# REMOVAL OF HEAVY METALS FROM DYE EFFLUENT USING ACTIVATED CARBON PRODUCED FROM COCONUT SHELL

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**ABSTRACT**

The ability of activated carbon produced from coconut shell to remoe mercury Hg (II), Lead Pb (II) and Copper Cu (II) from dye effluent was investigated. The activated carbon was produced through chemical activation processes by using zinc chloride (ZnCl$_2$). The adsorption capacity was determined as a function of adsorbent dosage. The adsorption Isotherms of the studied metals on adsorbent were also determined and compared with the Langmair models. The activated carbon produced showed excellent effecency in removing Hg (II) and Pb (II) with percentage removal up to 80 % at low adsorbent dosage of 2 g. In contrast, only about 29 % removal of Cu (II) was achieved at adsorbent dosage of 2 g. The study also showed that the adsorption of Hg (II), Pb (II) and Cu (II) by the activated carbon is dependent on the dosage of the adsorbent and the initial metal concentration. The use of cocnut shell for activated carbon also helps in solving the problem of over abundance of cocnut shell as agricultural waste.

**Key Words:**     **Heavy Metals; Dye Effluent; Activated Carbon; Coconut Shell.**

**INTRODUCTION**

The increase in industrial activities has caused many water bodies to receive loads of heavy metals that exceed the maximum permissible limit for wastewater discharge designed to protect the enviroment, human and animals (Iqual and Saeed, 2007). Pollution by heavy metal ions, including mercury (Hg), lead (Pb) and copper (Cu), has become a major hazard issue due to their possible toxic effects (Aydin et al, 2008). The risks of Hg(II) exposure, for instance, may contribute to adverse effects on central nervous system, pulmonary kidney functions and chromosomes (Rao et al, 2009).  Pb(II) on the other hand can bioaccumulate through the food chain(Qui et al,2008), while  Prolonged inhalation of Cu(II) spray is claimed to cause an increase in the risk of lung cancer (Aydin et al, 2008). Based on Enviromental Quality act 1974, maximum permisible limits for Hg(II), Pb(II) and Cu(II) in drinking water are 0.005mg/L,0.10mg/L and 0.20mg/L respectively.

Hg(II), Pb(II) and Cu(II) are released into the aqueous enviroment through variety of sources such as metal smelters, effluents from plastics, textiles, microelectronics and wood preservatives producing industries and useages of fertilizers and pesticides (Bhatti *et al*,2007). These metals cannot be degraded or destroyed, but can be remove from these water bodies. Conventional methods for removing heavy metals include filtration, chemical precipitation and ion exchange, electochemical deposition and membrane process. However, these methods are either inefficient or expensive especially when the concentration of the heavy metal ion is low, in the range of 1-100mg/L (Bhatti *et al*,2007).

Activated carbon is a microcrystalline, non-graphitic form of carbon with a porous structure that has been processed to develop its internal porosity (Hassler, 1974). This material can be characterized by a large specific surface area of 500-2500 $m^2/g$. This is the most important physical property of activated carbon because it allows the physical adsorption of gases or vapors and dissolved or dispersed substances from liquids. Activated carbons (AC) are an effective adsorbent for many pollutant compounds (organic, inorganic, and biological) of concern in water and wastewater treatment (Hassler *et al* 1974). The major use of activated carbon is in solution purification and for the removal of taste, color, odors and other objectionable impurities from liquids, water supplies and vegetable and animal oils. In recent years it has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of activated carbon for control of air and water pollution. Activated carbon is a broad-spectrum agent that effectively removes toxic and biorefractive substances such as insecticides, herbicides, chlorinated hydrocarbons, and phenols, typically present in many water supplies. The use of activated carbons is perhaps the best broad-spectrum control technology available at present. (Bagreev *et al*, 2001).

Any carbonaceous material (natural or synthetic) with high carbon content can be used as raw material for preparation of AC. The most common raw materials are agricultural byproducts such as wood, sawdust, rice husk, nut shells, fruit pits, and charcoal, brown and bituminous coals, lignite, peat, bone, paper mill waste (lignin), and synthetic polymers like PVC, are used for manufacturing of activated carbon. In fact, any carbonaceous low-cost materials (of animal, plant, or mineral origin) with high carbon and low ash content can simply be changed into activated carbon under the proper thermal decomposition process (Bagreev *et al*, 2001)..

