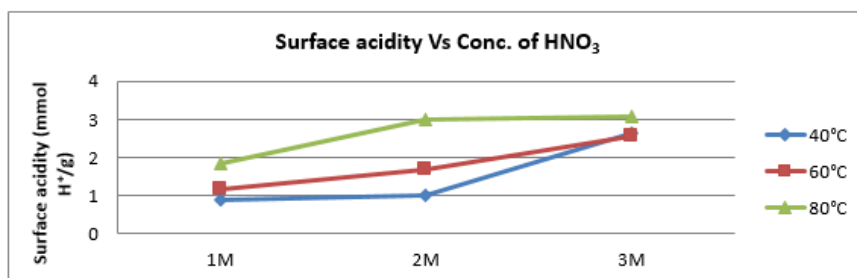
Figure 2: A. gives a detail explanation of the effect of 40°C treatment temperature on the surface acidity of the adsorbent. It was observed that at the three treatment times with 3 M HNO<sub>3</sub>, a high surface acidity was gotten. However, at 30 minutes treatment time, all concentration of the acid gave high surface acidity value. It was observed that 2 hours treatment using 1 M and 2 M of the acid respectively does not show much effective on the surface acidity. B. shows the effect of 60°C treatment temperature on the surface acidity of the adsorbent. It was observed that using 3 M HNO<sub>3</sub> for the treatment for 1 hour and 2 hours gave a good surface acidity on the adsorbent. 30 minutes treatment at this temperature was determined not to be very effective in increasing the acidic surface of the adsorbent. However, 1 hour and 2 hours using 1 M and 2 M of the acid respectively gave similar fair surface acidity value. C. Explains the effect of 80°C treatment temperature on the surface acidity. It reveals that 2 hours treatment using 1 M and 2 M of the acid gave the best surface acidity value. These two conditions of treatment were also discovered to produce the highest surface acidity value of all the conditions determined.



A. Effect of 30 minutes treatment on the surface acidity

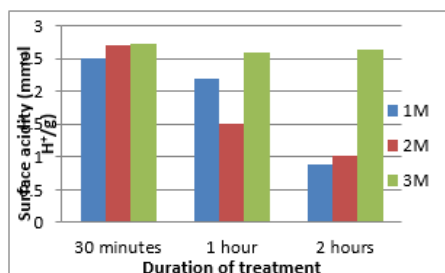


B. Effect of 1 hr treatment on the surface acidity

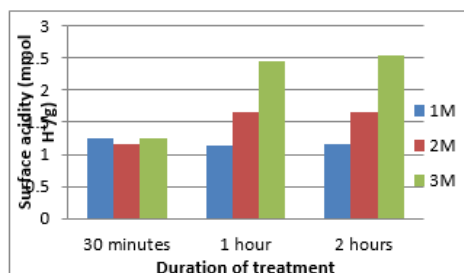


C. Effect of 2 hr treatment on the surface acidity

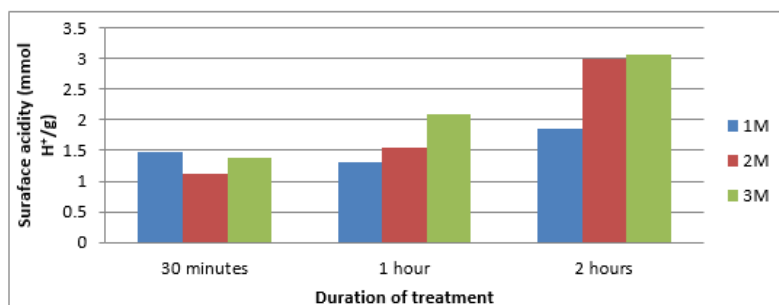
Fig.1. showing treatment effect on surface acidity at 30mins, 1hr and 2hrs respectively