There are two basic process of producing activated carbon; physical activation and chemical activation. In physical activation process, the processes of carbonization and activation take place in two separate steps. The activating medium mostly commonly used were certain oxidizing gases like steam, carbon dioxide , air etc. This is a high temperature process as compared to that of chemical activation (Kadlec *et al* 1970). In chemical activation, both the processes of carbonization and activation, takes place simultaneously. Here, the raw material which in most of the cases is of cellulosic nature, is impregnated or kneaded with certain inorganic salts and this impregnated mass is then carbonized at low temperatures to ultimately yield an active char, after washing with acid and water. The products obtained by the process of chemical activation are mostly used in liquid phase purification systems (Kadlec et al 1970).

Activated carbons can broadly be classification for general purpose based on their physical characteristics into: Powdered activated carbon (PAC), Granulated activated carbon (GAC), Extracted activated carbon (EAC), Impregnated carbon, Polymer coated carbon, etc.

Coconut husk and shells can be used for fuel and are sources of charcoal. Dried half coconut shells with husks are used to buff floors. Activated carbon manufactured from coconut shell is considered superior to those obtained from other sources. This is mainly because of small macrospores structure which renders it more effective for the adsorption of gas and vapor and for the removal of color, oxidants, impurities and odor of compounds. (www.wikipedia.org/activeatedcarbon).

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate) (Aydin *et al,* 2008). It is different from *absorption*, in which a substance diffuses into a liquid or solid to form a solution. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy. (Avon *et al*, 1997).

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases (Avon *et al*, 1997). On the other hand Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption. Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid) (Bcaoui, 2001). One of such isotherms is Langmuir isotherm. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.

2. Adsorbed molecules do not interact.

3. All adsorption occurs through the same mechanism.

4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

Langmuir isotherm can be written in linear form as:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K} + \frac{1}{Q_m} . C_e$$

Where $C_e$ is the metal equilibrium in liquid phase in mg/L

$q_e$ is the metal equilibrium concentration in adsorbed phase in mg/g

$Q_m$ and K are Langmuir constants representing the adsorption capacity (mg/g) and energy of adsorption respectively.

**METHODOLOGY**

**PRODUCTION OF ACTIVATED CARBON**

Some quantity of coconut shell was cleaned to remove impurities such as coconut fiber and sand, sun dried for 7 hours and then for about 3 – hours in an oven to obtain charcoal. The charcoal was crushed to 0.5 mm mesh size. About 200 g of this chrushed charcoal was introduced into 0.1 g/ml standard solution of Zinc Chloride ($ZnCl_2$) and stirred to form a paste/slurry. This was heated for about $1^1/_2$ hours and allowed to cool to room temperature thus impregnated with $ZnCl_2$. This is called doping.

10 g of the doped charcoal was heated in an electric furnace to 450 $^0$C for 1 hour and allowed to cool in air after which it was thoroughly washed to remove any traces of $ZnCl_2$. This process was repeated but with the furnace temperature set at 500 $^0$C, 550 $^0$C, 600 $^0$C, 650 $^0$C. The activated carbon thus produced was characterized and the average values obtained tabulated in table 1.

**ADSORPTION EXPERIMENTS: EFFECT OF ADSORBENT DOSAGE**

This experiment was carried out to study the adsorptive capacity of activated carbon produced on heavy metals such as Hg, Pb and Cu. The activated carbon used for this experiment was that produce at 550 $^0$C.
Concentrations of heavy metals (mg/L) in the effluent water were determined using the Atomic Adsorption Spectrometer. Then afterwards 100 mL of heavy metal solution (treated effluent water) was added into a conical flask. 10 ml of 0.5M $HNO_3$ was then added into the solution for digestion to occur. 2 g of activated carbon was then added into the mixture at room temperature. The conical flask was then placed on rotary shaker operated at 150 rpm for 18 hours. The filtrate (activated carbon) was then separated from the solution using filter paper. The final concentration of heavy metals (mg/L) in the treated effluent was then measured using Atomic Adsorption Spectrometer. The same procedures were then carried out for 4 g, 6 g, 8 g, 10 g and 12 g of activated carbon.

**RESULTS**

Table 1 Results of the average values of characterization

| Properties | Activated Carbon At 450 $^0$C (AC$^1$) | Activated Carbon At 500 $^0$C (AC$^2$) | Activated Carbon At 550 $^0$C (AC$^3$) | Activated Carbon At 600 $^0$C (AC$^4$) | Activated Carbon At 650 $^0$C (AC$^5$) |
|---|---|---|---|---|---|
| Ash Content (g) | 4.70 | 5.20 | 4.10 | 4.00 | 3.30 |
| PH Value | 6.52 | 6.58 | 6.53 | 6.53 | 6.52 |
| Surface Area ($m^2$/g) | 285.70 | 539.00 | 730.00 | 95.25 | 381.00 |
| Pore Volume ($cm^3$) | 1.20 | 1.14 | 1.14 | 1.17 | 1.17 |
| Bulk density (g/l) | 0.91 | 0.91 | 0.85 | 0.85 | 0.85 |

Table 2: Results for effect of adsorbent dosage on % removal of Lead (II) $Pb^{2+}$

| Adsorbent Dosage(g) | Initial Pb Conc.(mg/L) | Equilibrium Pb Conc. (mg/L) | Amount of Pb absorbed(mg/L) | % Removal of Pb |
|---|---|---|---|---|
| 2 | 0.34 | 0.07 | 0.27 | 80 |
| 4 | 0.34 | 0.05 | 0.29 | 85 |
| 6 | 0.34 | 0.06 | 0.28 | 83 |
| 8 | 0.34 | 0.04 | 0.30 | 88 |
| 10 | 0.34 | 0.04 | 0.30 | 88 |
| 12 | 0.34 | 0.04 | 0.30 | 88 |

Table 3: Results for effect of adsorbent dosage on % removal of Mercury (II) ion $Hg^{2+}$

| Adsorbent Dosage(g) | Initial Hg Conc.(mg/L) | Equilibrium Hg Conc. (mg/L) | Amount of Hg absorbed(mg/L) | % Removal of Hg |
|---|---|---|---|---|
| 2 | 0.21 | 0.04 | 0.17 | 81 |
| 4 | 0.21 | 0.03 | 0.18 | 86 |
| 6 | 0.21 | 0.03 | 0.18 | 86 |
| 8 | 0.21 | 0.03 | 0.18 | 86 |
| 10 | 0.21 | 0.03 | 0.18 | 86 |
| 12 | 0.21 | 0.02 | 0.19 | 90 |

Table 4: Results for effect of adsorbent dosage on % removal of Copper (II) ions $Cu^{2+}$

| Adsorbent Dosage(g) | Initial Cu Conc.(mg/L) | Equilibrium Cu Conc. (mg/L) | Amount of Cu absorbed(mg/L) | % Removal of Cu |
|---|---|---|---|---|
| 2 | 0.38 | 0.27 | 0.11 | 29 |
| 4 | 0.38 | 0.27 | 0.11 | 29 |
| 6 | 0.38 | 0.28 | 0.12 | 32 |
| 8 | 0.38 | 0.28 | 0.12 | 32 |
| 10 | 0.38 | 0.28 | 0.12 | 32 |
| 12 | 0.38 | 0.28 | 0.12 | 32 |

## % Removal VS Adsorbent Dosage
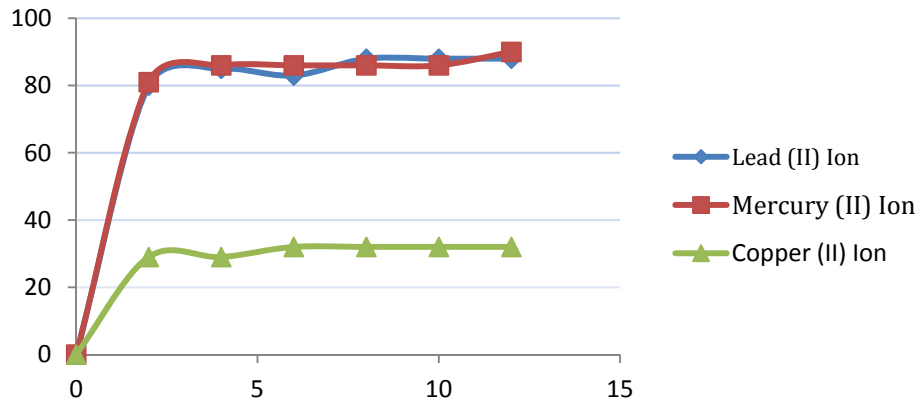


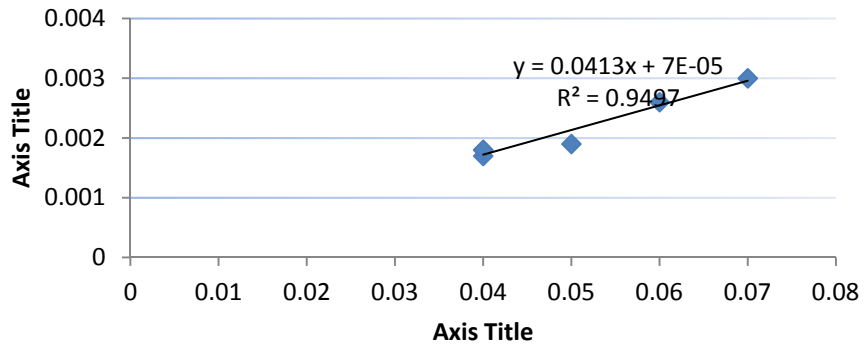Figure 1: graph of % removal of adsorbate vs. adsorbent dosage