A. Effect of 40°C treatment temperature on the surface acidity



B. Effect of 60°C treatment temperature on the surface acidity



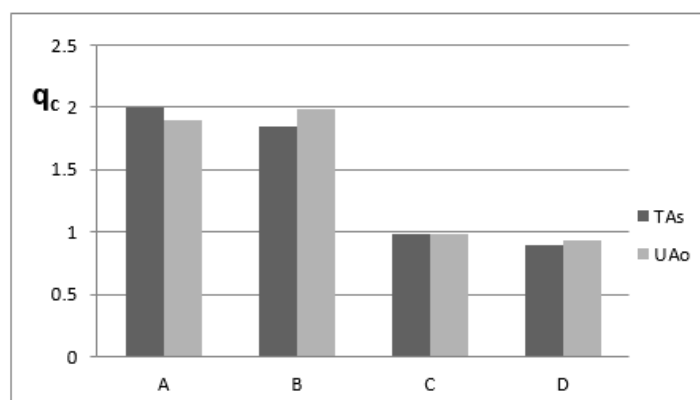
C. Effect of 80°C treatment temperature on the surface acidity

Fig.2. Effect of 40°C, 60°C and 80°C treatment temperatures of surface acidity

### 3.3 Effect of Acidic Treatment of the Adsorbent on Adsorption

**Figure 3** explained the equilibrium adsorption capacity ( $q_c$ ) for adsorption of lead was found to be higher with the acid treated adsorbent. That means the adsorbent with the highest surface acidity adsorbs more lead than the untreated adsorbent [14] reported that increasing the acidic functional groups on Activated Carbon surfaces enhances chelating ability with heavy metal species. This further reveals that acidic treatment of the adsorbent displays beneficial effects on the adsorption of lead. [15]. Strelko [15] reported that oxidation of Activated Carbon using nitric acid increases the adsorption capacity by a factor of 4 (for  $\text{Cu}^{2+}$ ). In the adsorption of 2,4-Dichlorophenol, the untreated adsorbent displayed a better adsorption capacity than the treated adsorbent. This indicates that surface acidity has a negative effect on the adsorption of 2,4-DCP. Santiago et al [16] reported that activated carbon treated with nitric acid destroyed basic sites considerably and subsequently decreased the uptake of phenol from aqueous solution. In his study, it was believed that destruction of basic sites eventually lead to reduce catalytic activity of phenol and this trend is consistent with dilute phenol solution. In this work, it is believed that the untreated adsorbent gave a better adsorption capacity for 2,4-DCP adsorption because the acidic treated adsorbent may have destroyed the existing basic group of the adsorbent which is considered more favorable for uptake of organic (especially phenols) from aqueous solution.

Category **C** and **D** in **figure 3** showed the adsorption capacity of the treated adsorbent and the untreated adsorbent in the adsorption of lead and 2, 4-DCP from equal mixture of 20mg/L of the two solutions. It is observed that in Lead adsorption, both the treated and the untreated adsorbent gave equal adsorption capacity. However, their adsorption capacities were low. It can be suggested that the low adsorption capacity was as a result of the fact that both lead and the 2, 4-DCP were competitively and simultaneously adsorbed. The untreated adsorbent still shows a little better uptake for 2, 4-DCP as compared to treated adsorbent



**Fig.3.** shows the effect of the treated adsorbent with the highest surface acidity and the untreated adsorbent on the adsorption capacity of Lead (Pb) and 2, 4-Dichlorophenol

TAS = Treated adsorbent with the highest surface acidity, UAO = Untreated adsorbent

$q_c$  = Equilibrium adsorption capacity ,

A = Adsorption of lead from 20mg/L lead solution

B = Adsorption of 2,4-DCP from 20mg/L 2,4-DCP solution

C = Adsorption of lead from 20mg/L equimixture lead/2, 4-DCP solution

D = Adsorption of 2,4-DCP from 20mg/L equimixture lead/2,4-DCP solution

#### 4. Conclusions

This research was conducted to investigate the sorptive properties of coconut shell derived-activated carbon. The produced activated carbon was subjected to acidic treatment in various conditions of treatment to examine the optimal treatment condition that demonstrated greater absorptivity. It has been shown that acidic treatment of the coconut shell activated carbon using 3 M  $\text{HNO}_3$  and at  $80^\circ\text{C}$  for duration of 2 hours gave a more effective treatment on the surfaces of the carbon. In the adsorption study, the surface acidic treatment of activated carbon from coconut shell enhances adsorption capacity for lead. In the case of 2, 4-Dichlophenol adsorption, acidic treated adsorbents gave negative effect on the adsorption capacity. Therefore, for heavy metal adsorption, increasing the acidic surface of the adsorbent will give a favorable effect on the adsorption but unfavorable for organic pollutant uptake.

#### References

- [1] Strand, Gert. "Activated carbon for purification of alcohol." *Malmö, Sweden* (2001).
- [2] Lua, Aik Chong, and Jia Guo. "Microporous oil-palm-shell activated carbon prepared by physical activation for gas-phase adsorption." *Langmuir* 17, no. 22 (2001): 7112-7117.
- [3] Ahmadvour, A., and D. D. Do. "The preparation of active carbons from coal by chemical and physical activation." *Carbon* 34, no. 4 (1996): 471-479.
- [4] Nasrin, R. K., C. Marta, S. Giselle, and G. Janusz. "Production of micro-and mesoporous activated carbon from paper mill sludge. I. Effect of zinc chloride activation." *Carbon* 38, no. 14 (2000): 1905-1915.
- [5] Arriagada, R., R. Garcia, M. Molina-Sabio, and F. Rodriguez-Reinoso. "Effect of steam activation on the porosity and chemical nature of activated carbons from Eucalyptus globulus and peach stones." *Microporous Materials* 8, no. 3-4 (1997): 123-130.
- [6] Rhoda H.G., Idayonbe O. (2015). *Advances in Chemical Engineering and Sciences* 5, 51-61.
- [7] Mianowski, A., M. Owczarek, and A. Marecka. "Surface area of activated carbon determined by the iodine adsorption number." *Energy sources, part A* 29, no. 9 (2007): 839-850.
- [8] ASTM International. "Standard Test Method for Determination of Iodine Number of Activated Carbon. ASTM D4607-14." (2014).
- [9] Duckhee Lee (2013). Preparation of a sulfonated carbonaceous material from lignosulfonate and its usefulness as an esterification catalyst. *Molecules*. 18: 8168-8180
- [10] Li, Bingzheng, Zhiping Lei, and Zhanggen Huang. "Surface-treated activated carbon for removal of aromatic compounds from water." *Chemical engineering & technology* 32, no. 5 (2009): 763-770.
- [11] Lartey, R. B., Francis Acquah, and K. S. Nketia. "Developing national capability for manufacture of activated carbon from agricultural wastes." *Ghana Eng* 3 (1999): 45-50.
- [12] Guo, Jia, and Aik Chong Lua. "Textural and chemical properties of adsorbent prepared from palm shell by phosphoric acid activation." *Materials chemistry and physics* 80, no. 1 (2003): 114-119.
- [13] Radovic L R, Moreno-Castilla C, Rivera-Utrilla J. In: L.R. Radovic (Ed.), *Chemistry and Physics of Carbon*. 2001: 27, Marcel Dekker, New York:Chapter 4.
- [14] Yin, Chun Yang, Mohd Kheireddine Aroua, and Wan Mohd Ashri Wan Daud. "Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions." *Separation and purification technology* 52, no. 3 (2007): 403-415.
- [15] Strelko Jr, Vladimir, and Danish J. Malik. "Characterization and metal sorptive properties of oxidized active carbon." *Journal of colloid and interface science* 250, no. 1 (2002): 213-220.
- [16] Santiago, Marta, Frank Stüber, Agustí Fortuny, Azael Fabregat, and Josep Font. "Modified activated carbons for catalytic wet air oxidation of phenol." *Carbon* 43, no. 10 (2005): 2134-2145.