## Chart Title



$y = 0.0413x + 7E{-}05$
$R^2 = 0.9497$

Figure 2: showing Langmuir isotherm for lead (II) ion

## Langmuir isotherm for mercury (II) ion



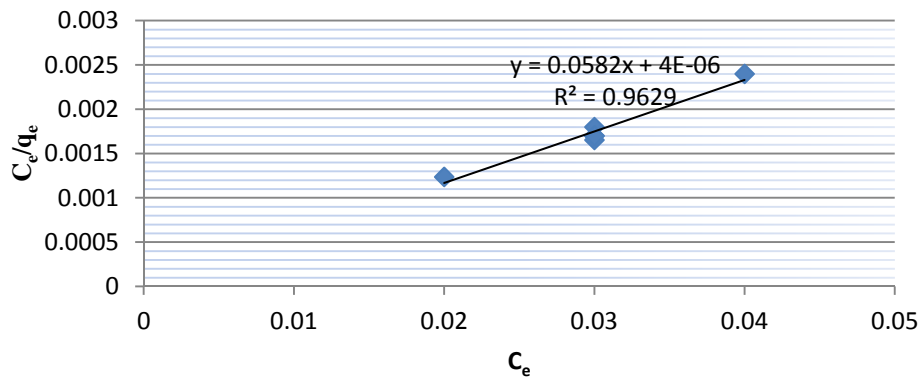$y = 0.0582x + 4E{-}06$
$R^2 = 0.9629$

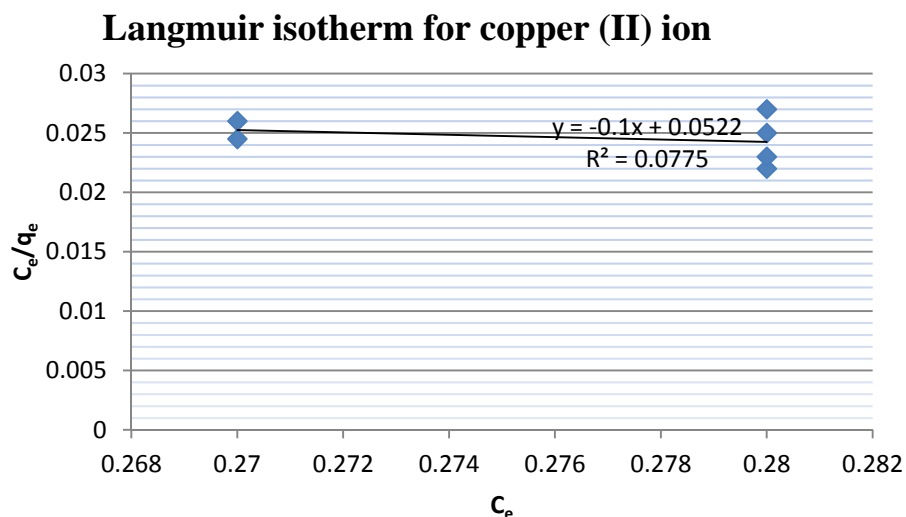Figure 3: showing Langmuir isotherm for mercury (II) ion

Figure 4: showing Langmuir isotherm for copper (II) ion

**Discussion of Results**

**Characterization:** Five different characteristics of activated carbon carried out (ash content, ph, surface area, and pore volume and bulk density) show remarkable differences between activated carbon produced at different temperatures. From table 1 the average % ash content was found to increase from 4.7 g for $AC^1$ to 5.2 g for $AC^2$ and decreases afterward to 3.3 for $AC^5$. The pH results are almost neutral but slightly acidic. The surface area increases remarkably from 285.70 $cm^3$ for $AC^1$ to 730.00 $cm^3$ for $AC^3$ but decreases at $AC^4$ and $AC^5$. $AC^3$ was found to have the highest surface area 730 $m^2$/g. Also it has ash content of 4.1 %, bulk density of 0.85 g/mL, and pore volume of 1.14 $cm^3$ with a corresponding pH of 6.53. Hence the optimum temperature for producing activated carbon was found to be 550 $^0$C. Thus this was for adsorption. This is because it has the best surface area which is the available area for adsorption or chemical reactions. These micro pores (surface area) also provide superb condition for adsorption since adsorption materials can interact with many surfaces.

**Effect of Adsorbent Dosage:** The effect of adsorbent dosage on the removal of Cu (II), Pb (II) and Hg (II) is presented in tables 2 to 4 and figure 1. Figure 1 shows that at low adsorbent dosage of 2 g, up to 80 % of Hg (II) and Pb (II) were removed from the effluent respectively. From a higher dosage of 4 g for Hg and 6 g for Pb, the % adsorption became virtually constant up to 12 g of the two heavy metals. Generally it can be concluded that higher dosage of adsorbent increases the % adsorption. This is because more surfaces and functional groups are available on the adsorbent on which the metals could interact with. These chemical groups were important in the formation of Van der Waals bonding as the functional groups played the main role in binding metals to the adsorbent during adsorption process. This provided more possibilities for adsorption to occur since there would be less competition between metals for the binding sites. The adsorption of Cu (II), however, did not record such higher % adsorption. Percentage of removal for Cu (II) was observed to increase gradually from 29 % to 32 % with the increase of adsorbent dosage from 2 g to 8 g. Lower Cu (II) removal may be due to the fact that the

adsorption of Cu (II) was limited to only monolayer adsorption. This is proved by calculation of correlation coefficient, $R^2$ value which is 0.077 from Langmuir isotherm in figure 4.

**Adsorption Isotherms:** The Langmuir isotherm was tested for Hg (II), Pb (II) and Cu (II). The applicability of each isotherm was evaluated by the value of correlation coefficient, $R^2$. Figs 2, 3 and 4 summarize the value of constants for Langmuir isotherm which were calculated from the best-fit lines. It can be concluded that the adsorption of Hg (II) and Pb (II) were best explained by Langmuir model as the value of correlation regression for both metals were 0.96 and 0.95 respectively. The value of Langmuir constant were found to be 24.4 mg/g, 17.24 mg/g and 10 mg/l for Lead (II) ion, Mercury (II) ion and Copper (II) ion respectively. This implies that 1 g of the activated carbon produced adsorbed 24.4 mg of Lead (II) ion, 17.24 mg of Mercury (II) ion and 10 mg of Copper (II) ion in the effluent water. This model (Langmuir isotherm) implies that the adsorptions of two of the metals were based on adsorption on heterogeneous surface. This was proved by higher adsorption of Hg (II) and Pb (II) in both experiments which is due to the greater tendency of these metals to be adsorbed onto the adsorbent surface since they undergo heterogeneous adsorption. Adsorption of Cu (II) can also be explained by Langmuir isotherm, the adsorption is limited to monolayer for Cu (II) and according to the correlation regression value of 0.077. It was observed that the adsorption of Cu (II) was in agreement with the percentage removal and also it is limited to only monolayer adsorption.

**Conclusion**

This research indicated that the coconut activated carbon produced through chemical activation using $ZnCl_2$ as activating agent could be used as an effective adsorbent material for the removal of Hg (II) and Pb (II) from effluent water. However, Cu (II) can only be removed at lower percentage. From the calculation based on Langmuir isotherm, Pb(II) ion show the highest adsorption capacity of 24.4mg/g, followed by Hg(II) and Cu(II) with adsorption capacity of 17.24 mg/g and 10 mg/g, respectively. It can also be concluded that the adsorption of Hg (II), Pb (II) and Cu (II) by coconut activated carbon is dependent on the adsorbent dosage. In adsorption isotherm analysis, the Langmuir model provides better correlation coefficient for Pb (II) and Hg while correlation coefficient for Cu (II) was low. This suggests that the adsorption is limited to monolayer for Cu (II) and heterogeneous for Pb (II) and Hg (II). These results were in agreement with the percentage removal and also maximum adsorption capacity of each of the metals. In this study, coconut shell used to produce activated carbon was locally sourced and abundantly available. Hence the activated carbon prepared from coconut shell would be an economically useful tool and as an alternative to the commercially available activated carbon in the treatment of effluent water containing Hg (II) and Pb (II).

**RECOMMENDATION**

Adsorption capacity of activated carbon had been found to be dependent on the adsorbent dosage in the course of this research but other variables such as adsorbate concentration, pH variation, activating reagents, temperature etc have their own effect on adsorption capacity. Hence this prompts the use of different model to carry out analysis of the adsorption capacity (Langmuir isotherm, Fruendlich isotherm, BET analysis etc). It is therefore recommended that further work on these models be conducted to study the adsorption capacity of activated carbon from coconut shell on heavy metals.

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